

# Theoretical Study on the Mechanism of the Cycloaddition Reaction between Alkylidene Carbene and Ethylene

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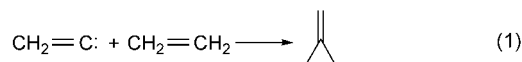
The mechanism of cycloaddition reaction between singlet alkylidene carbene and ethylene has been investigated with second-order Moller-Plesset perturbation theory (MP2). By using 6-31G\* basis, geometry optimization, vibrational analysis and energetics have been calculated for the involved stationary points on the potential energy surface. The results show that the title reaction has two major competition channels. An energy-rich intermediate (INT) is firstly formed between alkylidene carbene and ethylene through a barrier-free exothermic reaction of 63.62 kJ/mol, and the intermediate then isomerizes to a three-membered ring product (P1) and a four-membered ring product (P2) via transition state TS1 and TS2, in which energy barriers are 47.00 and 51.02 kJ/mol, respectively. P1 is the main product.

**Keywords** alkylidene carbene, cycloaddition reaction, second-order Moller-Plesset perturbation theory, potential energy surface

## Introduction

Cycloaddition has been long and widely used and rapidly advanced in organic chemistry. Especially since Woodward and Hoffmann put forward the orbital symmetry rule, which has deepened the understanding of such kind of reaction, the mechanism investigation using the rule has been one of the most interesting topics for experimentalists as well as theoreticians. Since unsaturated carbene was recognized as an active intermediate in 1960s, it has not only attracted much attention from theoretical chemists, but also been practically applied to organic chemistry.<sup>1,2</sup> For example, it provides simple and direct synthesis of small-ring, highly strained compounds, as well as those which could be hardly synthesized through conventional ways.<sup>2</sup> Apeloig and Fox *et al.*<sup>3,4</sup> have ever extensively studied the stereoselectivity of the alkylidene carbene addition to olefins using experimental and theoretical methods, as well as the rearrangement of alkylidene carbene.<sup>5,6</sup> In a previous paper, we explored the mechanism of cycloaddition reaction between alkylidene carbene and asymmetric  $\pi$  systems.<sup>7</sup> But there is still no report on the mechanism of the cycloaddition reaction between alkylidene carbene and symmetric  $\pi$  systems. Here, based on its activity, we choose alkylidene carbene and ethylene as model molecules to further explore the mechanism of the cycloaddition reaction between alkylidene carbene and symmetric  $\pi$  systems. The results indicate that cycloaddition between them has two leading reactions, (1) and (2) as shown below, which are similar to the results from Apeloig and Fox *et al.*,<sup>3,4</sup> with a main

product of three-membered ring conformation. Furthermore, it is found that the reaction (2) becomes a competition to reaction (1).



## Calculation methods

MP2/6-31G\*<sup>8</sup> implemented in Gaussian98 package was employed for all the involved calculations. Full optimization and harmonic vibrational analysis were performed for the stationary points on the reaction profile. Zero point energy correction was included in energy calculations. In order to explicitly establish the relevant species, IRC<sup>9,10</sup> was also run for all the transition states appearing on the cycloaddition energy surface profile.

