QUANTUM MECHANICAL STUDY OF THE INSERTION REACTION BETWEEN CYCLOPROPENYLIDENE WITH R-H (R=F, OH, NH₂, CH₃)

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ABSTRACT

To further reveal the reactivity of cyclopropenylidene with R-H compounds, mechanisms of four reactions between cyclopropenylidene and R-H (R=F, OH, NH₂, CH₃) have been systematically investigated employing the second-order Møller-Plesset perturbation theory (MP2) method. Geometry optimization, vibrational analysis, and energy property for the involved stationary points on the potential energy surface have been calculated. All the mechanisms of four reactions are identical to each other. Based on the calculated results, there are three steps (step a, b, and c) along the reaction between cyclopropenylidene and R-H. For the first step, cyclopropenylidene is inserted into R-H to form an three-membered ring intermediate. For the second step, the three-membered ring is opened to form a carbene intermediate. With regard to the third step, it is H-transfered processes, the ultimate product is alkyne.

Keywords: Carbene, Cyclopropenylidene, Reaction mechanism, MP2 method.

1. INTRODUCTION

Carbene can be defined as divalent carbon intermediates. The carbon of carbene 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, therefore, the studies of carbene have attracted more attentions theoretically and experimentally[1-8].

C₃H₂ is a class of highly unsaturated carbenes, which are of great interest for the chemistry of carbon-rich gas-phase environments. There are three isomers (propynylidene, propadienylidene and cyclopropenylidene) located on its potential energy surface. Propynylidene is the only C₃H₂ isomer with triplet electronic ground state, and propadienylidene and cyclopropenylidene are in singlet state[9-11]. All of them can be interconverted by photolysis[12,13]. The structural characters, thermochemistry, and isomerization of C₃H₂ carbene has been investigated extensively[14-16]. It was reported that the singlet cyclopropenylidene is the most stable isomer among three species[17-22]. Moreover, some theoretical investigations have been carried out involving the propadienylidene-cyclopropenylidene isomerization reaction[23,24]. The mechanism of C₃H₂ carbene formation has been proposed by Goulay et al. using tunable vacuum ultraviolet photoionization and time-resolved mass spectrometry[25]. These highly reactive carbene molecules are fundamentally important not only within the context of organic chemistry, but also within the context of the chemistry of the interstellar medium[26,27].

Recently, it was reported that cyclopropenylidene could act as ligand in palladium catalysed coupling reactions[28]. By appending π-electron–donating amino groups to the triangular skeleton, a cyclopropenylidene derivative which is stable at room temperature has been prepared[29]. In 2011, gas-phase high-resolution absorption spectrum of cyclopropenylidene has also been observed using a Fourier transform infrared spectrometer[30].

Since cyclopropenylidene is a very important reactive species in organic chemistry, its addition reaction with unsaturated compound have been studied by us[31]. However, the insertion reaction of cyclopropenylidene with saturated single bond compound has not been systematically investigated. Due to the absence of experimental information, a theoretical investigation on the above reaction appears to be highly desirable and practical. In the present study, the reaction mechanism between cyclopropenylidene and R-H (R=F, OH, NH₂, CH₃) has been systematically investigated employing the second-order Møller-Plesset perturbation theory (MP2) method.

As mentioned below, there are three steps (step a, b, and c) in the insertion reaction between cyclopropenylidene and R-H. For the first step (step a), cyclopropenylidene is inserted into R-H to form a three-membered ring intermediate (INTa). For the second step (step b), aforementioned three-membered ring is opened to form a carbene intermediate (INTb). With regard to the third step (step c), it is H-transfered process, the ultimate product (P) is alkyne. The corresponding reaction mechanism has 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 cyclopropenylidene with R-H compounds as well as to enrich the available data for the relevant carbene chemistry.

