

Ab Initio Study of Mechanism of Forming Spiro-Heterocyclic Ring Compound Involving Si and Ge from Dichlorosilylene Germylidene ($\text{Cl}_2\text{Si}=\text{Ge}$:) and AcetoneDongting Liu, Hua Ji,[†] and Xiuhui Lu*School of Chemistry and Chemical Engineering, University of Jinan, Jiweilu 106, Jinan, Shandong 250022, P.R. China
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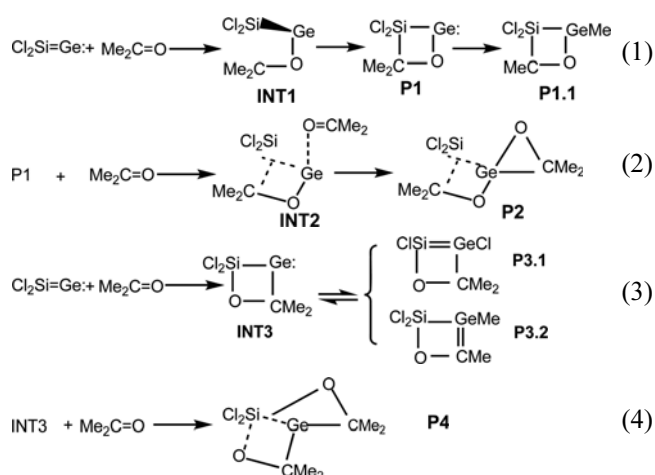
The mechanism of the cycloaddition reaction between singlet state dichlorosilylene germylidene ($\text{Cl}_2\text{Si}=\text{Ge}$:) and acetone has been investigated with B3LYP/6-31G* and B3LYP/6-31G** method, from the potential energy profile, we predict that the reaction has one dominant reaction pathway. The presented rule of the reaction is that the two reactants firstly form a Si-heterocyclic four-membered ring germylene through the [2+2] cycloaddition reaction. Because of the 4p unoccupied orbital of Ge atom in the Si-heterocyclic four-membered ring germylene and the π orbital of acetone forming a $\pi \rightarrow p$ donor-acceptor bond, the Si-heterocyclic four-membered ring germylene further combines with acetone to form an intermediate. Because the Ge atom in the intermediate hybridizes to an sp^3 hybrid orbital after the transition state, then, the intermediate isomerizes to spiro-heterocyclic ring compound involving Si and Ge (P4) via a transition state.

Key Words : Dichlorosilylene germylidene ($\text{Cl}_2\text{Si}=\text{Ge}$:), Spiro-heterocyclic ring compound, Reaction mechanism

Introduction

Unsaturated germylene is a kind of quite unstable active intermediate. The unsaturated germylene – germylidene was first produced by bombarding the tetramethylgermane (TMG) vapor using high-pressure steam pulse, which was found in 1997 by Clouthier group¹ of University of Kentucky. *Ab initio* study on the first unsaturated germylene – germylidene, they got this molecular structure,² electronic spectrum² and swinging fluorescence spectrum,² structure of its ground state,³ and the stimulated emission pumping (SEP) spectroscopy⁴ of the first excited singlet state of germylidene. Stogner and Grev have done extensive theoretical calculations⁵ on germylidene and the trans-bent germyne $\text{HC}\equiv\text{GeH}$ isomer with RHF/DZP and DHF/TZ(2df,2pd) method. They found that germylidene is the global minimum on the $\text{H}_2\text{C}=\text{Ge}$: potential energy surface, at the same time, the trans-bent germyne some 179.9 kJ/mol higher than germylidene in energy. The barrier to germyne isomerization was predicted to be only 29.3 kJ/mol and no stable linear germyne structures could be found. Regarding to the cycloaddition reaction of the unsaturated germylene, we have done some elementary discussion.^{6,7} But these studies are limited to the cycloaddition reaction of germylidene ($\text{H}_2\text{C}=\text{Ge}$:) and its derivatives. There are no reports on the cycloaddition reaction of silylene germylidene ($\text{H}_2\text{Si}=\text{Ge}$:) and its derivatives at present, and it is a new branch of unsaturated germylene's cycloaddition reaction. It is quite difficult to investigate the mechanisms of cycloaddition reaction directly by experimental methods due to the high activity of silylene germylidene, the theoretical study is more practical. To explore the mechanism of cycloaddition reaction between silylene germylidene (include its

derivatives) and the asymmetric π -bonded compounds, taking into account the diversity of halogenated silylene germylidene ($\text{X}_2\text{Si}=\text{Ge}$:, X=F, Cl, Br), dichlorosilylene germylidene ($\text{Cl}_2\text{Si}=\text{Ge}$:) and acetone were selected as model molecules, and its mechanism was investigated and analyzed theoretically. The results show that there are four possible pathways of the cycloaddition reaction (considering the chlorine transfer and methyl transfer simultaneously) as follows:



The research result indicates the laws of cycloaddition reaction between silylene germylidene ($\text{H}_2\text{Si}=\text{Ge}$:) and its derivatives and the asymmetric π -bonded compounds, which are significant for the synthesis of small-ring and spiro-heterocyclic ring compound involving Si and Ge. The study extends the research area and enriched the research content of germylene chemistry.

Computational Methods

B3LYP/6-31G* and B3LYP/6-31G**⁸ implemented in the Gaussian package is employed to locate all the stationary points along the reaction pathways. Subsequently, the frequency calculation is performed on the optimized geometries at the level of B3LYP/6-31G* and B3LYP/6-31G**. All energies reported in this work are corrected by the zero-point energy. The frequency calculation confirms the nature of the equilibrium geometries and transition states, and in order to explicitly establish the relevant species, the intrinsic reaction coordinate (IRC)^{9,10} is also calculated for all the transition states appearing on the cycloaddition energy surface profile.

Results and Discussions

Theoretical calculations indicate that the geometric parameters, which appear in the cycloaddition reactions (1)-(4) between dichlorosilylene germylidene ($\text{Cl}_2\text{Si}=\text{Ge}$:) and acetone, are almost the same at the B3LYP/6-31G* and B3LYP/6-31G** levels, so are the mechanisms of cycloaddition reaction between dichlorosilylene germylidene ($\text{Cl}_2\text{Si}=\text{Ge}$:) and acetone with both B3LYP/6-31G* and B3LYP/6-31G** methods. Considering the accuracy of B3LYP/6-31G** method in energy calculation, the following discussions therefore are based on the results from B3LYP/6-31G** with respect to geometric parameters and energy, respectively.

Reaction (1): Channels of Forming the Si-Heterocyclic Four-Membered Ring Germylene (P1) and Me-Transfer

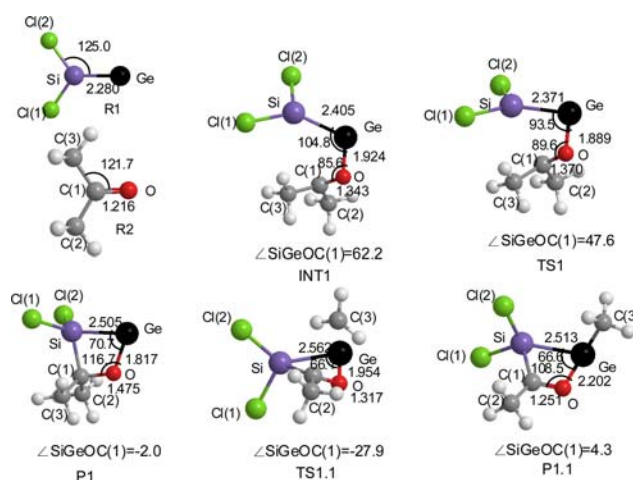


Figure 1. Optimized B3LYP/6-31G** geometrical parameters and the atomic numbering for the species in cycloaddition reaction (1). Lengths are in Å and angles in degree.

Product (P1.1). Theoretical calculations show that the ground state of dichlorosilylene germylidene is singlet state. The geometrical parameters of the intermediate (INT1), transition states (TS1, TS1.1, TS1.2) and products (P1, P1.1, P1.2) which appear in reaction (1) between dichlorosilylene germylidene and acetone are given in Figure 1. The energies are listed in Table 1, and the potential energy profile for the cycloaddition reaction is shown in Figure 2.

