

A THEORETICAL STUDY ON THE MECHANISM OF THE ADDITION REACTION BETWEEN CYCLOPROPENYLIDENE AND ETHYLENE

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ABSTRACT

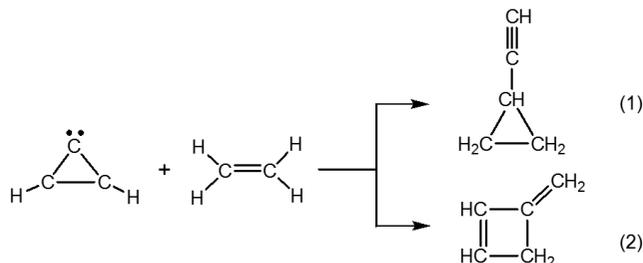
The reaction mechanism between cyclopropenylidene and ethylene has been systematically investigated employing the MP2/6-311+G* level of theory to better understand the cyclopropenylidene reactivity with unsaturated hydrocarbons. Geometry optimization, vibrational analysis, and energy property for the involved stationary points on the potential energy surface have been calculated. Energies of all the species are also further refined by the CCSD(T)/6-311+G* single-point calculations. Firstly, one important reaction intermediate (INTa) has been located via a transition state (TSa). After that, the common intermediate (INTb) for the two pathways (1) and (2) has been formed via TSb. At last, two different products possessing three- and four-membered ring characters have been obtained through two reaction pathways. In the reaction pathway (1), a three-membered ring alkyne compound has been obtained. As for the reaction pathway (2), a four-membered ring conjugated diene compound has been formed, which is the most favorable reaction to occur from the kinetic and thermodynamic viewpoints.

Keywords: Cyclopropenylidene, Ethylene, Addition reaction, Theoretical study.

1. INTRODUCTION

Carbene can be defined as a divalent carbon intermediate, where the carbene carbon is linked to two adjacent groups by covalent bonds and possesses two nonbonding electrons. It is well known that carbene plays an important role in organic chemistry, especially for the addition reaction with C=C and C=O double bond¹⁻⁴. Therefore, the studies of carbene have attracted more attentions theoretically and experimentally. For example, carbene can be used to provide simple and direct synthesis for small-ring, highly strained compounds, as well as those that are hardly synthesized through conventional ways⁵. The reactions between carbene or substituted carbene and some small molecules have been studied theoretically by Lu et al.⁶⁻⁸. Apeloig et al. extensively studied the mechanisms and stereoselectivity of carbene addition to olefin experimentally and theoretically⁹⁻¹⁰. Recently, the reactions between carbene and small-ring strained molecules, such as epoxyethane and azacyclopropane, have been investigated theoretically¹¹⁻¹².

As the simplest vinylidene carbenes, C₃H₂ is a class of highly unsaturated carbenes, which are of great interest for the chemistry of carbon-rich gas-phase environments. As displayed in Scheme 1, three isomers have been located on its potential energy surface. Here, propynylidene is the only C₃H₂ isomer with a triplet electronic ground state and the cyclopropenylidene and propadienylidene are in singlet state¹³⁻¹⁶. Moreover, all of them can be interconverted by photolysis¹⁷⁻¹⁹. The structural characters, thermochemistry, and isomerization of C₃H₂ carbenes have been investigated extensively^{13,18,20-22}. It was found that the singlet cyclopropenylidene is the most stable isomer among the three species²³⁻²⁶, which is lower in energy by about 42-59 and 59-92 kJ/mol than that of propadienylidene and propynylidene, respectively²⁷⁻³¹. These highly reactive carbene molecules are fundamentally important not only within the context of organic chemistry^{32,33}, but also within the context of the chemistry of the interstellar medium³⁴⁻³⁸. Recently, the formation mechanism of the C₃H₂ carbenes have been proposed by Goulay et al. using tunable vacuum ultraviolet photoionization and time-resolved mass spectrometry³⁹.



Scheme 1. The three isomers of C₃H₂.

In consideration of the high reactivity and the importance of addition reaction involving C₃H₂ carbenes, we have explored the reaction between propadienylidene and alkene using theoretical calculations⁴⁰. However, less is known about the reaction mechanism between cyclopropenylidene and unsaturated hydrocarbon compound to the best of our knowledge. In the absence of experimental information, a theoretical investigation on the above reaction appears to be highly desirable. Therefore, in the present study, the reaction mechanism between cyclopropenylidene and ethylene has been systematically investigated employing the second-order Moller-Plesset perturbation theory (MP2) method so as to better understand the cyclopropenylidene reactivity with unsaturated C=C compounds. As a result, for the addition reaction between cyclopropenylidene and ethylene, two different products characterized by three- and four-membered rings have been obtained via two different reaction pathways. The corresponding reaction mechanisms have been clarified detailedly. Hopefully, the present results not only can promote the progress of the relevant experiments, but also can provide insights into the reactivity of C₃H₂ carbene with unsaturated compounds containing C=C double bonds as well as to enrich the available data for the relevant carbene chemistry.