2. CALCULATION METHOD

The second-order Møller-Plesset perturbation theory (MP2) method[32] in combination with the 6-311+G* basis set has been employed to locate all the stationary points along the reaction pathways. Frequency analysis 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 the 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 insertion reaction. For the sake of simplicity, the energetic results at the CCSD(T)/6-311+G*//MP2/6-311+G* level have been mainly discussed below if not noted otherwise.

All the calculations have been performed using Gaussian 98 program[33].

3. RESULTS AND DISCUSSION

The reactive mechanisms are similar to each other at the selected level of theory for the four reactions of cyclopropenylidene with F-H, OH-H, NH₂-H, and CH₃-H, which were named as reaction (1), (2), (3), and (4), respectively. For the sake of simplicity, the following discussions are mainly based on the reaction between cyclopropenylidene and F-H.

The geometric parameters for the reactants (cyclopropenylidene and R-H), transition states (TS), intermediates (INT), and products (P) involved in the reactions are displayed in Figure 1. The calculated relative energies for the available stationary points have been summarized in Table 1. The profile of reaction (1) is illustrated in Figure 2.
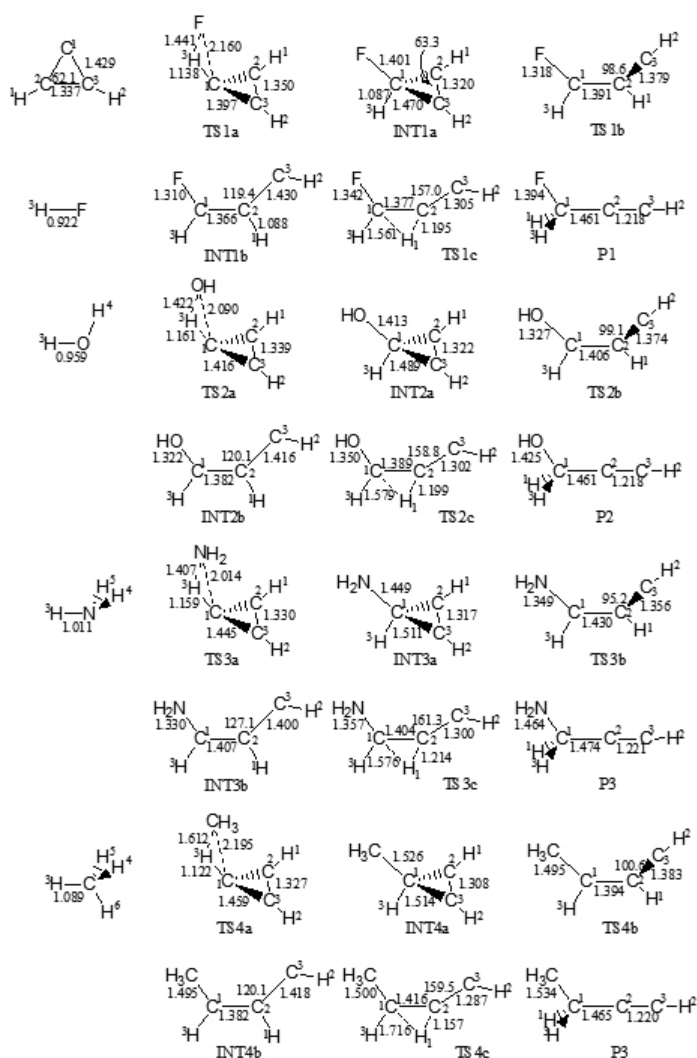
Figure 1. Optimized structures of the reactants (cyclopropenylidene and R-H), transition states (TS), intermediates (INT), and product (P) in reaction pathways at the MP2/6-311+G* level of theory, where the bond length and bond angle are in angstrom and degree, respectively.
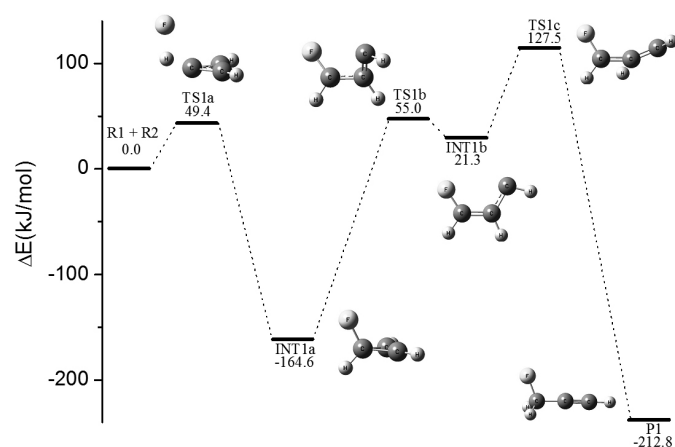