We can obtain from vibrational analysis that the unique imaginary frequencies of the transition states TS1 and TS1.1 are 92.9i and 663.8i, respectively, and therefore these transi-

Table 1. Zero point energy (ZPE, hartree), total energies (E_T , hartree) and relative energies (E_R , kJ/mol) for the species from B3LYP/6-31G* and B3LYP/6-31G** method

Reaction	Species	ZPE	B3LYP/6-31G*		ZPE	B3LYP/6-31G**	
		B3LYP/6-31G*	^a E_T	E_R	B3LYP/6-31G**	^a E_T	E_R
^b Reaction (1)	R1+R2	0.08808	-3477.96868	0.0	0.08772	-3477.97756	0.0
	INT1	0.08962	-3477.99769	-76.2	0.08920	-3478.00679	-76.7
	TS1(INT1-P1)	0.08988	-3477.99496	-69.0	0.08944	-3478.00399	-69.4
	P1	0.09157	-3478.04338	-196.1	0.09121	-3478.05227	-196.2
	TS1.1(P1-P1.1)	0.08703	-3477.93758	81.6	0.08677	-3477.94904	74.9
	P1.1	0.10285	-3478.02099	-137.3	0.08746	-3478.04589	-179.4
	^c Reaction (2)	P1+R2	0.17566	-3671.11498	0.0	0.17495	-3671.13274
INT2		0.17778	-3671.14331	-74.4	0.17676	-3671.16158	-75.7
TS2(INT2-P2)		0.17801	-3671.11866	-9.7	0.17725	-3671.13671	-10.4
P2		0.17773	-3671.14156	-69.8	0.17718	-3671.13682	-10.7
^b Reaction (3)		R1+R2	0.08808	-3477.96868	0.0	0.08772	-3477.97756
	INT3	0.09090	-3478.04361	-196.7	0.09043	-3478.05305	-198.2
	TS3.1 (INT3-P3.1)	0.09055	-3478.03776	-181.4	0.09024	-3478.04699	-182.3
	P3.1	0.09066	-3478.03953	-186.0	0.09034	-3478.04877	-187.0
	TS3.2(INT3-P3.2)	0.08869	-3478.01647	-125.5	0.08827	-3478.02629	-127.9
	P3.2	0.08842	-3478.04276	-194.5	0.08793	-3478.05283	-197.6
^d Reaction (4)	INT3+R2	0.17499	-3671.11521	0.0	0.17417	-3671.13352	0.0
	INT4	0.17778	-3671.15775	-111.7	0.17706	-3671.17614	-111.9
	TS4(INT4-P4)	0.17695	-3671.13896	-62.4	0.17626	-3671.15743	-62.8
	P4	0.17820	-3671.16155	-121.7	0.17753	-3671.15996	-69.4

^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 $E_R = E_T - E_{(INT3+R2)}$

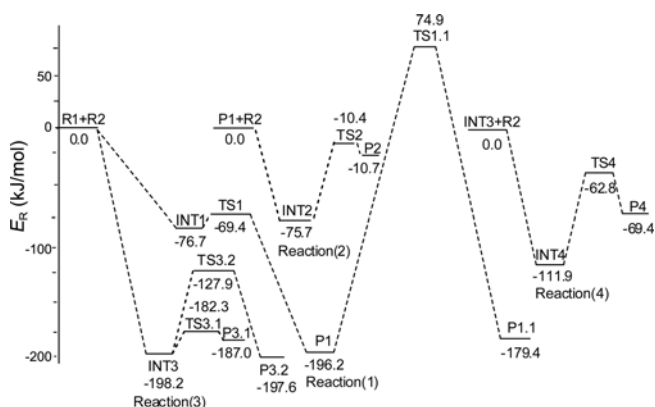


Figure 2. The potential energy surface for the cycloaddition reactions between dichlorosilylene germylidene and acetone with B3LYP/6-31G**.

tion states can be affirmed as the real ones. According to the calculations of the IRC (with the step-length of $0.1 \text{ amu}^{-1/2} \text{ bohr}$) for TS1 and TS1.1, and the further optimization of the primary IRC results, TS1 connects INT1 with P1, and TS1.1 connects P1 with P1.1. According to Figure 2, it can be seen that the reaction (1) consists of three steps: the first step is that the two reactants (R1, R2) form an intermediate (INT1), which is a barrier-free exothermic reaction of 76.7 kJ/mol. The second step is that the intermediate (INT1) isomerizes to a Si-heterocyclic four-membered ring germylene (P1) through transition state (TS1) with an energy barrier of 7.3 kJ/mol. The third step is the methyl-transfer reaction of P1, forming the products P1.1 *via* transition state TS1.1 with an energy barrier of 271.1 kJ/mol. Because the energy of P1.1 is 16.8 kJ/mol higher than that of P1, so the transfer reaction of $\text{P1} \rightarrow \text{P1.1}$ is prohibited in thermodynamics at normal temperature and pressure, and the reaction (1) will end with product P1.