## Results and discussion

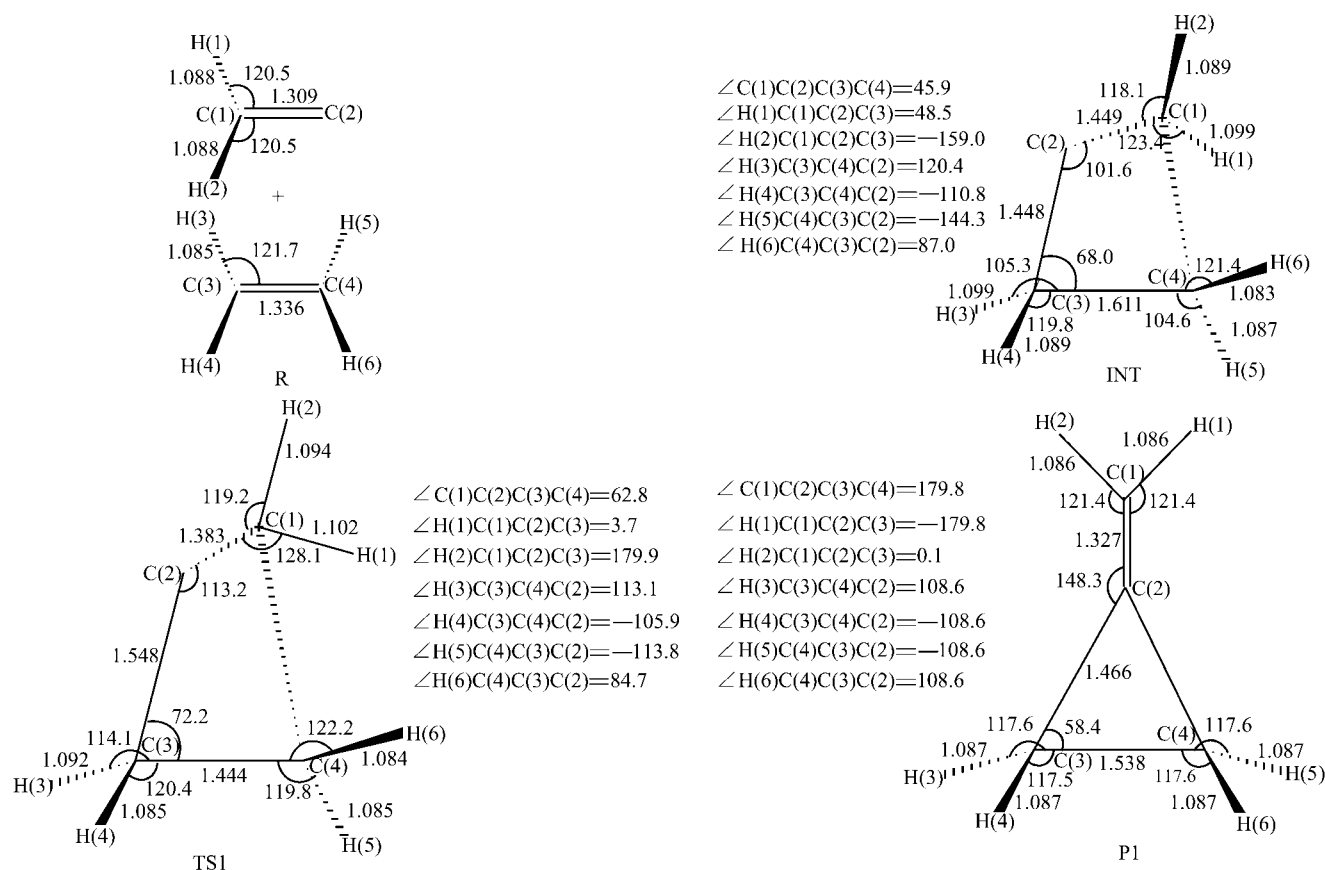
### Reaction (1)

Theoretical calculations indicate that the ground state of alkylidene carbene is singlet. The geometric parameters of the reaction intermediate (INT), transition state (TS1) and product (P1) in the cycloaddition (1) with ethylene are shown in Figure 1, and the energies is shown in Table 1.

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**Figure 1** The geometrical parameters and the atomic numbering for the species in cycloaddition reaction (1) at MP2/6-31G\* level. Lengths are in 0.1 nm and angles in degree.

**Table 1** The electronic structure energies ( $E_{SE}$ ), zero-point energies ( $E_{ZP}$ ), total energies ( $E_T$ ) and relative energies ( $E_R$ ) for the species of the cycloaddition reaction between alkylidene carbene and ethylene at MP2/6-31G\* level

Species	$E_{SE}/\text{a.u.}$	$E_{ZP}/\text{a.u.}$	$E_T/\text{a.u.}$	$E_R/(\text{kJ} \cdot \text{mol}^{-1})$
R	-155.27060	0.07620	-155.19440	0.0
INT	-155.30564	0.08701	-155.21863	-63.62
TS1	-155.28575	0.08502	-155.20073	-16.62
P1	-155.39670	0.08726	-155.30944	-302.04
TS2	-155.28292	0.08372	-155.19920	-12.60
P2	-155.41018	0.08838	-155.32180	-334.49

