THEORETICAL STUDY OF THE MECHANISM OF CYCLOADDITION REACTION BETWEEN DICHLORO-SILYLENE CARBENE($\text{Cl}_2\text{Si}=\text{C}:$) AND ACETONE

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ABSTRACT

The mechanism of the cycloaddition reaction between singlet dichloro-silylene carbene and acetone has been investigated with DFT, 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)//B3LYP/6-31G* method. From the potential energy profile, it can be predicted that the reaction has two competitive dominant reaction pathways. The channel (I) consists of two steps: (1) the two reactants firstly form a four-membered ring intermediate through a barrier-free exothermic reaction of 307.1 kJ/mol; (2) four-membered ring intermediate then isomerizes to a CH_3 -transfer product via a transition state with energy barrier of 11.3 kJ/mol. The process of channel (II) is as following: on the basis of four-membered ring intermediate created between the two reactants, four-membered ring intermediate further reacts with acetone to form the intermediate through a barrier-free exothermic reaction of 165.8 kJ/mol; Then, intermediate isomerizes to a silicic bis-heterocyclic product via a transition state, for which the barrier is 57.6 kJ/mol.

Keywords: Dichloro-silylene carbene; Cycloaddition reaction; Potential energy surface;

1. INTRODUCTION

Since unsaturated carbene was recognized as an active intermediate in 1960s, it has not only attracted much attention from theoretical chemists but also has been practically applied to organic chemistry.^[1, 2] For example, it has been proved that unsaturated carbene can provide a simple and direct way for synthesizing the small-ring, highly strained compounds as well as those that can hardly be synthesized through conventional ways.^[2] So far, depth exploration has been done on the rearrangement reaction of alkylidene carbene,^[3, 4] and the insertion reaction of alkylidene carbene has also been studied.^[5, 6] Apeloig and Fox have made experimental and theoretical studies on the 3-dimensional selectivity of substituting groups from the products of the vinylidene-olefins addition reaction of alkylidene carbene.^[7, 8] Meanwhile, we have done a relatively systematic theoretical study on the cycloaddition reaction of alkylidene carbene.^[9–13] However, studies of unsaturated carbene have so far been limited to vinylidene and its reactions and there has been no published report of studies of silylene carbene and its derivatives ($\text{X}_2\text{Si}=\text{C}:$, $\text{X}=\text{H}, \text{CH}_3, \text{F}, \text{Cl}, \text{Br}, \dots$). It is a new branch of unsaturated carbene chemistry. It is quite difficult to investigate mechanisms of cycloaddition reaction directly by experimental methods due to the high activity of silylene carbene; therefore, the theoretical study is more practical. To explore the rules of cycloaddition reaction between silylene carbene and the asymmetric π -bonded compounds, considering the variety of the halogenate silylene carbene, dichloro-silylene carbene and acetone were selected as model molecules. The cycloaddition reaction mechanism was investigated and analyzed theoretically. The results show that this reaction proceeds in the following four possible pathways(considering the methyl transfer):

2. Calculation Methods

B3LYP /6-31G*^[14] implemented in the Gaussian 03^[15] package is employed to locate all the stationary points along the reaction pathways. Zero-point energy and CCSD(T) are included for the energy calculations. Full optimization and vibrational analysis are done for the stationary points on the reaction profile. In order to further confirm the correctness of the relevant species, vibration analysis are included, and the intrinsic reaction coordinate (IRC)^[16, 17] 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 the three-membered ring product P1

The geometrical parameters for the intermediates (INT1a and INT1b), transition states (TS1a and TS1b) and product (P1) appearing in reaction(1) between dichloro-silylene carbene and acetone 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.

Fig. 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.

Fig. 2: The potential energy surface for the cycloaddition reactions between dichloro silanylene carbene and acetone with CCSD(T)/B3LYP/6-31G*.