Reaction (2): Channel of Forming Spiro-Heterocyclic Ring Compound Involving Si and Ge (P2). In reaction (2), the Si-heterocyclic four-membered ring germylene (P1) further reacts with acetone (R2) to form a spiro-heterocyclic ring compound involving Si and Ge (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

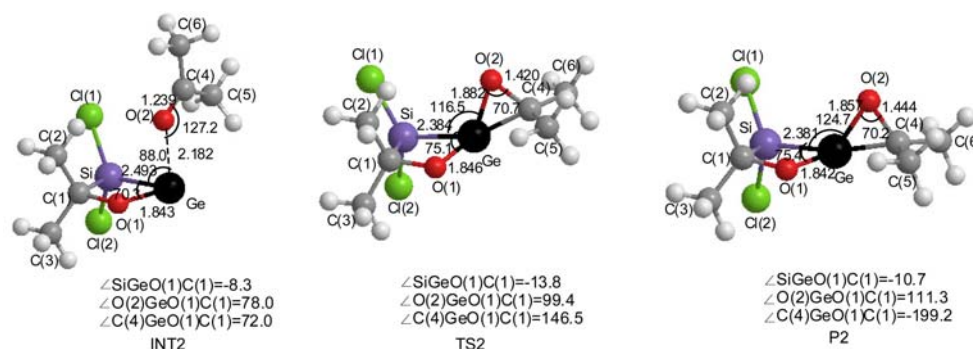


Figure 3. Optimized B3LYP/6-31G** geometrical parameters of INT2, TS2, P2 and the atomic numbering for cycloaddition reaction (2). Lengths are in Å and angles in degree.

energy profile for the cycloaddition reaction is shown in Figure 2.

We can obtain from vibrational analysis that the unique imaginary frequencies of the transition state TS2 is $25.0i$, and therefore the transition state can be affirmed as the real one. According to the calculations of the IRC (with the step-length of $0.1 \text{ amu}^{-1/2} \text{ bohr}$) for TS2, and the further optimization of the primary IRC results, TS2 connects INT2 with P2. According to Figure 2, it can be seen that the process of reaction (2) is as follows: on the basis of P1 formed on the reaction (1) between R1 and R2, the P1 further reacts with acetone to form an intermediate (INT2), which is a barrier-free exothermic reaction of 75.7 kJ/mol; next, the intermediate (INT2) isomerizes to a spiro-heterocyclic ring compound involving Si and Ge (P2) *via* a transition state (TS2) with an energy barrier of 65.3 kJ/mol. Because the energy of P2 is 65.0 kJ/mol higher than that of INT2, so reaction (2) terminate in the intermediate INT2.

Reaction (3): Channels of Forming Si-Heterocyclic Four-Membered Ring Germylene (INT3) and Cl-Transfer Product (P3.1) and Me-Transfer Product (P3.2). The geometrical parameters of Si-heterocyclic four-membered ring germylene (INT3), transition states (TS3.1, TS3.2) and products (P3.1 and P3.2) which appear in reaction (3) between dichlorosilylene germylidene and acetone are given in Figure 4. The energies are listed in Table 1, and the potential energy profile for the cycloaddition reaction is shown in Figure 2.

We can obtain from vibrational analysis that the unique imaginary frequencies of the transition states TS3.1 and TS3.2 are $42.9i$ and $357.4i$, and therefore the transition states can be affirmed as the real ones. According to the calculations of the IRC (with the step-length of $0.1 \text{ amu}^{-1/2} \text{ bohr}$) of TS3.1 and TS3.2, and the further optimization of the primary IRC results, TS3.1 connects INT3 with P3.1. TS3.2 connects INT3 with P3.2. According to Figure 2, it can be seen that reaction (3) consists of three steps: the first step is that the two reactants (R1, R2) form a Si-heterocyclic four-membered ring germylene (INT3), which is a barrier-free exothermic reaction of 198.2 kJ/mol. The second and third steps are that the INT3 undergoes Cl-transfer and methyl transfer *via* transition states TS3.1 and TS3.2 with an energy barriers of 15.9 and 70.3 kJ/mol, resulting in the formation

