Theoretical study on the cycloaddition reaction mechanism between azacyclopropenylidene and ethylene

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The mechanism of the cycloaddition reaction between azacyclopropenylidene and ethylene was systematically investigated employing the second-order Møller-Plesset perturbation theory (MP2) method in order to better understand the reactivity of azacyclopropenylidene with the unsaturated compound ethylene. Geometry optimizations and vibrational analyses were performed for the stationary points on the potential energy surfaces of the system. From the potential energy profile, it is predicted that the cycloaddition reaction has three competitive pathways: (I) reaction of azacyclopropenylidene with ethylene to form a carbene compound P1 in two steps; (II) formation of an allene compound P2 from the two reactants in three steps; (III) after the formation of P1 by the reaction of azacyclopropenylidene with ethylene, further reaction of P1 with ethylene to form a stable bicyclic compound P3.

Keyword: Azacyclopropenylidene, Reaction mechanisms, MP2 method.

INTRODUCTION

Cyanopolyene molecules HC_nN have been detected in the interstellar space by radio telescopes for a long time [1-9]. This class of molecules plays an important role in astronomy and interstellar chemistry due to their astrophysical abundance and rather large dipole moments. One of the interesting cyanopolyenes, the molecule HCCN, was studied by electron spin resonance and UV/IR spectroscopy since the 1960s [10,11]. For the first time, Guélin *et al*. detected HCCN in the carbon star envelope IRC+10216, and discussed its formation mechanism [12]. Later, in 1996, HCCN was observed in the interstellar space [13]. A lot of experimental and computational methods were applied for finding out the structures and the relative energies of some isomers of the HCCN system. Many studies have revealed that there exist many isomers with different kinds of geometries (linear, bent or cyclic) or different multiplicity (singlet or triplet) having similar energies of the HCCN molecules [14-23]. Lee *et al*. have characterized the quasilinear triplet, bent singlet, and cyclic singlet HCCN isomers and determined their molecular properties with a series of highly accurate *ab initio* levels of theory [24]. The cyclic HCCN isomer, generally named as azacyclopropenylidene, is the most stable isomer of all singlet molecules. In addition, the cyclic HCCN isomer has been found to be an intermediate between the interconversion of other isomers on the hypersurface of neutral, anionic, and cationic species where the barriers are feasible [25,26]. Recently, vibrational spectroscopic constants and fundamental vibrational frequencies for isotopologues of the azacyclopropenylidene isomer have been investigated [27].

In 1998, matrix generations of singlet azacyclopropenylidene and singlet bromocyanocarbene (BrCCN) were reported by Maier and co-workers [28]. Casavecchia *et al*. reported the dynamics of a reaction of the nitrogen atom with an unsaturated hydrocarbon by combining crossed molecular beam experiments and *ab initio* molecular orbital calculations. They found that azacyclopropenylidene is one of the products of the reaction of the nitrogen atom with C_2H_2 in the upper atmosphere of Titan [29]. Thus, azacyclopropenylidene seems to be a good candidate for astrophysical detection, considering the various possible formation pathways and its large dipole moment [30]. Computational investigation of HCCN molecules will be very helpful to elucidate the reactivity and kinetic stability of these molecules. We have studied the reactions between azacyclopropenylidene and small ring compounds [31,32]. The calculational results demonstrated that azacyclopropenylidene can insert into small ring compounds to form ring-expanded products. However, no attention has been paid to the reactivity of azacyclopropenylidene with active species containing double bond compounds

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until now. In the present study, we have performed a comprehensive theoretical investigation of the reaction mechanism between azacyclopropenylidene and ethylene by employing the second-order Møller-Plesset perturbation theory (MP2) method in order to better understand the azacyclopropenylidene reactivity. The present results will enrich the available data for the relevant azacyclopropenylidene chemistry and discuss the possibility of formation of larger molecules by means of azacyclopropenylidene in the interstellar space.

CALCULATION METHOD

The second-order Møller-Plesset perturbation theory (MP2) method [33] in combination with the 6-311+G* basis set was employed to locate all stationary points along the reaction pathways without imposing any symmetry constraints. Frequency analyses were carried out to confirm the nature of minima and transition states. For example, the intermediates (IM) in the reactions are local minima with no imaginary frequencies. The transition states (TS) have only one imaginary frequency. The spin multiplicities of all transition states are singlet. Moreover, intrinsic reaction coordinate (IRC) calculations were also 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, were corrected with the zero-point vibrational energy (ZPVE) corrections.