Table 1: Zero point energy(ZPE/ a.u), total energies (E_T /a.u) 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	^b E_R	^a E_T	^b E_R
Reaction(1)	R1+R2	0.090041	-1440.89863	0.0	-1438.61067	0.0
	INT1a	0.093552	-1440.99069	-239.9	-1438.67006	-155.9
	TS1a(INT1a-P1)	0.092161	-1440.96511	-174.5	-1438.64990	-103.0
	INT1b	0.094424	-1441.02107	-321.5	-1438.71632	-277.4
	TS1b(INT1b-P1)	0.093479	-1441.00309	-274.3	-1438.69648	-225.3
	P1	0.094840	-1441.05383	-407.5	-1438.74031	-340.4
Reaction(2)	R1+R2	0.090041	-1440.89863	0.0	-1438.61067	0.0
	INT1a	0.093552	-1440.99069	-239.9	-1438.67006	-155.9
	TS2(INT1a-P2)	0.091988	-1440.96768	-181.3	-1438.64893	-100.5
	P2	0.094208	-1441.02985	-344.5	-1438.72024	-313.9
	TS2.1(P2-P2.1)	0.091546	-1440.92686	-74.1	-1438.61384	-8.3
	P2.1	0.094968	-1441.05928	-421.8	-1438.74771	-359.8
Reaction(3)	P2+R2	0.178237	-1634.10123	0.0	-1631.21423	0.0
	INT3	0.182260	-1634.11425	-34.2	-1631.22338	-24.0
	TS3(INT3-P3)	0.181999	-1634.09530	15.6	-1631.21200	5.9
	P3	0.184095	-1634.17604	-196.4	-1631.29711	-217.6
Reaction(4)	R1+R2	0.090041	-1440.89863	0.0	-1438.61067	0.0
	INT4	0.093858	-1441.03344	-353.9	-1438.72762	-307.1
	TS4 (INT4-P4)	0.093383	-1441.03103	-347.6	-1438.72332	-295.8
	P4	0.096338	-1441.16180	-691.0	-1438.85200	-633.6
Reaction(5)	INT4+R2	0.177887	-1634.10482	0.0	-1631.22162	0.0
	INT5	0.183663	-1634.16974	-170.4	-1631.28478	-165.8
	TS5(INT5-P5)	0.182762	-1634.14086	-94.6	-1631.26285	-108.2
	P5	0.185301	-1634.22022	-303.0	-1631.34749	-330.5

$$^a E_T = E(\text{Species}) + \text{ZPE}, \quad ^b E_R = E_T - E_{(R1+R2)}, \quad ^c E_R = E_T - E_{(P2+R2)}, \quad ^d E_R = E_T - E_{(INT4+R2)}$$

The unique imaginary frequency of the transition state TS1a and TS1b are 365.4i and 276.9i, and therefore the transition states can be affirmed as the real ones. IRC (with the step-length of 0.1 amu^{1/2}bohr) analysis confirms that TS1a connects INT1a and P1, and TS1b connects INT1b and P1. According to Fig. 2, it can be intuitively seen that reaction (1) has two reaction pathways a and b, the two pathways are all composed of two steps: the first one is that the two reactants (R1, R2) firstly form intermediates INT1a and INT1b, which are barrier-free exothermic reactions with ΔE of 155.9 kJ/mol and 277.4 kJ/mol; and the second one is an isomerization of intermediates INT1a and INT1b to a three-membered ring product P1 via transition states TS1a and TS1b, with energy barriers of 52.9 kJ/mol and 52.1 kJ/mol. Because there is energy barrier difference of 0.8 kJ/mol between path a and b, so path a and b are the two competitive reaction pathway.

3.2. Reaction(2): channels of forming four-membered ring product P2 and CH₃-transfer product P2.1

The geometrical parameters for the transition states (TS2, TS2.1) and products (P2, P2.1) appearing in reaction(2) between dichloro-silylene carbene and acetone 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.

Fig. 3: Optimized B3LYP/6-31G* geometrical parameters of TS2, TS2.1, P2, P2.1 and the atomic numbering for cycloaddition reaction(2). Lengths are in Å and angles in degree.

The unique imaginary frequencies of the transition states TS2 and TS2.1 are 159.5i and 653.9i, respectively. Therefore, these transition states can be affirmed as the real ones. Their IRC (with the step-length of 0.1 amu^{1/2}bohr) analysis confirms that TS2 connects INT1a and P2; TS2.1 connects P2 and P2.1.