Figure 2. Reaction profile for the reaction (1) between cyclopropenylidene and F-H at the CCSD(T)//MP2/6-311+G* level of theory.

Table 1: The calculated relative energy (in kJ/mol) for the four reactions with respect to the isolated reactants at the MP2/6-311+G* level of theory considering the ZPVE corrections [a]

Reactions		Relative Energies	
R=F	**TS1a**	**INT1a**	**TS1b**
	43.2/49.4	-169.9/-164.5	76.2/55.0
	INT1b	**TS1c**	**P1**
	-44.6/21.3	152.3/127.5	-217.7/-212.8
R=OH	**TS2a**	**INT2a**	**TS2b**
	107.9/114.2	-159.6/-151.8	52.6/36.9
	INT2b	TS2c	P2
	16.7/-0.8	129.5/109.3	-214.7/-207.1
R=NH₂	**TS3a**	**INT3a**	**TS3b**
	160.1/164.8	-157.6/-147.5	-11.5/-19.8
	INT3b	**TS3c**	**P3**
	-35.9/-46.7	86.0/72.9	-233.0/-223.0
R=CH₃	**TS1a**	**INT4a**	**TS4b**
	192.0/194.6	-186.8/-149.2	21.1/8.0
	INT1b	**TS4c**	**P4**
	21.5/-1.7	108.6/90.2	-258.9/-245.8

[a] The data after the slash refer to the results at the CCSD(T)//MP2/6-311+G* level of theory considering the ZPVE corrections.

3.1 Step (a): insertion reaction to form a three-membered ring intermediate

The first intermediate INT1a occurs along the reaction (1) via a barrier of 49.4 kJ/mol. The calculated unique imaginary frequency of transition state TS1a in the insertion reaction of step (1a) is 899i cm^{-1} at the MP2/6-311+G* level of theory. As shown in Figure 1, in TS1a, the distance between C^1 and H^3 is 1.138 Å, and the bond length of F-H^3 has been elongated significantly to 1.441 Å. Thus, in the transition state TS1a, a new C^1–H^3 bond is to be formed and the F–H^3 bond is to be broken simultaneously. IRC calculations have been performed on the basis of the calculated TS1a to investigate the interaction between the reactants (cyclopropenylidene and F-H) and intermediate INT1a in the step (1a) process (see Figure 3).
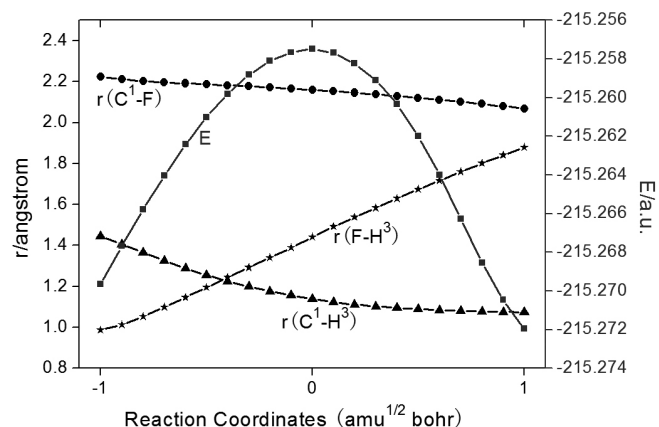

Figure 3. The selected bond lengths and energy changes along the reaction coordinates of step (1a) between cyclopropenylidene and F-H.