All calculations were performed using Gaussian 98 program [34].

RESULTS AND DISCUSSION

As displayed in Scheme 1, three possible pathways for the title reaction were proposed. The geometric parameters for the reactants (azacyclopropenylidene (R1) and ethylene (R2)), transition states (TS), intermediates (IM), and products (P) involved in the pathways (I), (II), and (III) are displayed in Fig. 1. The calculated relative energies for the available stationary points are summarized in Table 1. The corresponding reaction profile is illustrated in Fig. 2.

Pathway (I): formation of a carbene compound P1

There are step (a) and step (1) along the reaction pathway (I), where step (a) is a common step for the pathways (I) and (II).

The first intermediate IMa was formed along the reaction pathways (I) and (II) *via* a barrier of 51.7 kJ/mol. The calculated unique imaginary frequency

of the transition state TSa in the cycloaddition process of step (a) is 491i cm^{-1} at the MP2/6-311+G* level of theory.

As shown in Fig. 1, in TSa, the distance of C^1-C^3 and C^1-C^4 is 0.1930 and 0.2514 nm, respectively. The distance of C^3-C^4 in the R2 fragment is 0.1378 nm, which is elongated by 0.0039 nm in comparison with the isolated R2 molecule. Thus, in TSa, two new bonds of C^1-C^3 and C^1-C^4 are to be formed and the C^3-C^4 bond is to be simultaneously transformed from double bond to single bond. As shown in Fig. 3, these changes can be further validated by IRC calculations on the basis of TSa.
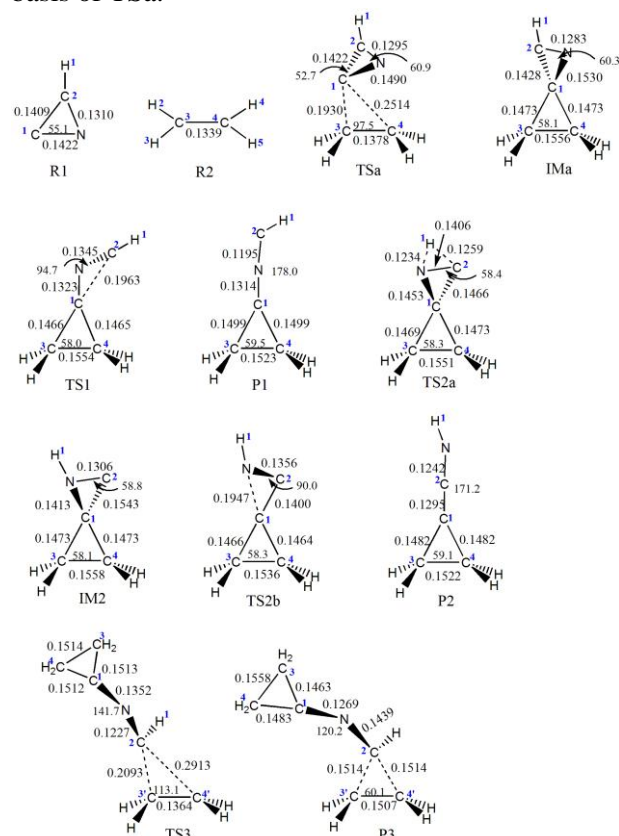

Fig. 1. Optimized structures of the reactants (azacyclopropenylidene and ethylene), transition states (TS), intermediates (INT), and products (P) in the reaction pathways (I), (II), and (III) at the MP2/6-311+G* level of theory, where bond length and bond angle are in angstrom and degree, respectively.

Qualitatively, the cycloaddition process can be understood ensuing from the frontier molecular orbital theory since the frontier orbitals (e.g., HOMO) of a chemical species are very important to define their reactivity and to determine the way in which the molecule interacts with other species [35]. As displayed in Fig. 4, the weak strength of the C^3-C^4 bond can be reflected from the HOMO of ethylene. Obviously, it is characterized by the π antibonding orbital. As for azacyclopropenylidene,

the activity of the C^1 site can be reflected from the largest contributions of the C^1 atom to the components of the whole HOMO. Therefore, the C^1 atom of azacyclopropenylidene can react with the C^3-C^4 bond of ethylene to form the spiro intermediate IMa.

