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A theoretical study on the mechanism of the reaction between azacyclopropenylidene and oxirane

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Abstract: The reaction mechanism between azacyclopropenylidene and oxirane was systematically investigated employing the second-order Møller–Plesset perturbation theory (MP2) method to understand better the reactivity of azacyclopropenylidene with the three-membered ring compound oxirane. Geometry optimization, vibrational analysis, and energy property for the involved stationary points on the potential energy surface were calculated. The energies of all the species were also further corrected by CCSD(T)/6-311+G* single-point calculations. The calculational results showed that there are two possible reaction pathways. From the kinetic viewpoint, the first pathway is primary. From the viewpoint of thermodynamics, the second dominates.

Keywords: azacyclopropenylidene; oxirane; reaction mechanism; MP2 method.

INTRODUCTION

Much attention has recently been paid to carbon chain molecules containing heteroatoms (N,[1–8] O,[9,10] S,[11–13] and Si[14–16]) due to their astrophysical abundance and interesting spectroscopic properties. A typical example is cyanopolyacetylenes, $HC_{2n+1}N$, in which $HC_{11}N$ is one of the largest carbon chain molecules observed in interstellar medium.[17] In contrast to $HC_{2n+1}N$ cyanopolyacetylenes, systematic studies on $HC_{2n}N$ molecules containing an even number of carbon atoms were relatively scarce. Despite this, $HC_{2n}N$ molecules and their geometrical isomers are still very important, as they are good candidates for astrophysical observations by microwave and infrared spectroscopy due to their rather large dipole moments. An exciting fact is that HC_2N was observed in interstellar space.[18] Many experimental and computational methods were utilized in studies on the structures and the relative energies of some isomers of this system. Numerous studies revealed that many isomers of HC_2N molecules of

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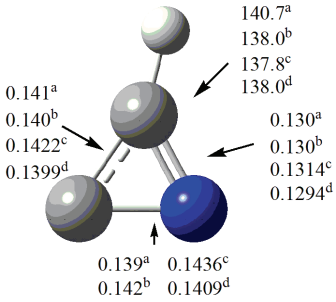
similar energies exist with different kinds of geometries (linear, bent or cyclic) or different multiplicities (singlet or triplet).[19–30] Inostroza *et al*. characterized quasi-linear triplet, bent singlet, and cyclic singlet HC_2N isomers and determined their molecular properties in a series of highly accurate *ab initio* level of theory investigation.[27] In addition, the cyclic HC_2N isomer was found to be an intermediate between the interconversion of the bent HCCN and an unknown bent HCNC on the hypersurface of neutral, anionic, and cationic species where barriers are feasible.[31] The most stable singlet state of the HC_2N molecule is named azacyclopropenylidene and its structure, which was confirmed by spectroscopy and calculation, is displayed in Scheme 1.



Scheme 1. Geometrical parameters for azacyclopropenylidene calculated at diverse levels. The bond lengths are in nm and the bond angle in degree (a: B3LYP/6--311++G**;[28] b: MP2/6-311++G**;[28] c: QCISD(T)/ /D95**;[21] d: CCSD(T)/cc-pVTZ[30]).

In 1998, matrix generations of singlet azacyclopropenylidene and singlet bromocyanocarbene (BrCCN) were researched by Maier and co-workers.[32] Casavecchia *et al*. reported the dynamics of a reaction of 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 nitrogen atom with C_2H_2 in the upper atmosphere of Titan.[33] Thus, azacyclopropenylidene seems to be a good candidate for astrophysical detection, considering these various possible formation pathways and its large dipole moment.[34]

Computation of HC_2N molecules would be very helpful in the elucidation of the reactivity and kinetic stability of these molecules, but less attention has been paid to the reactivity of azacyclopropenylidene with active species containing small ring compounds until now. In the present study, a comprehensive theoretical investigation of the reaction mechanism between azacyclopropenylidene and oxirane was performed by employing the second-order Møller–Plesset perturbation theory (MP2) method in order to understand better the reactivity of azacyclopropenylidene. To the best of our knowledge, this study is the first report of the reaction mechanism between azacyclopropenylidene and small ring compounds. The present results will enrich the available data for the relevant azacyclopropenylidene chemistry and discuss the possibility of the formation of larger molecules by means of azacyclopropenylidene in interstellar space.

