

Theoretical Study on the Reaction Mechanism of Azacyclopropenylidene with Epoxypropane: An Insertion Process

Xiaojun Tan,^{*} Weihua Wang,[†] and Ping Li^{†,*}

College of Biological Science and Technology, University of Jinan, Jinan, Shandong 250022, People's Republic of China

^{*}E-mail: chm_tanxj@ujn.edu.cn

[†]School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, Shandong 273165, People's Republic of China. ^{*}E-mail: lpsdu@sdu.edu.cn

Received February 3, 2014, Accepted May 16, 2014

The reaction mechanism between azacyclopropenylidene and epoxypropane has been systematically investigated employing the second-order Møller-Plesset perturbation theory (MP2) method to better understand the reactivity of azacyclopropenylidene with four-membered ring compound epoxypropane. Geometry optimization, vibrational analysis, and energy property for the involved stationary points on the potential energy surface have been calculated. It was found that for the first step of this reaction, azacyclopropenylidene can insert into epoxypropane at its C-O or C-C bond to form spiro intermediate IM. It is easier for the azacyclopropenylidene to insert into the C-O bond than the C-C bond. Through the ring-opened step at the C-C bond of azacyclopropenylidene fragment, IM can transfer to product P1, which is named as pathway (1). On the other hand, through the H-transferred step and subsequent ring-opened step at the C-N bond of azacyclopropenylidene fragment, IM can convert to product P2, which is named as pathway (2). From the thermodynamics viewpoint, the P2 characterized by an allene is the dominating product. From the kinetic viewpoint, the pathway (1) of formation to P1 is primary.

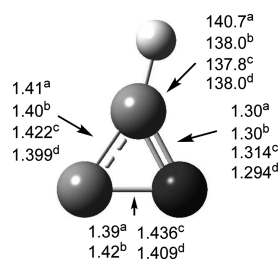
Key Words : Azacyclopropenylidene, Epoxypropane, Reaction mechanism, Molecular orbital

Introduction

Carbon chain molecules containing heteroatoms (N,¹⁻⁸ O,^{9,10} S,¹¹⁻¹³ Si¹⁴⁻¹⁶) have been paid much attention recently due to their astrophysical abundance and interesting spectroscopic properties. A typical example is cyanopolyacetylenes HC_{2n+1}N, in which HC₁₁N is one of the largest carbon chain molecules observed in interstellar medium.¹⁷ In contrast to cyanopolyacetylenes HC_{2n+1}N, systematic studies on the molecules HC_{2n}N containing *even* number of carbon atoms were relatively scarce. In spite of this, the HC_{2n}N molecules and their geometrical isomers are still very important species of astrophysical importance, where they are good candidates for astrophysical observation by microwave and infrared spectroscopy due to the rather large dipole moments of these molecules. What's exciting is that HC₂N has been observed in interstellar space.¹⁸ A lot of experimental and computational methods were carried out for the structures and the relative energies of some isomers of this system. Many studies have revealed that there are many isomers with different kinds of geometries (linear, bent or cyclic) or different multiplicities (singlet or triplet) having similar energies for the HC₂N molecules.¹⁹⁻³⁰ Lee *et al.* have characterized the quasilinear triplet, bent singlet, and cyclic singlet HC₂N isomers and determined their molecular properties with a series of highly accurate *ab initio* levels of theory.²⁷ In addition, the cyclic HC₂N isomer was found to be an intermediate between the interconversion of the bent HCCN and the unknown bent HCNC on the hypersurface of neutral, anionic, and cationic

species, where the barriers are feasible.³¹ For the most stable singlet state of HC₂N molecule, it has been displayed in Scheme 1, which has been confirmed by spectroscopy and calculation.

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 C₂H₂ in the upper atmosphere of Titan.³³ Thus, the azacyclopropenylidene seems to be a good candidate for astrophysical detection, considering these various possible formation pathways and its large dipole moment.³⁴



Scheme 1 Geometrical parameters for azacyclopropenylidene calculated at the diverse levels, where bond lengths are in Å and bond angles in degree (^a: B3LYP/6-311++G**²⁸; ^b: MP2/6-311++G**²⁸; ^c: QCISD(T)/D95**²¹; ^d: CCSD(T)/cc-pVTZ³⁰).