As displayed in Fig. 1, compared with the isolated azacyclopropenylidene, the bond length of C^1-C^2 in IMa is extended by 0.0019 nm. The angle of C^1NC^2 in IMa is 60.3º, which is lower by 1.6º relative to that of the isolated azacyclopropenylidene. Therefore, the ring-tension of the R1 fragment in IMa is larger than that of the isolated R1. Because of the existing large tension in the three-membered ring, the C^1-C^2 bond in IMa will be broken. Therefore, the second step of the pathway (I) is the C^1-C^2 bond cleavage, followed by the formation of P1.
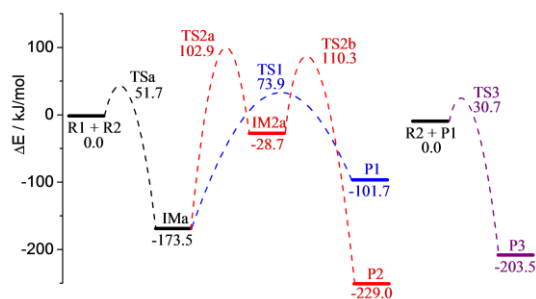

Fig. 2. Reaction profiles for the cycloaddition reaction pathways (I), (II), and (III) between azacyclopropenylidene and ethylene at the MP2/6-311+G* level of theory
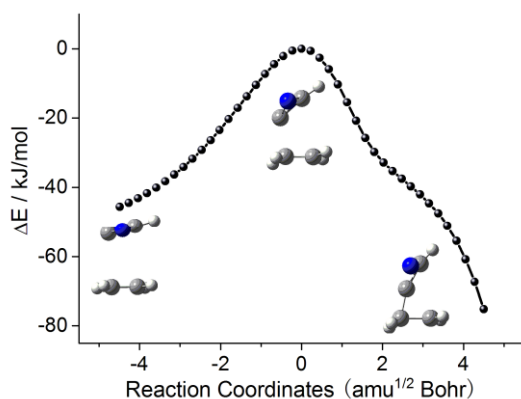

Fig. 3. IRC of TSa and geometry evolution.

Through the cleavage of the C^1-C^2 bond, IMa can be converted to P1 *via* TS1, where the barrier is 247.4 kJ/mol. The calculated unique imaginary frequency of TS1 is 435i cm^{-1}. IRC calculations were performed on the basis of the calculated TS1

to investigate the interactions between IMa and P1 in step (1) of the process (see Fig. 5).

As shown in Figs. 1 and 5 for the angle of C^1NC^2 in IMa, it increases along with the reaction. At the same time, the bond distance of C^1-C^2 increases along with the reaction process, implying the breakage of the three-membered ring involving C^1C^2N.
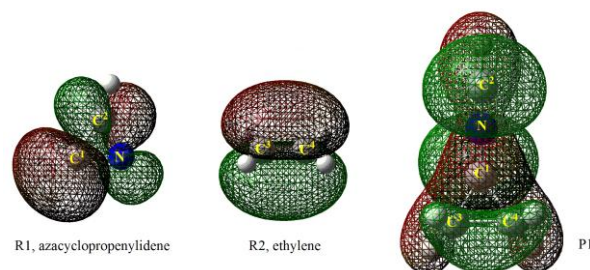

Fig. 4. Calculated HOMO orbitals for azacyclo-propenylidene, ethylene, and P1.

In P1, the C^2 adopts sp^2 hybridization, it has a pair of lone electrons, making the P1 exhibit a carbene character. Therefore, P1 is very active, it is not only the product of pathway (I), but also the reactant of pathway (III). In the following reaction process, P1 can further react with ethylene to form the product P3.
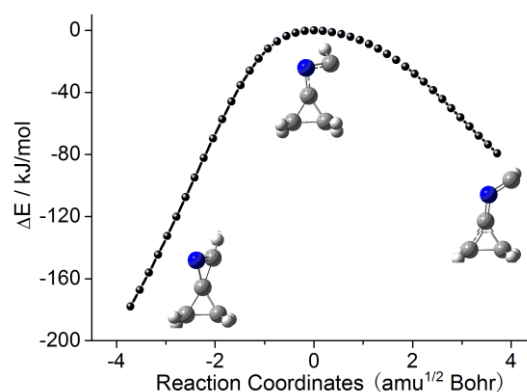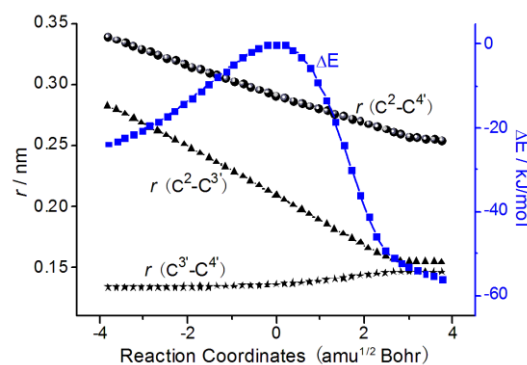

