

Ab initio study of mechanism of forming a spiro-heterocyclic ring compound with Si and Ge between dimethylsilylene germylidene ($\text{Me}_2\text{Si}=\text{Ge}:$) and acetone

Xiuhui Lu · Zhenxia Lian · Yongqing Li · Zhina Wang

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Abstract The mechanism of the cycloaddition reaction between singlet state dimethylsilylene germylidene ($\text{Me}_2\text{Si}=\text{Ge}:$) and acetone has been investigated with CCSD(T)//B3LYP/6-31G* method. From the potential energy profile, it could be predicted that the reaction has one dominant reaction pathway. The reaction rules presented are that the two reactants first 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 happens sp^3 hybridization after transition state, then, the intermediate isomerizes to a spiro-heterocyclic ring compound with Si and Ge *via* a transition state.

Keywords Dimethylsilylene germylidene ($\text{Me}_2\text{Si}=\text{Ge}:$) · Potential energy profile · Spiro-heterocyclic ring compound

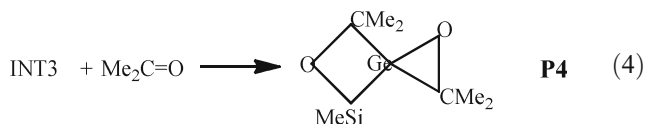
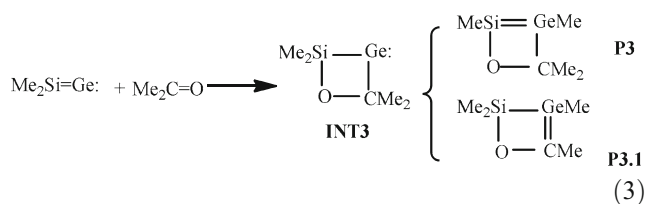
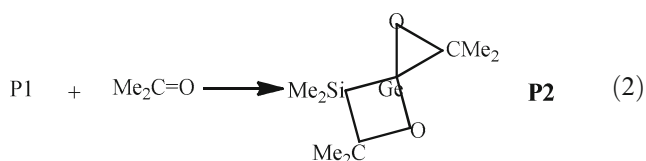
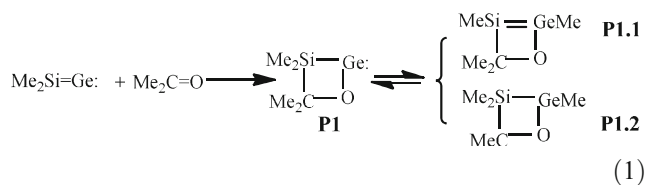
Introduction

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 spectrum [2] and oscillatory fluorescence decay [2] of jet-cooled germylidene ($\text{H}_2\text{C}=\text{Ge}:$), and learnt the ground state [3] of $\text{H}_2\text{C}=\text{Ge}:$ and $\text{D}_2\text{C}=\text{Ge}:$, the stimulated emission pumping (SEP) spectroscopy [4] of the first excited singlet state of germylidene. Stogner and Grev have published the extensive ab initio calculations [5] 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^{-1} higher in energy. The barrier to germyne isomerization was predicted to be only 7 kcal mol^{-1} 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 [6, 7], but these studies are limited to the cycloaddition reaction of methylene germylene ($\text{H}_2\text{C}=\text{Ge}:$) and its derivatives. There are no reports on the cycloaddition reaction of silylene germylene ($\text{H}_2\text{Si}=\text{Ge}:$) 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 silylene germylene, therefore, the theoretical study is more practical. To explore the rules of cycloaddition reaction between silylene germylene (include its derivatives) and the asymmetric π -bonded compounds, dimethylsilylene germylidene

X. Lu (✉) · Z. Lian · Y. Li · Z. Wang
School of Chemistry and Chemical Engineering,
University of Jinan,
Jinan, Shandong 250022, People's Republic of China
e-mail: lxh@ujn.edu.cn

($\text{Me}_2\text{Si}=\text{Ge}$) and acetone were selected as model molecules. The cycloaddition reaction mechanism (considering the methyl transfer simultaneously) was investigated and analyzed theoretically. The results show that the cycloaddition reaction consists of four possible pathways, as follows:



The research result indicates the law of cycloaddition reaction between dimethylsilylene germylidene ($\text{Me}_2\text{Si}=\text{Ge}$: , include its derivatives) and the asymmetric π -bonded compounds, which is significant for the synthesis of small-ring and spiro-heterocyclic ring compounds with Si and Ge. The study extends research area and enriched the research content of germylene chemistry.