Computation of HC_2N molecules will be very helpful to elucidate the reactivity and kinetic stability of these molecules, but less attention has been paid to the reactivity of azacyclopropenylidene with the active species containing small ring compounds until now. In the present study, we have performed comprehensive theoretical investigations of the reaction mechanism between azacyclopropenylidene and epoxyp propane by employing the second-order Møller-Plesset perturbation theory (MP2) method in order to better understand the azacyclopropenylidene reactivity. To the best of our knowledge, this study is the first report of the reaction mechanism between azacyclopropenylidene and four-membered ring compounds. 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 interstellar space.

Calculation Method

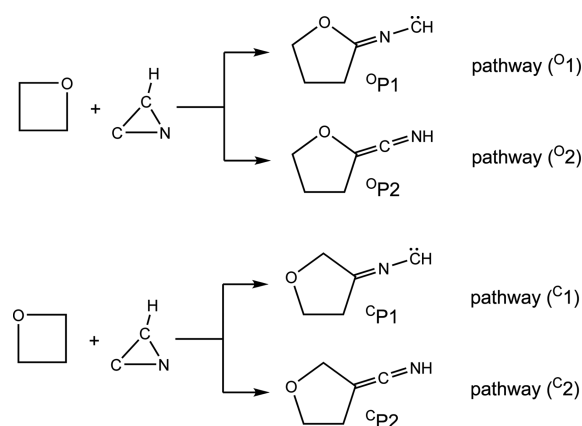
The MP2 method and the 6-311+G* basis set have been employed to locate all the stationary points along the reaction pathways. Frequency analyses have been carried out to confirm the nature of the minima and transition states at the MP2/6-311+G* level of theory, *i.e.*, all the reactants, intermediates, and products have been characterized by no imaginary frequency. 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 zero-point vibrational energy (ZPVE).

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

Results and Discussion

Azacyclopropenylidene can insert into epoxyp propane at its C-O or C-C bond. For the sake of simplicity, we mainly discuss the reaction mechanisms based on the pathways of azacyclopropenylidene insertion into epoxyp propane at its C-O bond, which is marked with superscript "O". As for the pathways of insertion into C-C bond, we mark it with superscript "C".

As displayed in Scheme 2, four possible reaction pathways for the insertion reaction between azacyclopropenylidene and epoxyp propane have been proposed. The geometric parameters for the reactants (azacyclopropenylidene (R1) and epoxyp propane (R2)), transition states (TS), intermediates (IM), and products (P) involved in the pathways (^O1), (^O2), (^C1), and (^C2) are displayed in Figure 1. Correspondingly, the calculated relative energies for the available stationary points have been summarized in Table 1. The corresponding reaction profile of the pathways (^O1) and (^O2) are illustrated in Figure 2. The reaction mechanisms of the pathways (^O1) and (^O2) are similar to the pathways (^C1) and (^C2), respectively. For the sake of simplicity, the following



Scheme 2. The proposed four reaction pathways for the insertion reaction between azacyclopropenylidene and epoxyp propane.

discussions are mainly based on the pathways (^O1) and (^O2).

Insertion Process to form Spiro Intermediate IM. The first intermediate ^OIM in the reaction between azacyclopropenylidene and epoxyp propane is formed *via* a barrier of 203.0 kJ/mol. The calculated unique imaginary frequency of the transition state ^OTS in the insertion process is 629i cm^{-1} at the MP2/6-311+G* level of theory.

As shown in Figure 1, in ^OTS, the distances of C¹-O and C¹-C⁵ are 2.049 and 2.208 Å, respectively. The distance of O-C⁵ in R2 fragment of ^OTS is elongated significantly to 1.950 Å. Thus, in the transition state ^OTS, two new bonds of C¹-O and C¹-C⁵ are to form and the O-C⁵ bond is to break simultaneously. In other words, it's the process of C¹ atom of R1 fragment insertion into the O-C⁵ bond of R2 fragment that resulted in the formation of a spiro intermediate ^OIM. Moreover, as shown in Figure 3, those changes can be further validated by the IRC calculations on the basis of ^OTS. Similarly, azacyclopropenylidene can insert into epoxyp propane at its C³-C⁴ to form a spiro intermediate ^CIM.