CALCULATION METHOD

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

To further refine the calculated energy parameters, single point energy calculations were 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 I, both levels gave consistent results for the calculated reaction profile of the insertion reaction. For the sake of simplicity, mainly the energetic results at the CCSD(T)//MP2/6-31+G* level are discussed below if not noted otherwise.

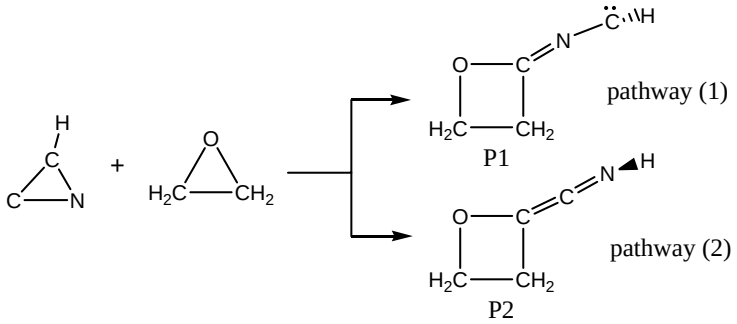
All the calculations have been performed using the Gaussian 98 program.[35]

TABLE I. The calculated relative energy (in kJ mol^{-1}) with respect to the isolated reactants at the MP2/6-311+G* level of theory considering the ZPVE corrections; the data in the brackets refer to the results at the CCSD(T)//MP2/6-311+G* level of theory considering the ZPVE corrections

Pathway	Relative Energy			
	TS	IM		
	171.0 (173.2)	–273.4 (–255.6)		
Pathway (1)	TS1	P1		
	–87.8 (–93.3)	–181.3 (–186.0)		
Pathway (2)	TS2a	IM2a	TS2b	P2
	8.9 (19.3)	–126.0 (–124.9)	–57.8 (–60.8)	–260.0 (–255.8)

RESULTS AND DISCUSSION

The two proposed possible reaction pathways for the insertion reaction between azacyclopropenylidene and oxirane are displayed in Scheme 2. The geometric parameters for the reactants (azacyclopropenylidene (R1) and oxirane (R2)), transition states (TS), intermediates (IM), and products (P) involved in



Scheme 2. The two proposed reaction pathways for the insertion reaction between azacyclopropenylidene and oxirane.

pathways (1) and (2) are shown in Fig. 1. Correspondingly, the calculated relative energies for the available stationary points are summarized in Table I. The corresponding reaction profile is illustrated in Fig. 2.

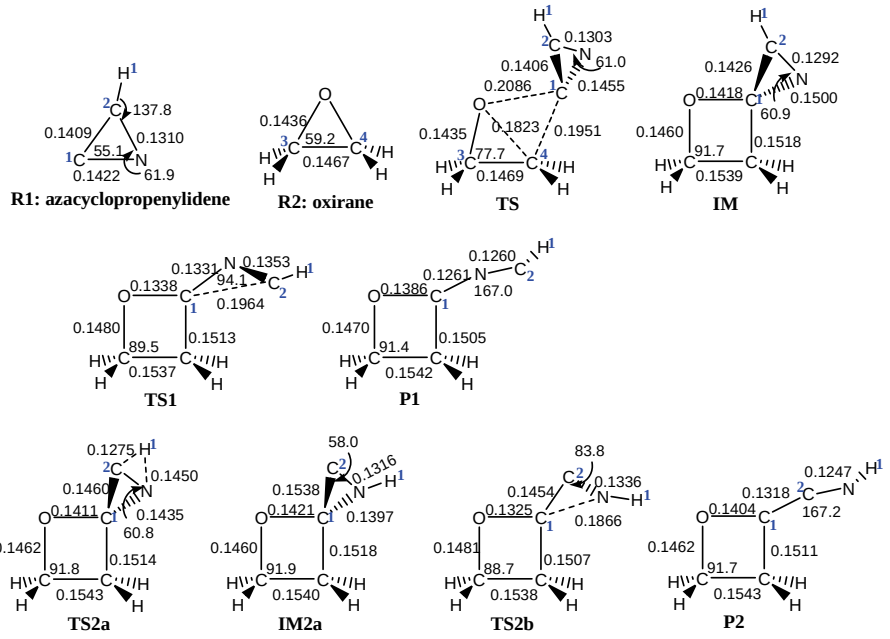


Fig. 1. Optimized structures of the reactants (azacyclopropenylidene and oxirane), transition states (TS), intermediates (IM), and products (P) in reaction pathways (1) and (2) at the MP2/6-311+G* level of theory, in which the bond lengths and bond angles are in nm and degree, respectively.