Calculation methods

B3LYP/6-31G* [8] implemented in the Gaussian 98 package [9] 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(CCSD(T)// B3LYP/6-31G*) are included for the energy calculations. To explicitly establish the relevant species, the intrinsic reaction coordinate (IRC) [10, 11] is also calculated for all the transition

states appearing on the cycloaddition energy surface profile.

Results and discussion

Reaction (1): channels of forming the Si-heterocyclic four-membered ring germylene (P1) and Me- transfer Products (P1.1 and P1.2)

Theoretical calculations show that the ground state of dimethylsilylene germylidene is singlet state. The geometrical parameters of dimethylsilylene germylidene(R1), acetone (R2), intermediate (INT1), transition states (TS1, TS1.1, TS1.2), and products (P1, P1.1, P1.2) appearing in reaction (1) between dimethylsilylene germylidene and acetone are given in Fig. 1. The energies are listed in Table 1, and the potential energy surface for the cycloaddition reaction is shown in Fig. 2. According to Fig. 2, it can be seen that reaction (1) consists of four steps: the first one is that the two reactants (R1, R2) form an active intermediate (INT1), which is a barrier-free exothermic reaction of 82.0 kJ mol^{-1} . The second step is that the intermediate (INT1) isomerizes to a Si-heterocyclic four-membered ring germylene (P1) via the transition state (TS1) with an energy barrier of 34.0 kJ mol^{-1} . The next two steps are that the Si-heterocyclic four-membered ring germylene (P1) undergoes two methyl-transfer reactions via the transition states TS1.1 and TS1.2 with energy barriers of 148.5 and $173.8 \text{ kJ mol}^{-1}$ respectively, resulting in the formation of products (P1.1 and P1.2). The reaction of $\text{P1} \rightarrow \text{P1.1}$ and $\text{P1} \rightarrow \text{P1.2}$ is prohibited in thermodynamics at ordinary condition, because the energies of P1.1 and P1.2 are 56.3 and 47.8 kJ mol^{-1} higher than that of P1. And reaction (1) will be end in product P1.

Reaction (2): channel of forming spiro-heterocyclic ring compound with 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 with Si and Ge (P2). The geometrical parameters of intermediate (INT2), transition state (TS2), and product (P2) appearing in reaction (2) are given in Fig. 3. The energies are listed in Table 1, and the potential energy surface for the cycloaddition reaction is shown in Fig. 2. According to Fig. 2, it can be seen that the process of reaction (2) is as follows: on the basis of P1 formed in reaction (1), P1 further reacts with acetone to form an intermediate (INT2), which is also a barrier-free exothermic reaction of 71.9 kJ mol^{-1} . Then, the intermediate (INT2)