Qualitatively, we can explain the insertion process 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 determine the way in which the molecule interacts with other species.³⁶ As displayed in Figure 4, the weak strength of C-C and C-O bonds can be reflected from the HOMO of epoxyp propane. Obviously, all of them are characterized by the π antibonding orbital. As for azacyclopropenylidene, the activity of C¹ site can be reflected from the largest contributions on the C¹ atom to the components of the whole HOMO. Therefore, C¹ atom in azacyclopropenylidene can insert into the C-O bond or the C-C bond of epoxyp propane. Furthermore, polarized C-O bond is more active than the nonpolar C-C bond. It is easier for azacyclopropenylidene to insert into the C-O bond than it inserts into the C-C bond of epoxyp propane, which can be verified by the barrier high of this insertion process (203.0 and 235.0 kJ/mol for the insertion into C-O and C-C bond, respectively.).

As displayed in Figure 1, in ^OIM, the C² and N atoms adopt sp^2 hybridization. Compared with the isolated aza-

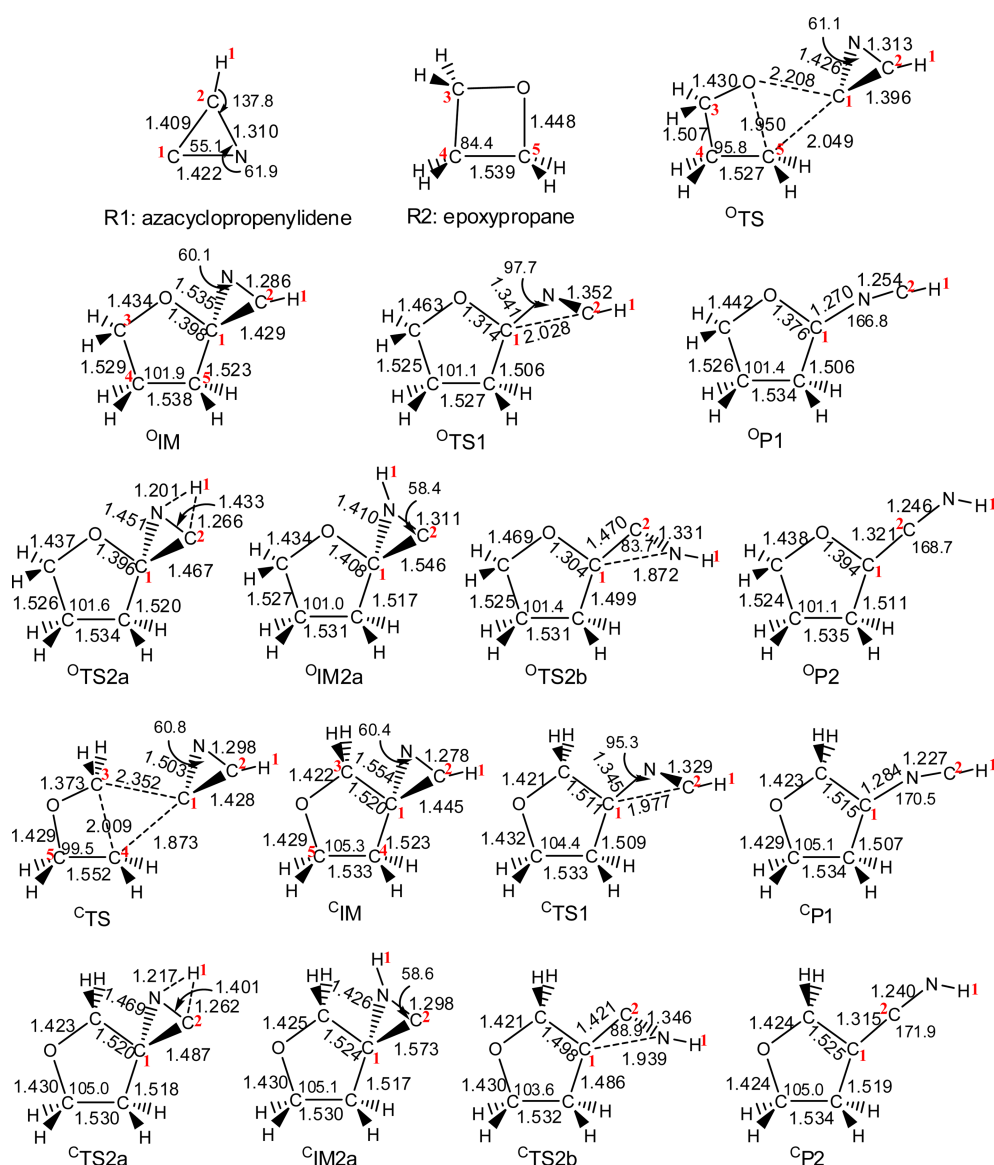


Figure 1. Optimized structures of the reactants (azacyclopropenylidene and epoxyp propane), transition states (TS), intermediates (IM), and products (P) in reaction pathways (^O1), (^O2), (^C1), and (^C2) at the MP2/6-311+G* level of theory, where the bond length and bond angle are in nm and degree, respectively.

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

Pathways	Relative Energies			