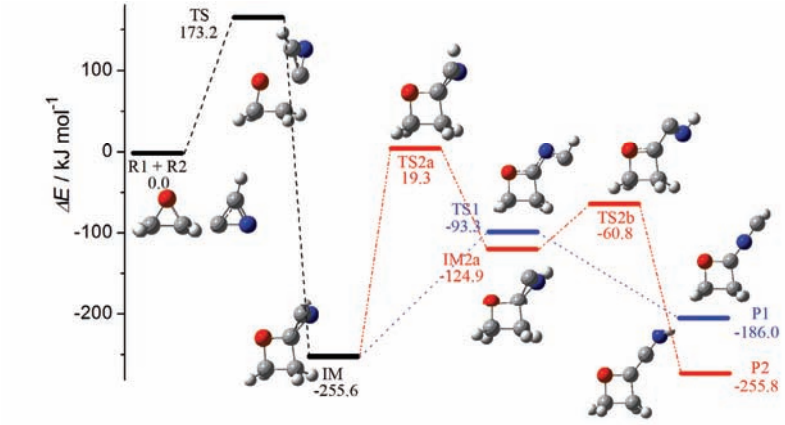


Fig. 2. Reaction profile for the reaction between azacyclopropenylidene and oxirane at the MP2/6-311+G* level of theory.

Insertion process to form a spiro intermediate IM

The first intermediate IM in the reaction between azacyclopropenylidene and oxirane was formed *via* a barrier of 173.2 kJ mol^{-1}. The calculated unique imaginary frequency of the transition state TS in the insertion process is 727*i* cm^{-1} at the MP2/6-311+G* level of theory.

As shown in Fig. 1, in the TS, the distance of C^1–O is 0.2086 nm, and C^1–C^4 is 0.1951 nm. The distance of O–C^4 in the R2 fragment of the TS has been elongated significantly to 0.1823 nm. Thus, in the transition state TS, two new bonds C^1–O and C^1–C^4 are to form and the O–C^4 bond is to break simultaneously. In other words, insertion of the C^1 atom of the R1 fragment into the O–C^4 bond of the R2 fragment is the process that resulted the formation of a spiro intermediate IM. Moreover, as shown in Fig. 3, these changes can be further validated by IRC calculations based on the TS.

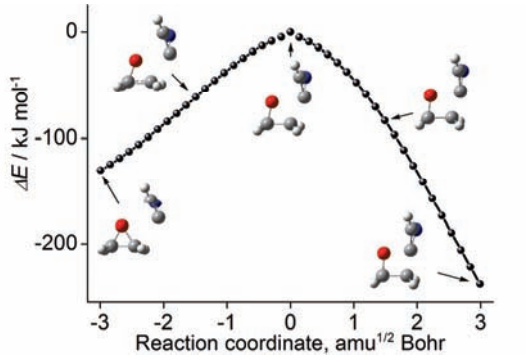


Fig. 3. IRC of TS and geometry evolution.

Qualitatively, the insertion process could be explained from the frontier molecular orbital theory since the frontier orbitals (*e.g.*, HOMO) of a chemical species are very important in defining their reactivity and determining the way in which the molecule interacts with other species.[36] As displayed in Fig. 4, the weak strength of the C–O bond can be deduced from the HOMO of oxirane. Obviously, the O–C^3 bond (or O–C^4 bond) is characterized by π antibonding orbital. As for azacyclopropenylidene, the activity of C^1 site could be deduced from the C^1 atom having the largest contributions to the components of the whole HOMO. Therefore, C^1 atom in azacyclopropenylidene could insert into the C–O bond of oxirane rather than into the C–C bond.

As shown in Fig. 1, C^2 and N adopt sp^2 hybridization in the IM. Compared with the isolated azacyclopropenylidene, the bond length of C^2–N in the IM is shortened by 0.0018 nm. The angle of C^{1}NC^2 in the IM is 60.9°, which is decreased slightly by 1.0° relative to that in isolated azacyclopropenylidene. Therefore, the ring-tension of the R1 fragment in the IM is larger than that of the iso-

lated R1. Due to the existing large tension in the three-membered ring, the C^1–C^2 bond in the IM will break. Through the ring-opening step at the C–C bond, the IM can transfer to product P1, which is designated as pathway (1). On the other hand, through H-transfer step and subsequent ring-opening step at the C–N bond, the IM can turn into product P2, which is designated pathway (2). Therefore, the IM is the common intermediate for pathway (1) and pathway (2).