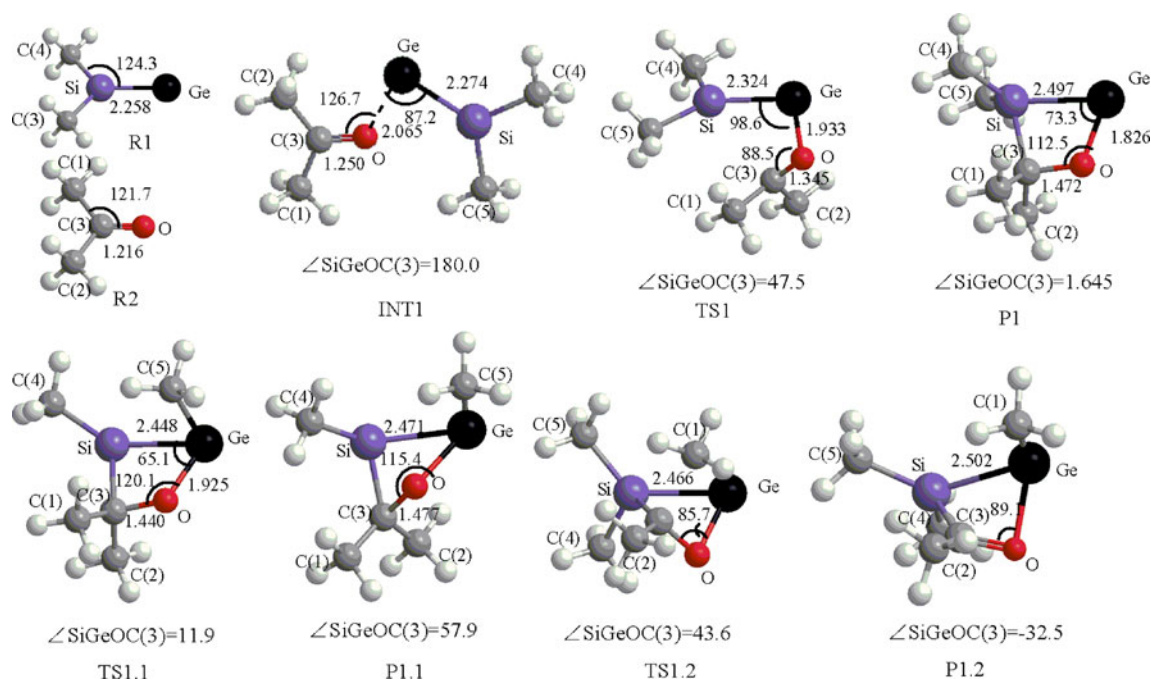


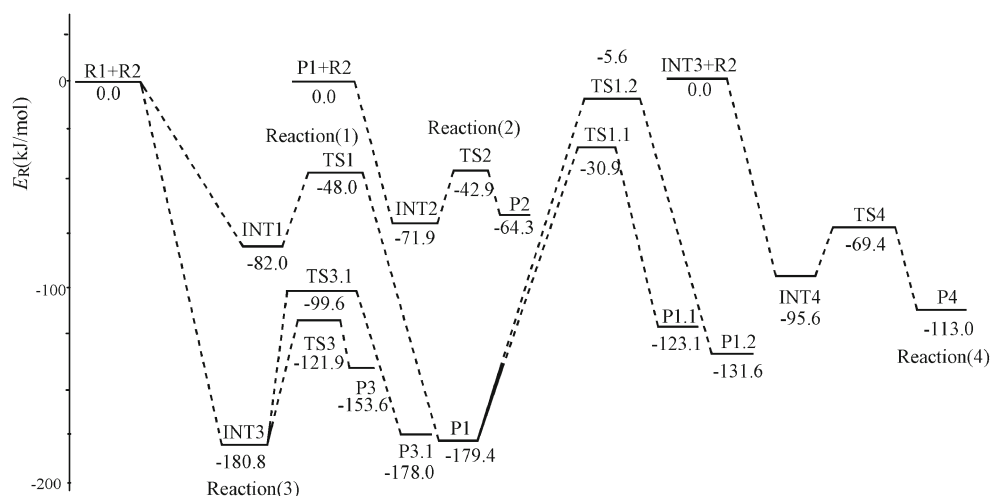
Fig. 1 Optimized B3LYP/6-31G* geometrical parameters and the atomic numbering for the species in cycloaddition reaction (1). Bond lengths and bond angles are in angstrom and degree, respectively