According to Fig. 2, it can be intuitively seen that reaction (2) is composed of three steps: the first one is that the two reactants firstly form an intermediate INT1a, which is a barrier-free exothermic reaction with ΔE of 155.9 kJ/mol; and the second one is an isomerization of intermediate INT1a to a four-membered ring product P2 via a transition state TS2, with an energy barrier of 55.4 kJ/mol; then the third step is the product P2 isomerizes to the CH₃-transfer product P2.1 via transition state TS2.1 with energy barriers of 305.6 kJ/mol. According to the comparison of reaction(2) with reaction(1), the energy barrier of TS2 are 2.5 and 3.3 kJ/mol higher than that of TS1a and TS1b, respectively. So reaction(2) and reaction(1) are the two competitive dominant reaction pathways.

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

In reaction(3), the four-membered ring product P2 further reacts with acetone (R2) to form the silicic bis-heterocyclic product 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. And the potential energy surface for reaction(3) is illustrated in Fig. 2.

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

The unique imaginary frequency of the transition state TS3 is 113.8i, and the transition state can therefore be affirmed as the real one. IRC (with the step-length of 0.1 amu^{1/2}bohr) analysis of TS3 confirms that TS3 connects INT3 and P3. According to Fig. 2, the process of Reaction(3) is as following: on the basis of P2 created from the reaction(2) between R1 and R2, P2 further reacts with acetone (R2) to form the intermediate INT3 through a barrier-free exothermic reaction of 24.0 kJ/mol. Then, INT3 isomerizes to a silicic bis-heterocyclic product P3 via a transition state TS3, for which the barrier is 29.9 kJ/mol. Compared reaction(3) with P2→P2.1 in reaction(2), it is realizing that the two reaction form a mutual competition reaction due to scrambling for P2 together. In reaction(3), the combination of P3 and R2 is just through a barrier-free exothermic reaction of 24.0 kJ/mol. However, in reaction(2), the energy barrier of P2→P2.1 is 305.6 kJ/mol. So, reaction(3) will be the dominant reaction pathway.

3.4. Reaction(4): channels of forming four-membered ring intermediate INT4 and CH₃-transfer product P4

The geometrical parameters for the intermediate(INT4), transition state (TS4) and product (P4) appearing in reaction(4) between dichloro-silylene carbene and acetone are given in Fig. 5. The energies are listed in Table 1, and the potential energy surfaces for the cycloaddition reaction are shown in Fig. 2.

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

The unique imaginary frequencies of the transition state TS4 is 357.0i. Therefore, the transition state can be affirmed as the real one. Its IRC (with the step-length of 0.1 amu^{1/2}bohr) analysis confirms that TS4 connects INT4 and P4.

According to Fig. 2, Reaction(4) consists of two steps: (1) the two reactants (R1, R2) firstly form an intermediate INT4 through a barrier-free exothermic reaction of 307.1 kJ/mol; (2) INT4 then isomerizes to CH₃-transfer product P4 via a transition state TS4 with energy barrier of 11.3 kJ/mol. Compared reaction(4) with reaction(1), reaction(2) and reaction(3), the energy barrier of TS4 is 41.6, 40.8 and 44.1 lower than that of TS1a, TS1b and TS2, so reaction(4) will be the dominant reaction channel.

3.5. Reaction(5): channels of forming silicic bis-heterocyclic product P5

In reaction(5), the four-membered ring intermediate INT4 further reacts with acetone (R2) to form the silicic bis-heterocyclic product P5. The geometric

parameters for the intermediate INT5, the transition state TS5 and the product P5 appearing in reaction(5) are given in Fig. 6. The energies are listed in Table 1. And the potential energy surface for reaction(5) is illustrated in Fig. 2.

Fig. 6: Optimized B3LYP/6-31G* geometrical parameters of INT5, TS5, P5 and the atomic numbering for cycloaddition reaction(5). Lengths are in Å and angles in degree.

The unique imaginary frequency of the transition state TS5 is 164.5i, and the transition state can therefore be affirmed as the real one. IRC (with the step-length of 0.1 amu^{1/2}bohr) analysis of TS5 confirms that TS5 connects INT5 and P5. According to Fig. 2, the process of Reaction(5) is as following: on the basis of INT4 created from the reaction(4) between R1 and R2, INT4 further reacts with acetone (R2) to form the intermediate INT5 through a barrier-free exothermic reaction of 165.8 kJ/mol. Then, INT5 isomerizes to a silicic bis-heterocyclic product P5 via a transition state TS5, for which the barrier is 57.6 kJ/mol. Compared reaction(5) with reaction(4), it is realizing that the two reaction form a mutual competition reaction due to scrambling for INT4 together. In reaction(5), the combination of INT4 and R2 is just through a barrier-free exothermic reaction of 165.8 kJ/mol. In reaction(4), the energy barrier of INT4 $\rightarrow$ P4 is only 11.3 kJ/mol. So, reaction(5) and reaction(4) are the two competitive dominant reaction pathways.