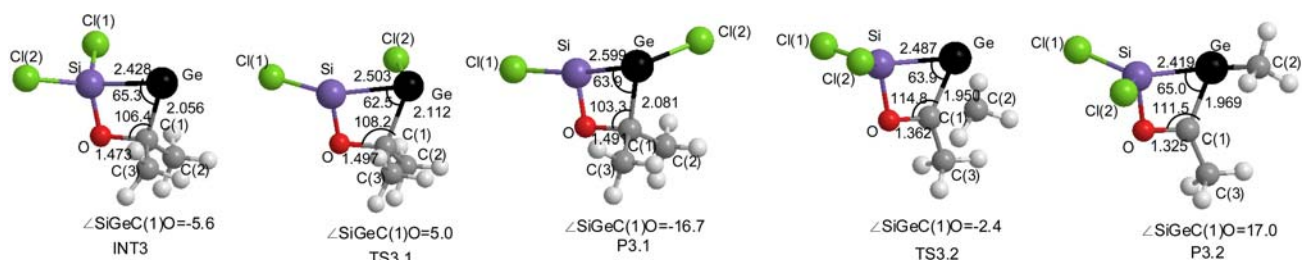


Figure 4. Optimized B3LYP/6-31G** geometrical parameters of INT3, TS3.1, P3.1, TS3.2, P3.2 and the atomic numbering for cycloaddition reaction (3). Lengths are in Å and angles in degree.

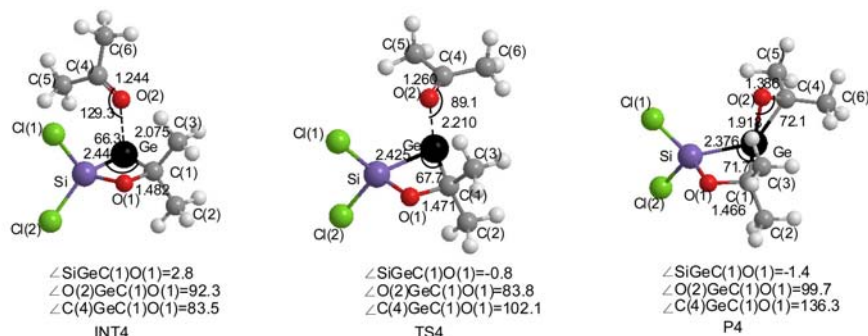


Figure 5. Optimized B3LYP/6-31G** geometrical parameters of INT4, TS4, P4 and the atomic numbering for cycloaddition reaction (4). Lengths are in Å and angles in degree.

of Cl-transfer and Me-transfer products (P3.1 and P3.2). Because of the higher energies of P3.1 and P3.2 than that of INT3 by 11.2 and 0.6 kJ/mol, the reactions of INT3→P3.1 and INT3→P3.2 are prohibitive in thermodynamics at ordinary condition. So reaction (3) terminate in the INT3.

According to Figures 1, 2 and 4, it can be seen that INT1 and INT3 isomerides, and the equilibrium distributions of INT1 and INT3 are $P_i(\text{INT1}) = K(\text{INT1})/K(\text{INT1}) + K(\text{INT3}) \approx 0.0$, $P_i(\text{INT3}) = K(\text{INT3})/K(\text{INT1}) + K(\text{INT3}) \approx 1.0$, respectively. So INT3 is main distribution.

Reaction (4): Channel of Forming Spiro-Heterocyclic Ring Compound Involving Si and Ge (P4). In reaction (4), the Si-heterocyclic four-membered ring germylene (INT3) further reacts with acetone (R2) to form a spiro-heterocyclic ring compound involving Si and Ge (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 profile for the cycloaddition reaction is shown in Figure 2.

We can obtain from vibrational analysis that the unique imaginary frequencies of the transition state TS4 is 73.5i, and therefore the transition state can be affirmed as the real one. According to the calculations of the IRC (with the step-

length of $0.1 \text{ amu}^{-1/2} \text{ bohr}$) for TS4, and the further optimization of the primary IRC results, TS4 connects INT4 with P4. According to Figure 2, it can be seen that the process of reaction (4) is as follows: on the basis of the two reactants (R1, R2) to form INT3, it further reacts with acetone (R2) to form an intermediate (INT4), which is a barrier-free exothermic reaction of 111.9 kJ/mol. And then intermediate (INT4) isomerizes to a spiro-heterocyclic ring compound involving Si and Ge (P4) *via* a transition state (TS4) with an energy barrier of 49.1 kJ/mol. Because the energy of P4 is 42.5 kJ/mol higher than that of INT4, the reaction of INT4→P4 is an endothermic reaction.