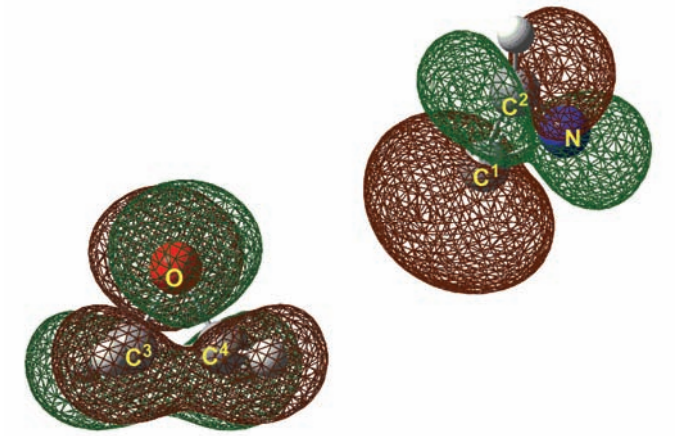


Fig. 4. The calculated HOMO orbitals for azacyclopropenylidene and oxirane.

Pathway (1): ring-opening process to form a carbene product

As mentioned above, the first step of pathway (1) is the formation of the IM. Through cleavage of the C^1–C^2 bond, the second step of pathway (1) is the conversion of the IM to P1 *via* TS1, where the barrier is 162.3 kJ mol^{-1}. The calculated only imaginary frequency of the transition state TS1 is 359*i* cm^{-1}. IRC calculations were performed based on the calculated TS1 to investigate the interactions between intermediate IM and product P1 in the pathway (1) process (see Fig. 5).

As shown in Figs. 1 and 5, the angle of C^1NC^2 in TS1 increases continuously along with the reaction. Simultaneously, the bond distance of C^1–C^2 increases along with the reaction process, implying the breakage of the three--membered ring involving C^1NC^2.

In P1, all the non-hydrogen atoms are located approximately on the same plane. The N atom adopts sp^2 hybridization and the bond length of C^1–N is 0.1261 nm, which is shorter than that of a normal C=N double bond. Moreover, the distance of N–C^2 (0.1260 nm) is shorter than that of a normal N–C single bond. Furthermore, the C^2 atom has a pair of lone electrons, making P1 exhibit the carbene characters. Therefore, from a thermodynamics viewpoint, P1 is not a

stable product, which can be demonstrated by the calculated energy (–186.0 kJ mol^{-1}).

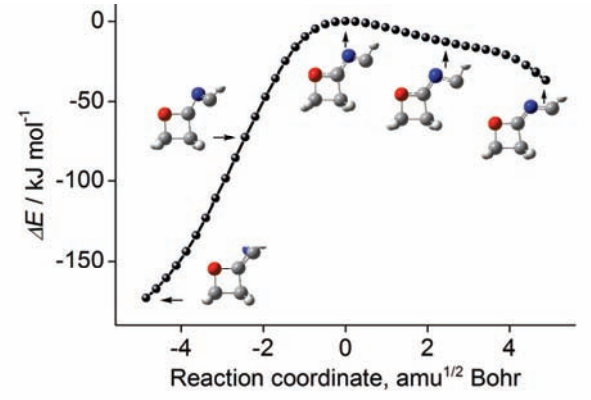


Fig. 5. IRC of TS1 and geometry evolution.

Pathway (2): H-transfer and ring-opening processes to form an allene product

The second step and the third step of pathway (2) are an H-transfer process to form the spiro intermediate IM2a, and a ring-opening process to form the allene product P2, respectively.

The second step of pathway (2) is hydrogen transfer from C^2 to the adjacent N, resulting in the conversion of IM into IM2a *via* TS2a. IRC calculations were performed based on the calculated TS2a and TS2b in the pathway (2) process (see Fig. 6). Here, the calculated barrier is 274.9 kJ mol^{-1} and the imaginary frequency of TS2a is 1281*i* cm^{-1}. In details, as shown in Figs. 1 and 6, the distance of C^2–H^1 in TS2a is elongated to 0.1275 nm, and the distance of N–H^1 reaches 0.1450 nm, indicating that the H^1 atom can transfer from C^2 to N.