3.5. Theoretical analysis and explanation of the dominant reaction channels

According to the above analysis, the cycloaddition reaction between singlet dichloro-silylene carbene and acetone has two competitive dominant reaction pathways. namely:

In the two reaction, the frontier molecular orbital of R1, R2, INT4 are shown in Fig. 7.

Fig. 7: The frontier molecular orbital of R1, R2, INT4

R1: dichloro-silylene carbene($\text{Cl}_2\text{Si}=\text{C}:$)
 R2: acetone

HOMO: Highest Occupied Molecular Orbital.
 LUMO: Lowest Unoccupied Molecular Orbital.

According to Fig. 7, the mechanism of two reaction could be explained with the molecular orbital diagram (Figs.8 and 9) and Figs. 5 and 6. According to Fig. 8 and 5, As dichloro-silylene carbene (R1) initially interacts with acetone (R2), the [2+2] cycloaddition of the bonding π -orbitals firstly results in a four-membered ring intermediate INT4. In the conformation of INT4,

atom C(1) is unsaturated, it stores high energy, due to the high energy, transfer reaction of methyl in the conformation have occurred from C(2) to C(1), leading to the more stable formation of CH_3 -transfer product P4 via transition state TS4. In the conformation of P4, C(1) hybridizes into sp^3 hybrid orbital and forms σ bond with three atoms neighboring, and forms π bond with C(2) synchronously, so, C(1) is saturated, this is the main reason why P4 is more stable than INT4.

The mechanism of reaction(5) could be explained with the molecular orbital diagram (Fig. 9) and Fig. 6. In the conformation of INT4, atom C(1) is unsaturated, as dichloro-silylene carbene (R1) initially interacts with oxygen side of the acetone (R2), C(1) in INT4 hybridizes into sp^2 hybrid orbital and forms intermediate INT5 with acetone (R2). As the reaction goes on, the dihedral angles $\angle \text{C(5)O(2)C(1)Si}$ (INT5: 1.2° , TS5: 81.0° , P5: 129.0°) gradually increase, and $\angle \text{C(5)O(2)C(1)}$ (INT5: 129.6° , TS5: 101.5° , P5: 61.9°) gradually decrease, the C(5)O(2) bond (INT5: $1.300\text{\AA}$, TS5: $1.345\text{\AA}$, P5: $1.446\text{\AA}$) gradually lengthens. These changes finally make INT5 isomerize to silicic bis-heterocyclic product P5 via transition state TS5. In the conformation of P5, C(1) hybridizes into sp^3 hybrid orbital and forms bonds with four atoms neighboring.

Fig. 8: A schematic interaction diagram for the frontier orbitals of $\text{Cl}_2\text{Si}=\text{C}:$ (R1) and $\text{Me}_2\text{C}=\text{O}$ (R2)

Fig. 9: A schematic interaction diagram for the frontier orbitals of INT4 and $\text{Me}_2\text{C}=\text{O}$ (R2)

4. CONCLUSION

On the basis of the potential energy surface obtained with the CCSD(T)//B3LYP/6-31G* method for the cycloaddition reaction between singlet dichloro-silylene carbene and acetone, it can be predicted that the reaction has two competitive dominant reaction pathways. Reaction(4) consists of two steps: (1) the two reactants (R1, R2) firstly form a four-membered ring intermediate INT4 through a barrier-free exothermic reaction of 307.1 kJ/mol; (2) INT4 then isomerizes to CH_3 -transfer product P4 via a transition state TS4 with energy barrier of 11.3 kJ/mol. The process of reaction(5) is as following: on the basis of INT4 created between R1 and R2, INT4 further reacts with acetone (R2) to form the intermediate INT5 through a barrier-free exothermic reaction of 165.8 kJ/mol; Then, INT5 isomerizes to a silicic bis-heterocyclic product P5 via a transition state TS5, for which the barrier is 57.6 kJ/mol.

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