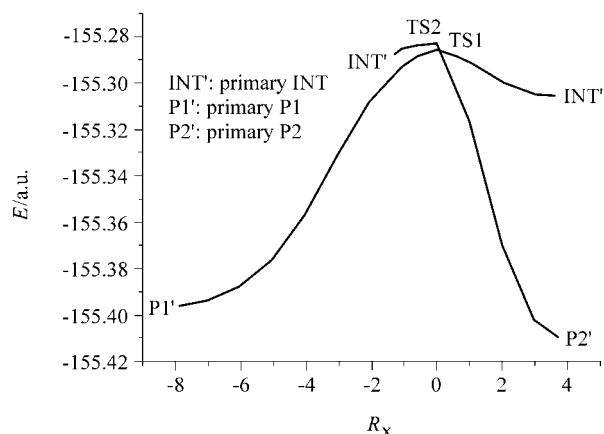
$${}^a E_T = E_{SE} + E_{ZP}$$

**Table 2** The harmonic vibrational frequencies for the transition states of the cycloaddition reaction between alkylidene carbene and ethylene at MP2/6-31G\* level

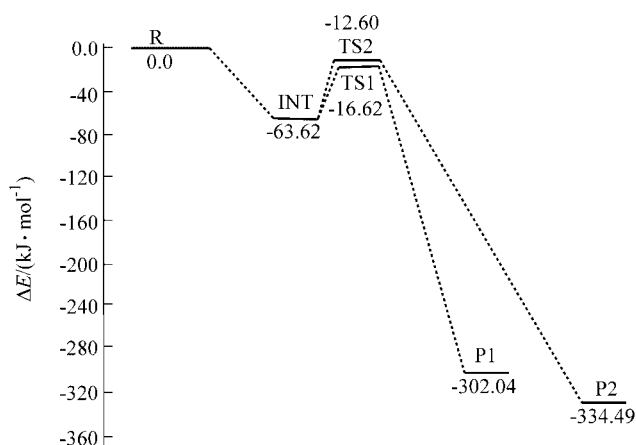
Transition state	Vibration frequency/ $\text{cm}^{-1}$								
TS1	-525.3	245.5	600.9	702.3	742.5	874.8	914.0	1029.8	
	1039.3	1102.2	1119.9	1152.3	1223.8	1244.4	1445.4	1529.5	
	1571.3	1623.7	3023.0	3154.9	3174.1	3221.3	3261.1	3323.6	
TS2	-684.9	264.4	728.5	851.8	893.7	920.3	944.0	1023.3	
	1031.8	1128.9	1178.7	1215.2	1255.5	1288.5	1413.6	1438.6	
	1510.3	1541.9	2310.2	3124.1	3128.9	3177.1	3183.7	3196.9	

Vibrational frequencies of the transition state (TS1) are listed in Table 2, where the frequency 525.3i could be confirmed as its unique imaginary frequency, and the transition state should be the real one. According to the calculation for the IRC of TS1 (illustrated in Figure 2), and the further optimization of primary IRC results, TS1 connects INT with P1.

Figure 3 illustrates the potential energy profile of reaction (1), according to Table 1. The figure shows directly that the reaction (1) consists of two steps: the first one is a barrier-free exothermic reaction of 63.62 kJ/mol, giving an energy-rich intermediate INT; then INT isomerizes to product P1, with a barrier of 47.00 kJ/mol. Since the barrier of the latter reaction is 16.62



**Figure 2** Curve of the intrinsic reaction coordinate of the cycloaddition reactions of alkylidene carbene with ethylene.

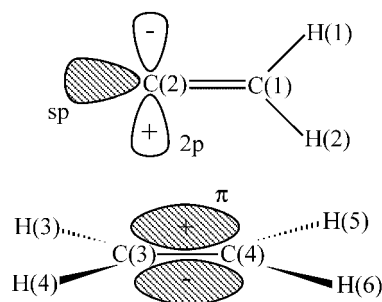


**Figure 3** Potential energy surface for the cycloaddition reactions of alkylidene carbene with ethylene at MP2/6-31G\* level.

kJ/mol lower than that of the reactants (R), the reaction will be easily finished.