As displayed in Figure 1, in INT1a, C^2 and C^3 adopt sp^2 hybridization. Compared with the isolated cyclopropenylidene, the bond length of C^1-C^3 in INT1a is prolonged by 0.041 Å. Because of large tension existing in the three-membered ring, the C^1-C^3 bond in INT1a should be disconnected. Therefore,

the second step of the reaction (1) is the C^1-C^3 bond opened process, resulting in the formation of the intermediate INT1b.

Additionally, as shown in Table 1, compared with the reactants, the energies of four transition states (TS1a, TS2a, TS3a, and TS4a) are 49.4 (R=H), 114.2 (R=OH), 164.8 (R=NH$_2$), and 194.6 (R=CH$_3$) kJ/mol, respectively. As a result, the relative orders in the step (a) process are as follows: R=H > R=OH > R=NH$_2$ > R=CH$_3$.

3.2 Step (b): ring-opened process to form a carbene intermediate

By disconnecting the bond of C^1-C^3, INT1a can be converted to INT1b via TS1b, where the barrier is 219.5 kJ/mol. The calculated unique imaginary frequency of transition state TS1b is 534i cm^{-1}. IRC calculations have been performed on the basis of the calculated TS1b to investigate the interactions between two intermediates INT1a and INT1b in the step (1b) process (see Figure 4).
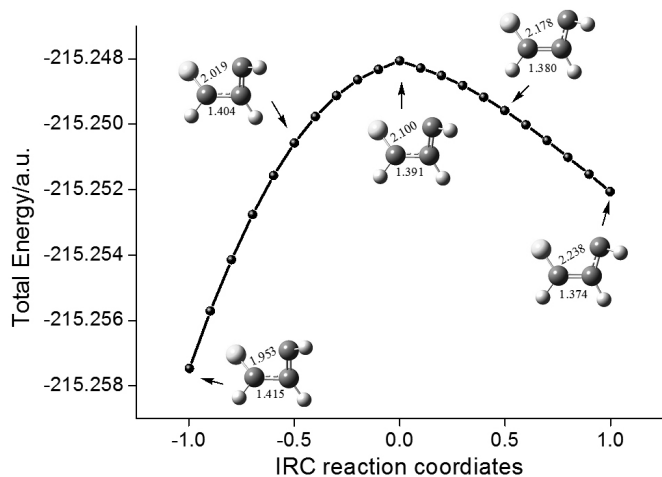

Figure 4. IRC of TS1b and geometry evolution.

As shown in Figure 1 and Figure 4, the angle of C^{1}C^{2}C^3 increased with the proceeding of the reaction. In addition, the distance of C^1-C^3 increased in the reaction progress, which implies the breakage of the three-membered ring of C^{1}C^{2}C^3.

In INT1b, all the atoms located on the same plane. The C^2 adopts sp^2 hybridization and the distance of C^1-C^2 is 1.366 Å, which is a typical C=C double bond length. On the other hand, the distance of C^2-C^3 (1.430 Å) is approximated to the typical C-C single bond length. As for the C^3 atom, it has a pair of lone electrons, which makes the INT1b exhibit carbene characters. In other words, INT1b is unstable and can be rearrange to a more stable structure.