2. CALCULATION METHOD

The MP2 method in combination with 6-311+G* basis set has been employed to locate all the stationary points along the reaction pathways. Frequency analyses have been carried out to confirm the nature of the minima and transition states. Moreover, intrinsic reaction coordinate (IRC) calculations have also been performed to further validate the calculated transition states connecting reactants and products. Additionally, the relevant energy quantities, such as reaction energies and barrier heights, have been corrected with the zero-point vibrational energy (ZPVE) corrections.

To further refine the calculated energy parameters, single point energy calculations have been performed at the CCSD(T)/6-311+G* level of theory based on the stationary points optimized at the MP2/6-311+G* level of theory. As summarized in Table 1, both levels can give consistent results for the calculated reaction profile of the addition reaction. For the sake of simplicity, the energetic results at the CCSD(T)/6-311+G*/MP2/6-311+G* level of theory have been mainly discussed below if not noted otherwise.

All the calculations have been performed using Gaussian 98 program⁴¹.

3. RESULTS AND DISCUSSION

As displayed in Figure 1, two possible reaction pathways for the addition reaction between cyclopropenylidene and ethylene have been proposed. Correspondingly, the calculated relative energies for the available stationary points have been summarized in Table 1.

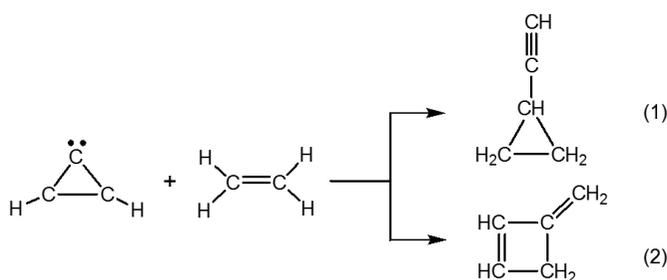


Figure 1. The proposed two reaction pathways for the addition reaction between cyclopropenylidene and ethylene.

Table 1: The calculated relative energies (in kJ/mol) with respect to the isolated reactants at the MP2/6-311+G* level of theory considering the ZPVE corr.

Pathways	Relative Energies			
Pathway (1)	TSa	INTa	TSb	INTb
	77.4(80.6)	-138.5(-113.7)	50.5(50.1)	45.0(36.2)
	TS1	P1		
	107.5(141.6)	-266.9(-238.4)		
Pathway (2)	TS2a	INT2a	TS2b	INT2b
	91.4(85.9)	-215.7(-201.4)	-36.(-11.6)	-17.1(-25.9)
	TS2c	P2		
	13.5(17.1)	-295.7(-282.5)		

^a The data in parentheses refer to the results at the CCSD(T)/6-311+G**/MP2/6-311+G* level of theory considering the ZPVE corrections.

3.1 Reaction pathway (1): three-membered ring product channel

The geometric parameters for the reactants (cyclopropenylidene and ethylene), transition states (TSa, TSb, and TS1), intermediates (INTa and INTb), and product (P1) involved in the reaction pathway (1) are displayed in Figure 2. Here, a three-membered ring product P1 has been obtained in this pathway. The corresponding reaction profile is illustrated in Figure 3.

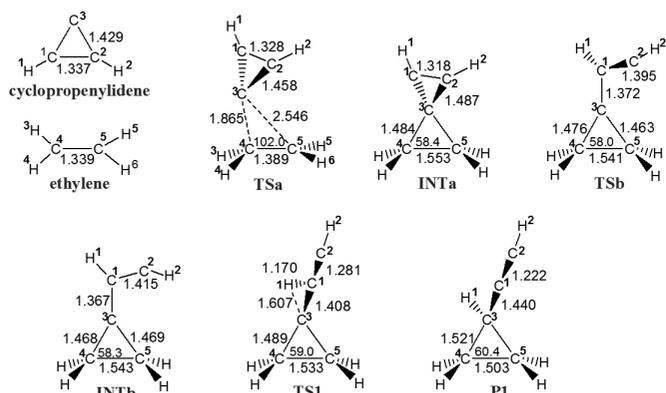


Figure 2. Optimized structures of the reactants (cyclopropenylidene and ethylene), transition states (TSa, TSb, and TS1), intermediates (INTa and INTb), and product (P1) in the reaction pathway (1) at the MP2/6-311+G* level of theory, where the bond length and bond angle are in angstrom and degree, respectively.