As IM, IM2a is a spiro intermediate. However, the bond between C^2 and N in IM2a is a single bond, whereas it is a double bond in IM. Therefore, there are

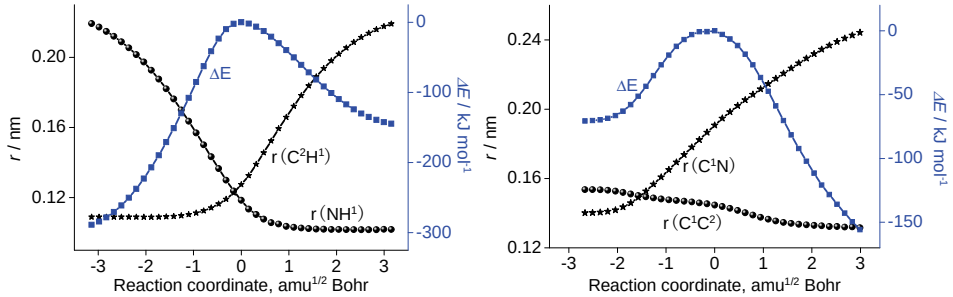


Fig. 6. Selected bond lengths and relative energy changes along the reaction coordinates based on the IRC of TS2a (left) and TS2b (right).

two unpaired electrons in the C^2 atom. In other words, IM2a has the character of an active carbene and can convert into a more stable configuration.

The third step of pathway (2) is a ring-opening process to form the allene product P2. Through cleavage of the C^1–N bond, IM2a is converted into P2 *via* TS2b, where the barrier is 64.1 kJ mol^{-1}. The calculated only imaginary frequency of the transition state TS2b is 429*i* cm^{-1}. As shown in Figs. 1 and 6, the bond distance of C^1–N in TS2b lengthens and the angle of C^1C^2N increases along with the reaction process, implying breakage of the three-membered ring involving C^1C^2N.

In P2, the bond length of C^1–C^2 is 0.1318 nm, which falls in the range intermediate between C=C and C≡C bond lengths. Similarly, the bond length of C^2–N (0.1247 nm) is between C=N and C≡N bond lengths. The three atoms, C^1, C^2 and N, are almost in the same line (the angle of C^1C^2N is 167.2°). Therefore, P2 has the typical structure of an allene. Along the reaction profile, P2 is the most stable species, which is exothermic with the value of 255.8 kJ mol^{-1} compared with those of the reactants.

CONCLUSIONS

In this study, the mechanism of the reaction between azacyclopropenylidene and oxirane was systematically investigated employing the MP2/6-311+G* level of theory. It is found that there are two pathways, denoted (1) and (2), which lead to the formation of two ultimate products, P1 and P2, respectively. The first step of the reaction is the formation of a common intermediate IM. The barrier heights of the rate-determining steps in reaction pathway (1) and (2) are 173.2 and 274.9 kJ mol^{-1}, respectively. Therefore, the reaction pathway (1) is the most favorable channel from the kinetic viewpoint. On the other hand, the corresponding two products P1 and P2 were stabilized by about 186.0 and 255.8 kJ mol^{-1} relative to the reactants, respectively. Therefore, the most favorable product P2 should be confirmed from the thermodynamic viewpoint.

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ИЗВОД

ТЕОРИЈСКО ИСПИТИВАЊЕ МЕХАНИЗМА РЕАКЦИЈЕ ИЗМЕЂУ АЗАЦИКЛОПРОПЕНИЛИДЕНА И ОКСИРАНА

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Механизам реакције између азациклопропенилидена и оксирана је систематски испитиван применом Møller–Plesset пертурбационе теорије другог реда (MP2). Циљ је био да се боље разуме реактивност азациклопропенилидена са једињењима која имају трочлани прстен, као што је оксиран. Израчунате су оптимизоване геометрије и енергије за одговарајуће стационарне тачке на површини потенцијалне енергије, и извршена вибрациона анализа. Енергије су затим додатно кориговане CCSD(T)/6-311+G* методом.

Прорачуни показују да су могућа два пута за одигравање реакције. Први је фаворизован са кинетичке а други са термодинамичке тачке гледишта.

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