3.3 Step (c): H-transferred process to form a product of alkyne

The reaction step (1c) is shifting H^1 atom from C^2 to adjacent C^1, with the result that INT1b is converted into P1 via TS1c, where the barrier is 106.2 kJ/mol. The calculated unique imaginary frequency of transition state TS1c is 1080i cm^{-1}. IRC curve have been performed on the basis of the calculated TS1c to investigate the interactions between two intermediates INT1b and P1 in the step (1c) process (see Figure 5). As shown in Figure 1 and Figure 5, the distance of C^2-H^1 in TS1c has been elongated to 1.195 Å, and the distance of C^1-H^1 has been shortened to 1.561 Å, which denotes the H^1 atom is transferred from C^2 to C^1. At the same time, the bond angle of C^{1}C^{2}C^3 in TS1c increased to 157.0°, suggesting the alkene structure of INT1b will transform into the alkyne of P1.

In P1, the distance of C^2-C^3 is 1.218 Å, which is the typical C≡C triple bond length. On the other hand, the three carbon atoms, C^1, C^2, and C^3, are in the same line, suggesting the P1 is the relatively stable product of alkyne. Among all intermediates in the reaction (1), the P1 is the most stable species along the reaction profile, whose energy is lower 212.8, 58.2, and 234.1 kJ/mol than that of reactants, INT1a, and INT1b, respectively. Similarly, for the situation of R=OH, NH$_2$, and CH$_3$, the respective product P2, P3, and P4, are the most stable species along the reaction profile, whose energy is lower 207.1, 223.0, and 245.8 kJ/mol than that of reactants, respectively.
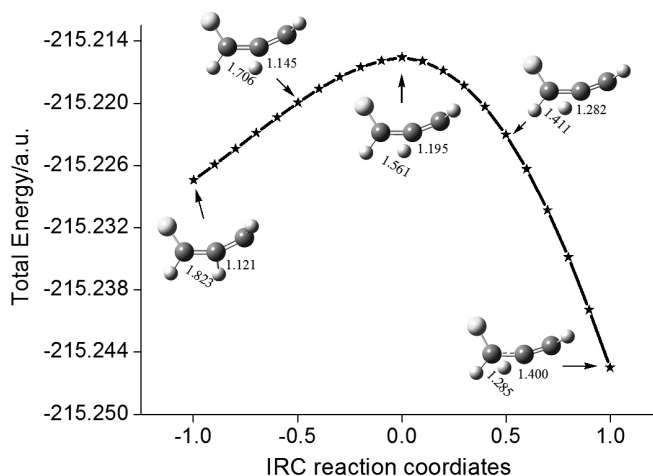

Figure 5. IRC of TS1c and geometry evolution.

As to the reaction (1), the barrier height of the three steps is 49.4, 219.6, and 106.2 kJ/mol, respectively. Therefore, the rate-determining step in the reaction (1) is the step (1b). For the situation of R=OH, NH$_2$, and CH$_3$, the rate-determining step is also step (b), whose barrier height is 188.7, 127.7, and 157.2 kJ/mol, respectively. From the dynamics viewpoint, the four reactions of cyclopropenylidene and R-H (R=F, OH, NH$_2$, CH$_3$) are considerably approximative.

4. CONCLUSIONS

In this study, the reaction mechanism between cyclopropenylidene and R-H (R=F, OH, NH$_2$, CH$_3$) have been systematically investigated employing the MP2/6-311+G* levels of theory. On the basis of this mechanism, the accurate energies caculation have been performed at the CCSD(T)/6-311+G* level of theory. According to the calculated results, the mechanism for the four reactions are similar with each other. There are three steps for the reaction between cyclopropenylidene and R-H. For the first step, cyclopropenylidene is inserted into R-H bond to form a three-membered ring intermediate. For the second step, a substituted carbene intermediate formed through a ring-opening process. As to the third step, the ultimate product alkyne formed in a H-transferred process. The rate-determining step for the four reactions is the step (b), i.e., an carbene formation in the ring-opening process, whose barrier height is 219.6, 188.7, 127.7, and 157.2 kJ/mol, respectively. In addition, the high stability of the product of alkyne suggests that the corresponding reaction is a favorable process thermodynamically, which provides an alternative approach to the formation of the alkyne.

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