The formation of the first intermediate INTa occurs along the pathway (1) via a barrier of 80.6 kJ/mol. As shown in Figure 2, the distances from C³ to C⁴ and C⁵ atoms in TSa are 1.865 and 2.546 Å, and the bond lengths of C¹-C², C²-C³, and C⁴-C⁵ are only slightly changed (1.328 vs 1.337, 1.458 vs 1.429, 1.389 vs 1.339 Å), respectively.

vs 1.339 Å) compared with the reactants, respectively. The smoothness of the full IRC shown in Figure 4 further indicates that TSa connects reactants and the three-membered ring intermediate INTa.

Due to the existence of tension in three-membered ring, the second step of the pathway (1) is that C²-C³ bond in INTa opens to form an intermediate INTb via TSb, where the barrier is 50.1 kJ/mol relative to the reactants.

In INTb, the C¹ atom adopts *sp*² hybridization and the C¹-C² and C¹-C³ bonds have been changed to the single and double bonds, respectively. As for the C² atom, it has a pair of lone electrons, making the INTb exhibit the carbene characters. In other words, INTb is unstable and can rearrange to a more stable structure.

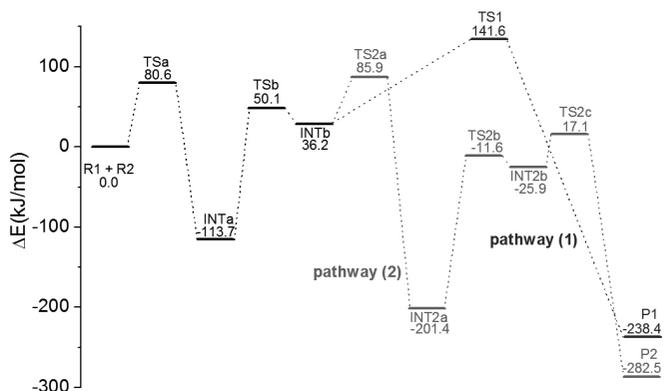


Figure 3. Reaction profiles for the addition reaction pathways (1) and (2) between cyclopropenylidene and ethylene at the CCSD(T)/6-311+G**/MP2/6-311+G* level of theory.

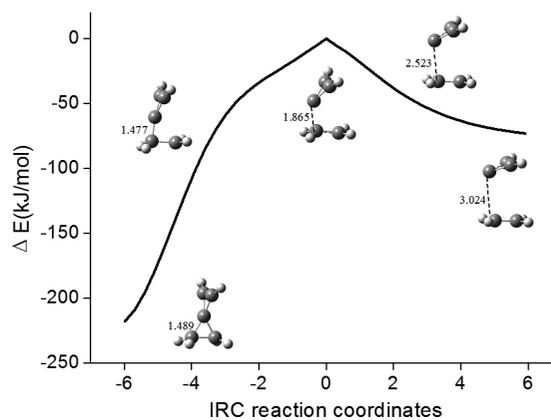


Figure 4. IRC of TSa and geometry evolution.

By shifting the H¹ atom on the C¹ atom to the adjacent C³ atom, INTb can be converted to P1 via TS1. Here, P1 is the most stable structure along the pathway (1). Obviously, in P1, the C³ atom is *sp*² hybridization and both the C¹ and C² atoms are *sp* hybridization. Therefore, the C¹-C² bond is a triple bond (1.222 Å), which is rather shorter than that of the bond between C¹ and C³ atoms (1.440 Å).

As mentioned above, three steps need to surmount transition state in the pathway (1). The corresponding barriers of the three steps are 80.6, 50.1, and 141.6 kJ/mol relative to the reactants, respectively. Therefore, the third step is the rate-determining step along the pathway (1).

3.2 Reaction pathway (2): four-membered ring product channel

The geometric parameters for the stationary points in the reaction pathway (2) are given in Figure 5. The corresponding reaction profile is illustrated in Figure 3. As illustrated in Figure 5, a four-membered ring product (P2) has been generated in the pathway (2).

Similar to the reaction pathway (1), the common intermediates INTa and

INTb have been formed successively in the pathway (2). As described above, in the pathway (1), INTb can be converted to P1 via TS1 by shifting the H¹ atom on the C¹ atom to the adjacent C³ atom. However, in the pathway (2), INTb can be converted to INT2a via TS2a by shifting the H¹ atom on the C¹ to the adjacent C² atom.