The mechanisms of the reaction (1) could be explained with the molecular orbital diagram (shown in Figure 4) and Figure 1. According to MO symmetry-adaptation rule, the insertion of the unoccupied 2p orbital of C(2) from the C(3) end of ethylene to the  $\pi$  orbital forms  $\pi \rightarrow p$  donor-acceptor bond between C(2)—C(3), meanwhile, electrons from  $\pi$  orbital of the alkylidene carbene interact with the  $\pi$  orbital of ethylene from side, resulting in the bond formation between C(1) and C(4). So a twisted four-membered ring intermediate INT is formed at first when alkylidene carbene reacts with ethylene. In the conformation of INT, the bond order values of C(2)—C(3) and C(1)—C(4) are 0.38934 and 0.18851, respectively, which are evidently different.

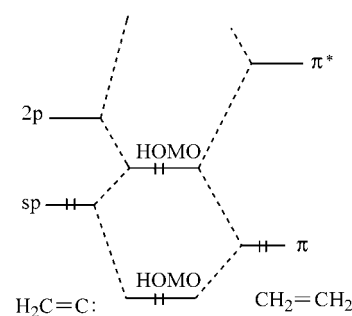
It is found that the two reactants directly generate the intermediate INT without a transition state, and we found there is indeed no transition state and any other intermediates through the calculation by gradually stretching the bond between C(2)—C(3) in the intermediate. We propose that such a result should be attributed to the strong binding between 2p unoccupied orbital of



**Figure 4** MO symmetry-adaptation of  $\text{H}_2\text{C}=\text{C}:$  and  $\text{H}_2\text{C}=\text{CH}_2$ .

alkylidene carbene and the electrons in  $\pi$  orbital of ethylene, as well as the reaction of the two  $\pi$  orbitals in alkylidene carbene and ethylene.

In the conformation of INT, the INT stores high energy since the sp lone electron pair in C(2) does not participate in the bond formation. So the system reduces its own energy by increasing the dihedral angles  $\angle\text{C}(1)\text{C}(2)\text{C}(3)\text{C}(4)$  (INT:  $45.9^\circ$ ; TS1:  $62.8^\circ$ ; P1:  $179.8^\circ$ ) and  $\angle\text{C}(1)\text{C}(2)\text{C}(3)$  (INT:  $101.6^\circ$ ; TS1:  $113.2^\circ$ ; P1:  $148.3^\circ$ ), and finally changes the INT into more stable product P1 via transition state TS1. In the conformation of P1, looped donor-acceptor bonds between sp lone electron pair of C(2) and  $\pi^*$  unoccupied orbital of C(3) end ( $\text{sp} \rightarrow \pi^*$ ), 2p unoccupied orbital of C(2) and  $\pi$  electrons of C(4) ( $\pi \rightarrow p$ ) are formed in P1, respectively, as shown in Figure 5, together with the  $\sigma$  and  $\pi$  double bonds of C(1)=C(2), which are responsible for the stability of P1.