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

Reaction	Species	ZPE	B3LYP/6-31G*		CCSD(T)//B3LYP/6-31G*	
			^a E_T	E_R	^a E_T	E_R
^b Reaction(1)	R1+R2	0.15862	-2637.25566	0.0	-2634.24244	0.0
	INT1	0.16057	-2637.28983	-89.7	-2634.27367	-82.0
	TS1(INT1-P1)	0.16090	-2637.27306	-45.7	-2634.26072	-48.0
	P1	0.16221	-2637.31773	-163.0	-2634.31076	-179.4
	TS1.1(P1-P1.1)	0.15970	-2637.26539	-25.5	-2634.25421	-30.9
	P1.1	0.16079	-2637.29708	-108.7	-2634.28934	-123.1
	TS1.2(P1-P1.2)	0.15897	-2637.25801	-6.2	-2634.24456	-5.6
^c Reaction(2)	P1+R2	0.24630	-2830.38933	0.0	-2826.80469	0.0
	INT2	0.24821	-2830.41285	-61.8	-2826.83206	-71.9
	TS2(INT2-P2)	0.24774	-2830.40206	-33.4	-2826.82103	-42.9
	P2	0.24897	-2830.40392	-38.3	-2826.82919	-64.3
^b Reaction(3)	R1+R2	0.15862	-2637.25566	0.0	-2634.24244	0.0
	INT3	0.16137	-2637.31986	-168.6	-2634.31131	-180.8
	TS3 (INT3-P3)	0.16093	-2637.29871	-113.0	-2634.28888	-121.9
	P3	0.16158	-2637.30946	-141.3	-2634.30096	-153.6
	TS3.1(INT3-P3.1)	0.15937	-2637.29423	-101.3	-2634.28037	-99.6
^d Reaction(4)	P3.1	0.15935	-2637.32437	-180.4	-2634.31025	-178.0
	INT3+R2	0.24546	-2830.39146	0.0	-2826.80524	0.0
	INT4	0.24799	-2830.42563	-89.7	-2826.84165	-95.6
	TS4(INT4-P4)	0.24712	-2830.41298	-56.5	-2826.83167	-69.4
	P4	0.24883	-2830.42565	-89.8	-2826.84829	-113.0

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

Fig. 2 The potential energy profile for the cycloaddition reactions between dimethylsilylene germylidene and acetone with CCSD(T)//B3LYP/6-31G*



isomerizes to a spiro-heterocyclic ring compound with Si and Ge (P2) via the transition state (TS2) with a energy barrier of 29.0 kJ mol⁻¹. Because the energy of P2 is 7.6 kJ mol⁻¹ higher than that of INT2, so the reaction of INT2→P2 is prohibited in thermodynamics at ordinary condition, and reaction (2) terminates in the intermediate INT2.

Reaction (3): channels of forming Si-heterocyclic four-membered ring germylene (INT3) and Me-transfer products (P3 and P3.1)

The geometrical parameters of Si-heterocyclic four-membered ring germylene (INT3), transition states (TS3, TS3.1) and products (P3, P3.1) appearing in reaction (3) between dimethylsilylene germylidene and acetone are given in Fig. 4. The energies are listed in Table 1, and the potential energy surface for the cycloaddition reaction is shown in Fig. 2. According to Fig. 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 180.8 kJ mol⁻¹. The second and third steps are that the INT3 undergoes methyl transfer via transition states TS3 and TS3.1 with an energy barriers of 58.9 and 81.2 kJ mol⁻¹, respectively, resulting in the formation of Me-transfer products (P3 and P3.1). The reaction of INT3→P3 and INT3→P3.1 are prohibited in thermodynamics at ordinary condition, because the energies of P3 and P3.1 are 27.2 and 2.8 kJ mol⁻¹ higher than that of INT3, and reaction (3) will end in intermediate INT3.

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

Reaction (4): channel of forming spiro-heterocyclic ring compound with Si and Ge (P4)

In reaction (4), the Si-heterocyclic four-membered ring germylene (INT3) further reacts with acetone (R2) to form a

Fig. 3 Optimized MP2/6-31G* geometrical parameters of INT2, TS2, P2 and the atomic numbering for the species in cycloaddition reaction (2). Bond lengths and bond angles are in angstrom and degree, respectively