As displayed in Figure 5, in INT2a, the C¹ atom adopts *sp* hybridization and the C-C bond lengths are 1.319 (C¹-C²) and 1.295 Å (C¹-C³), which are intermediate between the general C=C double bond (about 1.33 Å) and C≡C triple bond (about 1.20 Å), respectively. Due to the existence of tension in three-membered ring, the fourth step of the pathway (2) is that the C³-C⁵ bond in INT2a opens to form an intermediate INT2b via TS2b, where the barrier is -11.6 kJ/mol relative to the reactants. In addition, in TS2b, the distance between C³ and C⁵ atoms has been elongated to 1.714 Å, denoting the rupture of the C³-C⁵ bond. On the other hand, the distance between C¹ and C⁵ atoms is 1.953 Å, indicating the formation of the C¹-C⁵ bond.

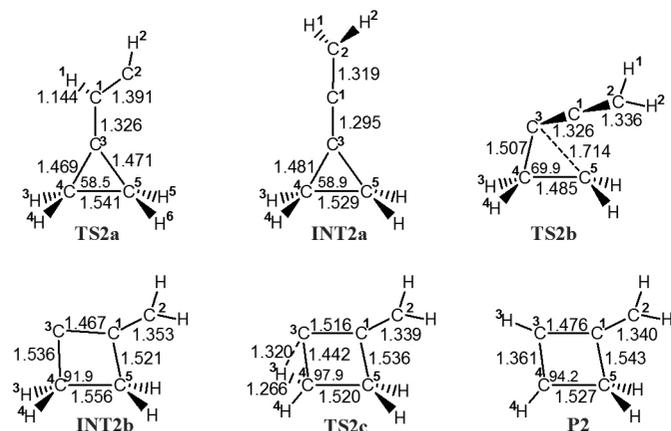


Figure 5. Optimized structures of the transition states (TS2a, TS2b, and TS2c), intermediates (INT2a and INT2b), and product (P2) in the reaction pathway (2) at the MP2/6-311+G* level of theory, where the bond length and bond angle are in angstrom and degree, respectively.

As displayed in Figure 5, INT2b is a four-membered ring structure, and there is a pair of lone electrons on the C³ atom. For this reason, INT2b is characteristic of carbene. The fifth step of the pathway (2) is that one H atom on the C⁴ atom of INT2b is transferred to the C³ atom to form a more stable structure P2 via TS2c, where the barrier is 17.1 kJ/mol relative to the reactants. Based on the analysis of the imaginary frequency and the calculation of the IRC, it can be proved that TS2c connects the INT2b and P2 indeed.

In P2, the bond lengths of C¹-C² and C³-C⁴ are 1.340 and 1.361 Å, respectively, which are slightly longer than that of the normal C=C double bond. At the same time, the bond length of C¹-C³ is 1.476 Å, which is slightly shorter than that of the normal C-C single bond. Moreover, further energy analyses suggest that P2 is lower in energy by about 282.5 kJ/mol than those of reactants. From the calculated bond length and the stability, P2 is a stable conjugated diene and it is the ultimate product of the pathway (2).

In summary, the barrier heights of the five steps in pathway (2) are 80.6, 50.1, 85.9, -11.6, and 17.1 kJ/mol relative to the reactants, respectively. Therefore, the third step is the rate-determining step along the pathway (2).

3.3 Comparisons of the two reaction pathways

As mentioned above, three- and four-membered ring products can be produced between cyclopropenylidene and ethylene through two different reaction pathways. The barrier heights of the rate-determining step in reaction pathways (1) and (2) are 141.6 and 85.9 kJ/mol relative to the reactants, respectively. Therefore, the reaction pathway (2) should be the most favorable reaction to occur kinetically. On the other hand, the corresponding products P1 and P2 have been stabilized by about 238.4 and 282.5 kJ/mol relative to the reactants, respectively. Therefore, the most favorable product P2 should be confirmed, implying that the reaction pathway (2) is also a favorable channel from the thermodynamic viewpoint.

4. CONCLUSIONS

In this study, the reaction mechanism between cyclopropenylidene and ethylene has been systematically investigated employing the MP2/6-311+G* level of theory. It was found that two products P1 and P2 characterized by the three- and four-membered ring structures have been produced via two different reaction pathways. The reaction pathway (2) should be the most favorable reaction to occur kinetically. Moreover, the corresponding products P1 and P2 have been stabilized by 238.4 and 282.5 kJ/mol relative to the reactants, respectively. Therefore, the pathway (2) should be the most favorable reaction to occur from the thermodynamic viewpoints.

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