Theoretical Analysis and Explanation of the Dominant Reaction Channel. According to the above analysis, reaction (4) should be the dominant reaction channel of the cycloaddition reaction between singlet dichlorosilylene germlydene and acetone



In the reaction, the frontier molecular orbitals of R1, R2 and INT3 are shown in Figure 6. According to Figure 6, the frontier molecular orbitals of R1, R2, INT3 can be expressed in schematic diagram 7 and 8. The mechanism of this reac-

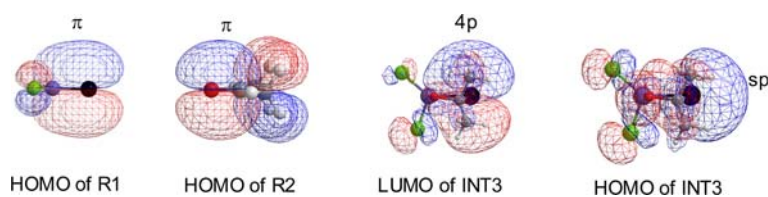


Figure 6. The frontier molecular orbitals of R1, R2, INT3.

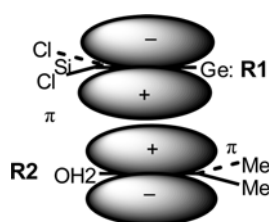


Figure 7. A schematic interaction diagram for the frontier orbitals of $\text{Cl}_2\text{Si}=\text{Ge}:(\text{R}1)$ and $\text{Me}_2\text{C}=\text{O} (\text{R}2)$.

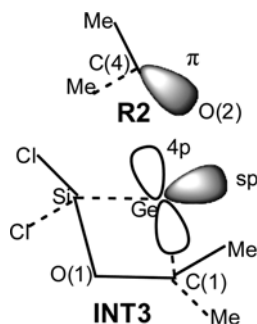


Figure 8. A schematic interaction diagram for the frontier orbitals of $\text{INT}3$ and $\text{Me}_2\text{C}=\text{O} (\text{R}2)$.

tion could be explained with the molecular orbital diagrams (Figs. 7 and 8), and the Figures 1, 4 and 5. According to Figure 7 and Figures 1 and 4, as dichlorosilylene germylidene initially interacts with acetone, the [2+2] cycloaddition of the bonding π -orbitals firstly results in a Si-heterocyclic four-membered ring germylene ($\text{INT}3$). Because $\text{INT}3$ is an active intermediate, $\text{INT}3$ could further react with acetone ($\text{R}2$) to form a spiro-heterocyclic ring compound involving Si and Ge ($\text{P}4$). The mechanism of this reaction could be explained with Figures 5 and 8, according to orbital symmetry matching condition, when $\text{INT}3$ interacts with acetone ($\text{R}2$), the 4p unoccupied orbital of the Ge atom in $\text{INT}3$ will insert the π orbital of acetone from oxygen side, then the shift of π -electrons to the p unoccupied orbital forms a $\pi \rightarrow \text{p}$ donor-acceptor bond, leading to the formation of intermediate ($\text{INT}4$). As the reaction goes on, because of $\angle \text{C}(4)\text{O}(2)\text{Ge}$ ($\text{INT}4$: 129.3° , $\text{TS}4$: 89.1° , $\text{P}4$: 72.1°) gradually decrease,

and the $\text{C}(4)\text{-O}(2)$ ($\text{INT}4$: 1.244 \AA , $\text{TS}4$: 1.260 \AA , $\text{P}4$: 1.386 \AA) bond gradually lengthen, the Ge in $\text{INT}4$ hybridizes to sp^3 hybrid orbital after the transition state ($\text{TS}4$), forming a spiro-heterocyclic ring compound involving Si and Ge ($\text{P}4$).

Conclusion

On the basis of the potential energy profile obtained with the B3LYP/6-31G** method for the cycloaddition reaction between singlet dichlorosilylene germylidene ($\text{Cl}_2\text{Si}=\text{Ge}:$) and acetone, 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 ($\text{R}1$, $\text{R}2$) form a Si-heterocyclic four-membered ring germylene ($\text{INT}3$), which is a barrier-free exothermic reaction of 198.2 kJ/mol . The second step is that $\text{INT}3$ further reacts with acetone ($\text{R}2$) to form an intermediate ($\text{INT}4$), which is also a barrier-free exothermic reaction of 111.9 kJ/mol . The third step is that $\text{INT}4$ isomerizes to a spiro-heterocyclic ring compound involving Si and Ge ($\text{P}4$) via a transition state ($\text{TS}4$) with an energy barrier of 49.1 kJ/mol . $\text{INT}4 \rightarrow \text{P}4$ is an endothermic reaction of 42.5 kJ/mol .

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