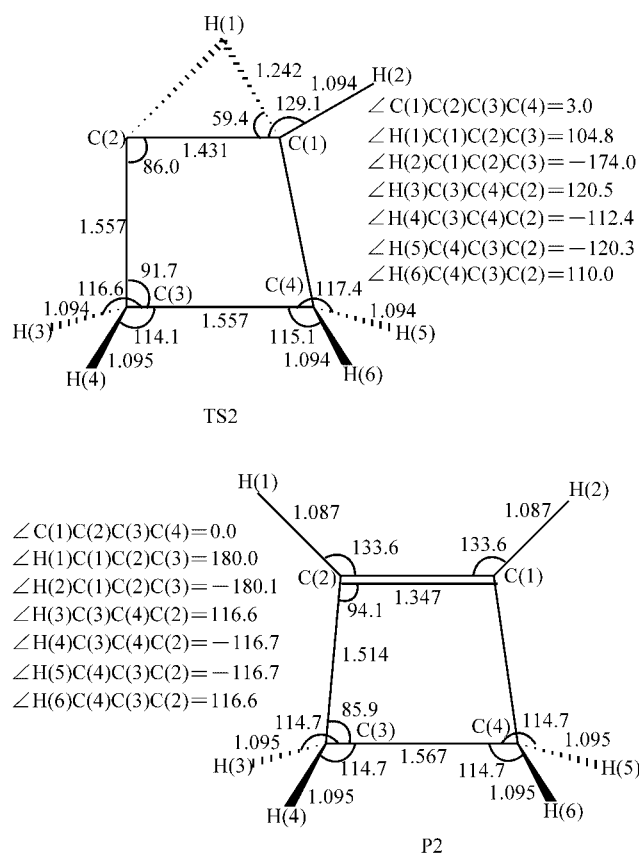
**Figure 5** A schematic interaction diagram for the frontier orbitals of  $\text{H}_2\text{C}=\text{C}:$  and of  $\text{H}_2\text{C}=\text{CH}_2$ .

## Reaction (2)

The energies of the transition state TS2 and product P(2) are listed in Table 1. The geometric parameters are shown in Figure 6.

Vibrational frequencies of the transition state (TS2) are listed in Table 2, where the frequency 684.9i could be confirmed as its unique imaginary frequency, and the transition state should be the real one. According to the calculation for the IRC of TS2 (illustrated in Figure 2), and the further optimization of primary IRC results, TS2 connects INT with P2.

Theoretical study indicates that the route of the reaction (2) is as follows: the two reactants form an energy-rich intermediate INT, a barrier-free exothermic



**Figure 6** Geometrical parameters of TS2, P2 and the atomic numbering for cycloaddition reaction (2) at MP2/6-31G\* level. Lengths are in 0.1 nm and angles in degree.

reaction of 63.62 kJ/mol; and then the INT isomerizes to four-membered ring product P2 via a transition state TS2, with a barrier of 51.02 kJ/mol.

Figure 3 includes the potential energy profile of reaction (2) according to Table 1. It can be concluded from the figure that the reaction (1) competes with reaction (2). Because the two reactions are both energy decreasing reaction, the two potential barrier energies, with a difference of only 4.02 kJ/mol, are lower than that of reactant (R). So it can be predicted from thermodynamics that they are competition reactions which can be simultaneously finished. But from the view of dynamics, the barrier energy of reaction (1) is 4.02 kJ/mol lower than that of reaction (2), which will make the velocity of the reaction of TS1 to P1 5 times higher than that of TS2 to P2 according to the exponential rule. Therefore, in the products of the cycloaddition, P1 will

be the main one.

The mechanism of reaction (2) could be analyzed with Figures 4, 5 and 1. Similar to reaction (1), the two reactants form a twisted four-membered ring intermediate INT at first. The INT has a high energy since the sp lone pair electrons in C(2) do not participate in the bond formation. That results in the migration of H(1) atom from C(1) to C(2) side and the subsequent change from INT to P2 via TS2. In the formed P2 conformation, the C(2) atom changes to sp<sup>2</sup> hybridization and forms  $\sigma$  bond with the neighbor three atoms, and forms  $\pi$  bond with C(1) atom simultaneously. So there are no sp lone pair electrons any longer in C(2) atom. That will make the P2 conformation much stable than INT.

## Conclusion

Based on the surface energy profile calculated with MP2/6-31G\* method for the cycloaddition reaction between singlet alkylidene carbene and ethylene, it can be predicted that there are two competition reactions in the cycloaddition. The route of the two reactions is as follows: the two reactants first give rise to an energy-rich intermediate (INT), which is formed through a barrier-free exothermic reaction of 63.62 kJ/mol, and then isomerize to 3-membered ring product P1 and 4-membered ring product P2 via transition state TS1 and TS2, with an energy barrier of 47.00 and 51.02 kJ/mol, respectively. The P1 will be the main product.

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