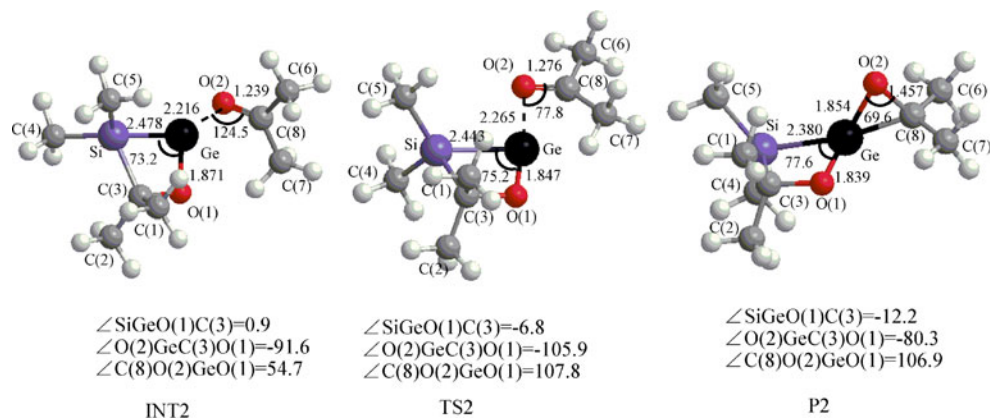
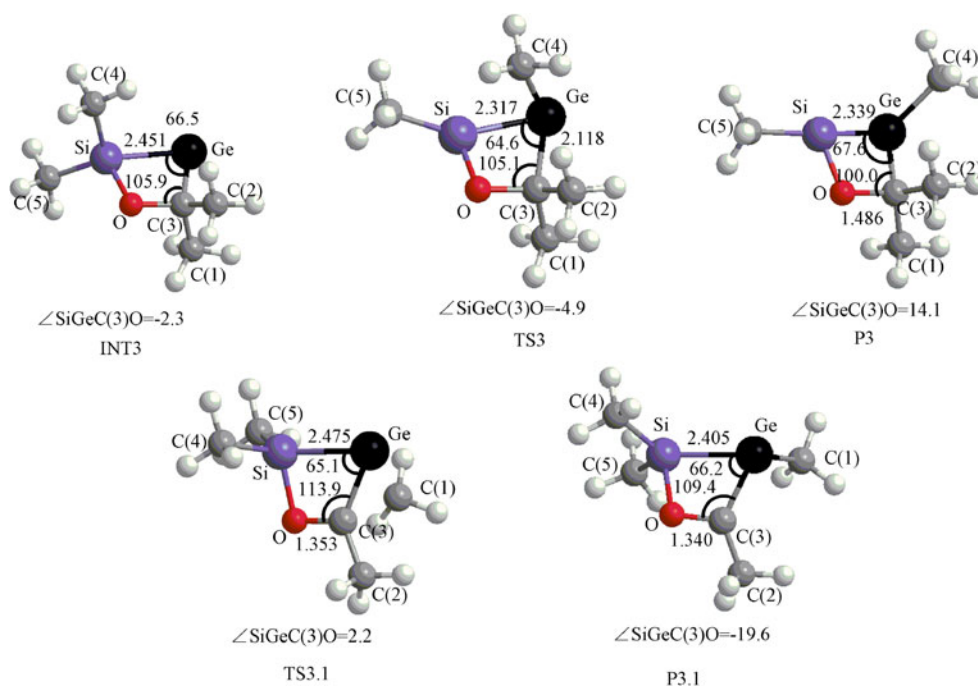
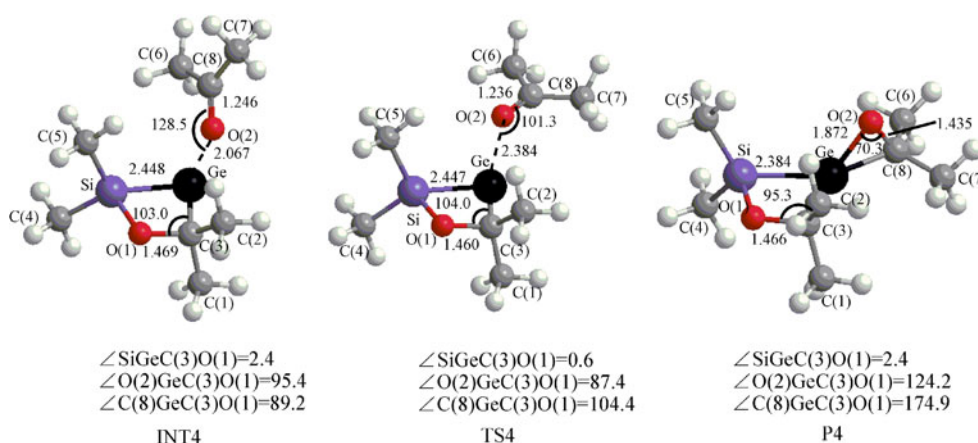


Fig. 4 Optimized B3LYP/6-31G* geometrical parameters of INT3, TS3, P3, TS3.1, P3.1 and the atomic numbering for the species in cycloaddition reaction (3). Bond lengths and bond angles are in angstrom and degree, respectively