Fig. 5. IRC of TS1 and geometry evolution.

Fig. 6. Selected bond lengths change along the reaction coordinates on the basis of the IRC of TS3.

Pathway (II): formation of an allene compound P2

As the common intermediate of pathway (I) and (II), IMa can transform to P2 *via* steps (2a) and (2b).

The reaction step (2a) is a hydrogen transfer process from C^2 to the adjacent N, resulting in the conversion of IMa into IM2a *via* TS2a. Here, the calculated barrier is 276.4 kJ/mol and the unique imaginary frequency of TS2a is 1464i cm^{-1}. In detail, as shown in Fig. 1, the distance of C^2-H^1 in TS2a is elongated to 0.1259 nm, and the distance of N-H^1 reaches 0.1234 nm, which indicates that the H^1 atom can be transferred from C^2 to N.

Similar to the C^1C^2N ring in IMa, the C^1C^2N ring in IM2a can be opened at its weaker bond. Through the break of the C^1-N bond, IM2a can be converted to P2 *via* TS2b, where the barrier is 139.0 kJ/mol. The calculated imaginary frequency of transition state TS2b is 921i cm^{-1}.
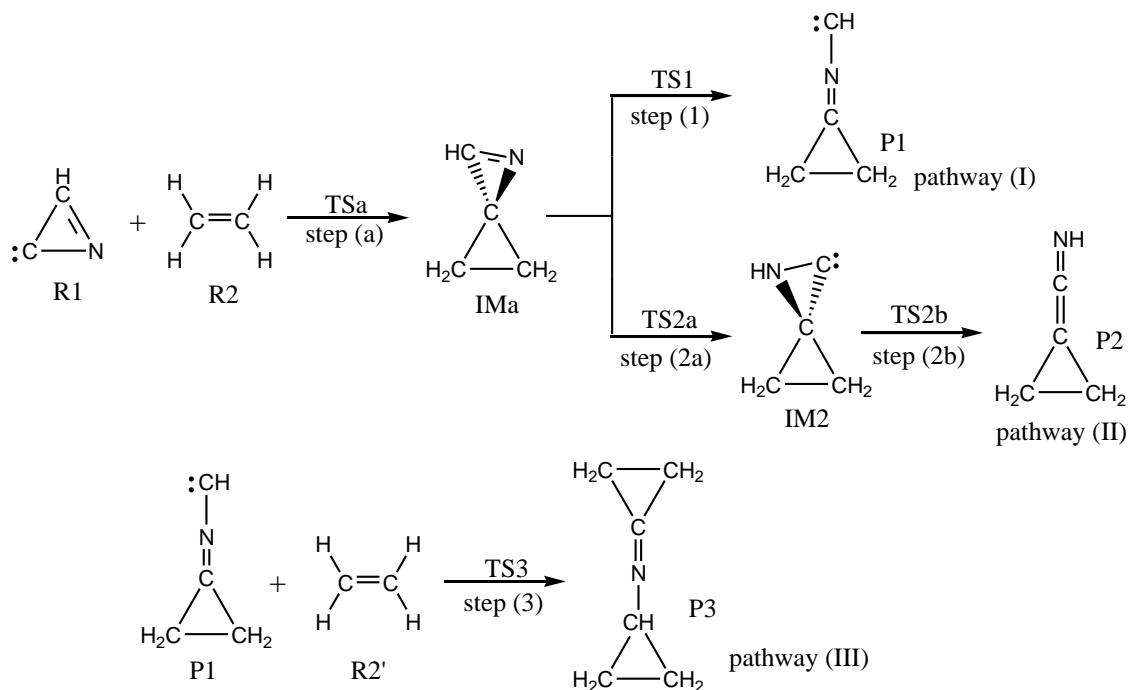
In P2, the bond length of C^1-C^2 is 0.1295 nm, which falls in the range of the intermediate between C=C and C≡C bond length. Analogously, the bond length of C^2-N (0.1242 nm) lies between those of the C=N and C≡N bonds. The three atoms C^1, C^2, and N are approaching the same line ($\angle C^1C^2N$ is 171.2°). Therefore, P2 is an allene structure. Along the reaction profile, P2 is exothermic with a value of 229.0 kJ/mol compared with that of the reactants.