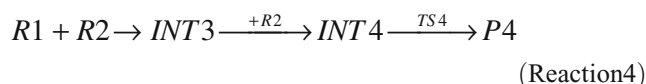
spiro-heterocyclic ring compound with Si and Ge (P4). The geometrical parameters of intermediate (INT4), transition state (TS4), and product (P4) appearing in reaction (4) are given in Fig. 5. The energies are listed in Table 1, and the potential energy surface for the cycloaddition reaction is shown in Fig. 2. According to Fig. 2, it can be seen that the process of reaction (4) is as follows: on the basis of INT3 formed in reaction (3), it further reacts with acetone (R2) to form an intermediate (INT4), which is a barrier-free exothermic reaction of 95.6 kJ mol⁻¹. And then intermediate (INT4) isomerizes to a spiro-heterocyclic ring compound with Si and Ge (P4) via a transition state (TS4) with an energy barrier of 26.2 kJ mol⁻¹.

Fig. 5 Optimized B3LYP/6-31G* geometrical parameters of INT4, TS4, P4 and the atomic numbering for the species in cycloaddition reaction (4). Bond lengths and bond angles are in angstrom and degree, respectively



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 dimethylsilylene germylidene and acetone. Namely:



In the reaction, the frontier molecular orbitals of R2 and INT3 are shown in Fig. 6. According to Fig. 6, the frontier molecular orbitals of R2, INT3 can be expressed in

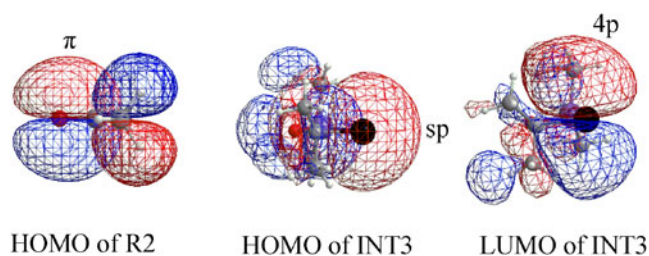


Fig. 6 The frontier molecular orbitals of R2, INT3

schematic diagram 7. The mechanism of this reaction could be explained with the molecular orbital diagram (Fig. 7) and Figs. 1, 4 and 5. According to Figs. 1 and 4, as dimethylsilylene germylidene initially interacts with acetone, due to the [2+2] cycloaddition of the bonding π -orbitals first results in a Si-heterocyclic four-membered ring germylene (INT3). Because INT3 is an active intermediate, INT3 further reacts with acetone (R2) to form a spiro-heterocyclic ring compound with Si and Ge (P4). The mechanism of this reaction could be explained with Fig. 7 and Fig. 5, according to orbital symmetry matching condition, when INT3 interacts with acetone (R2), the 4p unoccupied orbital of the Ge atom in INT3 will insert the π orbital of acetone from oxygen side, then the shift of π -electrons to the p unoccupied orbital gives a $\pi \rightarrow p$ donor–acceptor bond, leading to the formation of intermediate (INT4). As the reaction goes on, because of C(4)O(2)Ge (INT4: 128.5°, TS4: 101.3°, P4: 70.3°) gradually decrease, and the C(4)—O(2) (INT4: 1.236 Å, TS4: 1.246 Å, P4: 1.435 Å) bond gradually

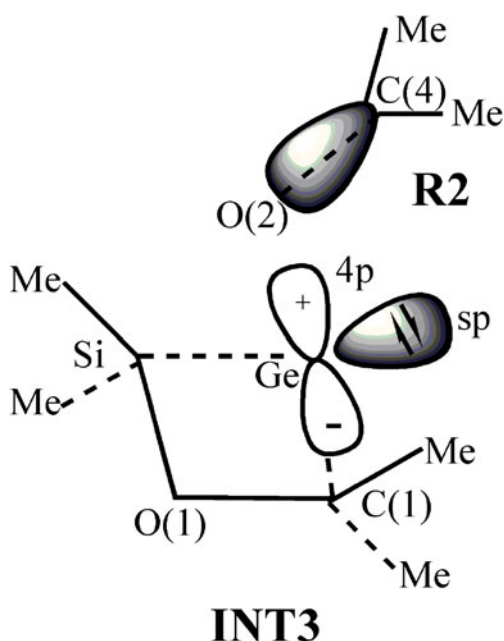


Fig. 7 A schematic interaction diagram for the frontier orbitals of INT3 and $\text{Me}_2\text{C}=\text{O}$ (R2)

elongate, the Ge in INT4 hybridizes to sp^3 hybrid orbital after the transition state (TS4), forming a spiro-heterocyclic ring compound with Si and Ge (P4).