Pathway (III): formation of a bicyclic compound P3

As mentioned earlier, P1 exhibits a carbene character; it can further react with ethylene to form the product P3, which is named as the pathway (III). The geometric parameters for the species involved in the pathway (III) are displayed in Fig. 1. The calculated relative energies for the available stationary points are summarized in Table 1.

As shown in Fig. 1, in TS3, the distance of C^2-$C^{3'}$ and C^2-$C^{4'}$ is 0.2093 and 0.2913 nm, respectively. The distance of $C^{3'}$-$C^{4'}$ in the R2' fragment (0.1364 nm) is by 0.0025 nm longer than that in the isolated R2' molecule. Thus, in the transition state TS3, two new bonds of C^2-$C^{3'}$ and C^2-$C^{4'}$ are formed and the $C^{3'}$-$C^{4'}$ bond is simultaneously transformed from double bond to single bond. As shown in Fig. 6, those changes can be further validated by IRC calculations on the basis of TS3. Furthermore, similar with the explanation of the R1 reaction with ethylene, the HOMOs of P1 and ethylene are displayed in Fig. 4. Along the reaction profile, P3 is the important stable species, which is exothermic with a value of 203.5 kJ/mol compared with that of the reactants.

Scheme 1. The proposed three pathways for the reaction between azacyclopropenylidene and ethylene

Table 1. The calculated relative energy (in kJ/mol) with respect to the isolated reactants

Pathways	Relative Energies			
Pathway (I)	TSa	IMa	TS1	P1
	51.7	-173.5	73.9	-101.7
Pathway (II)	TS2a	IM2a	TS2b	P2
	102.9	-28.7	110.3	-229.0
Pathway (III)	TS3	P3		
	30.7	-203.5		

CONCLUSIONS

The cycloaddition reaction between azacyclopropenylidene and ethylene has three competitive pathways (I), (II), and (III); the corresponding products are: carbene compound P1, allene compound P2, and bicyclic compound P3, respectively. On the basis of the potential energy surface obtained with the MP2/6-311+G* method, it can be predicted that pathway (III) is the competitive dominant channel. The pathway (III) consists of three steps: (1) the two reactants (azacyclopropenylidene and ethylene) first form a spiro intermediate IMa *via* transition state TSa with energy barrier of 51.7 kJ/mol; (2) IMa isomerizes to a carbene compound P1 *via* transition state TS1a with an energy barrier of 247.4 kJ/mol; (3) P1 further reacts with ethylene (R2') to form a bicyclic compound P3 *via* transition state TS3 with an energy barrier of 30.7 kJ/mol. From the thermodynamic viewpoint, P3 is the important product, with energy lower by 203.5 kJ/mol than that of the reactants.

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ТЕОРЕТИЧНО ИЗСЛЕДВАНЕ НА МЕХАНИЗМА НА ЦИКЛИЧНО ПРИСЪЕДИНЯВАНЕ МЕЖДУ АЗА-ЦИКЛОПРОПЕНИЛИДЕН И ЕТИЛЕН

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(Резюме)

Системно е изследван механизма на циклично присъединяване между аза-циклопропенилиден и етилен с помощта на пертурбационната теория на Møller-Plesset от втори порядък(MP2). Така се постига по-добро разбиране на реактивоспособността на аза-циклопропенилидена с ненаситени съединения (етилен). Направени са геометрична оптимизация и вибрационен анализ за определянето на стационарните точки на повърхността на потенциалната енергия на системата. От профилите на потенциалната енергия се предсказва, че за реакцията на циклично присъединяване има три конкурентни маршрута: (I) дву-етапна реакция с образуване на карбеново съединение P1; (II) образуване на аленово съединение P2 в два етапа от двата реагента; (III) реакция с образуване на стабилно би-циклично съединение P3 след образуване на съединението P1.