Compared to the dominant reaction channels of the cycloaddition reaction between dimethylsilylene germylidene ($\text{Me}_2\text{Si}=\text{Ge}:$) and acetone with the cycloaddition reaction between silylene carbene ($\text{H}_2\text{Si}=\text{C}:$) [12] and acetone, the cycloaddition reaction between silylene silylene ($\text{H}_2\text{Si}=\text{Si}:$) [13] and acetone, the result indicates that the mechanism of those three reactions are similar, the first step is that the [2+2] cycloaddition reaction between two reactants ($\text{R1}+\text{R2}$) generates a four-membered ring intermediate (INTa), then it further reacts with acetone to form another intermediate (INTb). Finally, the intermediate (INTb) isomerizes to a spiro-ring compound (P) via a transition state (TS). Their potential energy surface indicates that each step of the main reaction channel is spontaneous in thermodynamics. In the reaction $\text{R1} + \text{R2} \rightarrow \text{INTa}$, INTa ($\text{H}_2\text{Si}=\text{C} + \text{Me}_2\text{C}=\text{O}$) = $-585.9 \text{ kJ mol}^{-1}$; INTa ($\text{H}_2\text{Si}=\text{Si} + \text{Me}_2\text{C}=\text{O}$) = $-512.5 \text{ kJ mol}^{-1}$; INTa ($\text{Me}_2\text{Si}=\text{Ge} + \text{Me}_2\text{C}=\text{O}$) = $-180.8 \text{ kJ mol}^{-1}$. Therefore, the spontaneity of $\text{Me}_2\text{Si}=\text{Ge} + \text{Me}_2\text{C}=\text{O} \rightarrow \text{INTa}$ is less than that of the other two reactions. In the reaction $\text{INTa} + \text{R2} \rightarrow \text{P}$, P ($\text{H}_2\text{Si}=\text{C} + \text{Me}_2\text{C}=\text{O}$) = $-342.4 \text{ kJ mol}^{-1}$; P ($\text{H}_2\text{Si}=\text{Si} + \text{Me}_2\text{C}=\text{O}$) = $-152.1 \text{ kJ mol}^{-1}$; P ($\text{Me}_2\text{Si}=\text{Ge} + \text{Me}_2\text{C}=\text{O}$) = $-113.0 \text{ kJ mol}^{-1}$. Therefore, in this step the spontaneity of ($\text{Me}_2\text{Si}=\text{Ge} + \text{Me}_2\text{C}=\text{O}$) is also smaller than the other two reactions. In the process of $\text{INTb} \rightarrow \text{TS} \rightarrow \text{P}$, the barrier of ($\text{H}_2\text{Si}=\text{C} + \text{Me}_2\text{C}=\text{O}$) is 54.9 kJ mol^{-1} ; barrier of ($\text{H}_2\text{Si}=\text{Si} + \text{Me}_2\text{C}=\text{O}$) is 51.7 kJ mol^{-1} ; barrier ($\text{Me}_2\text{Si}=\text{Ge} + \text{Me}_2\text{C}=\text{O}$) = 26.2 kJ mol^{-1} . So the reaction between $\text{Me}_2\text{Si}=\text{Ge}:$ and $\text{Me}_2\text{C}=\text{O}$ is faster than that of the other two reactions.

Conclusions

On the basis of the potential energy surface the cycloaddition reaction between singlet dimethylsilylene germylidene ($\text{Me}_2\text{Si}=\text{Ge}:$) and acetone obtained with the CCSD(T)//B3LYP/6-31G* method can be predicted. 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 Si-heterocyclic four-membered ring germylene (INT3), which is a barrier-free exothermic reaction of $180.8 \text{ kJ mol}^{-1}$. The second step is that INT3 further reacts with acetone (R2) to form an intermediate (INT4), which is also a barrier-free exothermic reaction of 95.6 kJ mol^{-1} . The third step is that INT4 isomerizes to a spiro-heterocyclic ring compound with Si and Ge (P4) via a transition state (TS4) with an energy barrier of 26.2 kJ mol^{-1} .

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