	^O TS	^O IM		
Pathway (^O 1)	203.0	-350.1		
	^O TS1	^O P1		
Pathway (^O 2)	-162.0	-263.5		
	^O TS2a	^O IM2a	^O TS2b	^O P2
	-71.2	-201.0	-146.7	-347.1
	^C TS	^C IM		
Pathway (^C 1)	235.0	-323.0		
	^C TS1	^C P1		
	-91.8	-252.8		
Pathway (^C 2)	^C TS2a	^C IM2a	^C TS2b	^C P2
	-43.1	-179.3	-54.7	-364.2

cyclopropenylidene, the bond length of C²-N in ^OIM is shortened by 0.024 Å. The angle of C¹NC² in ^OIM is 60.1°, which is decreased slightly by 1.8° relative to that of the isolated azacyclopropenylidene. Therefore, the ring-tension of R1 fragment in ^OIM is larger than that of the isolated R1. Because of the existed large tension in the three-membered ring, the C¹-C² bond in ^OIM will open. Through the ring-opened step at the C¹-C² bond, ^OIM can convert to product ^OP1, which is named as pathway (^O1). On the other hand, through the H-transferred step and subsequent ring-opened step at the C-N bond, ^OIM can turn into product ^OP2, which is named as pathway (^O2). Therefore, ^OIM is the common intermediate for the pathway (^O1) and pathway (^O2). Similarly, ^CIM is the common intermediate for the pathway (^C1) and pathway (^C2). Namely, ^CIM can convert to products ^CP1 and ^CP2 through the C¹-C² bond break and the H-transferred step

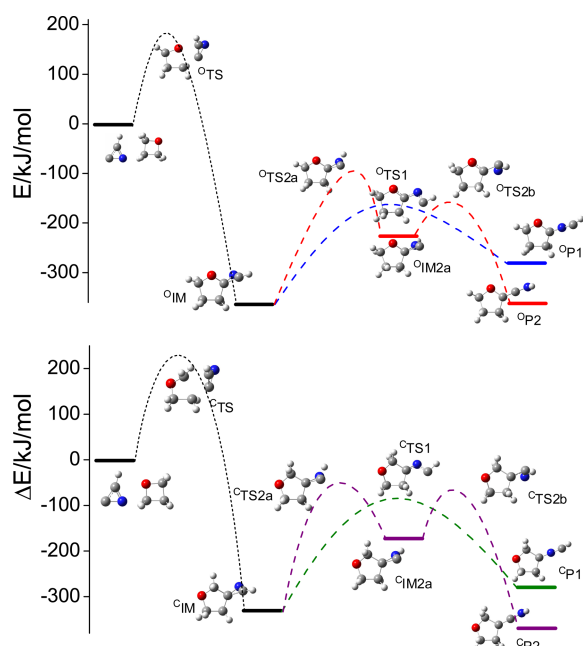


Figure 2. Reaction profiles for the pathways ($^{\circ}1$), ($^{\circ}2$) (top), and pathways ($^{\circ}1$), ($^{\circ}2$) (bottom) between azacycloprenylidene and epoxypropane at the MP2/6-311+G* level of theory.

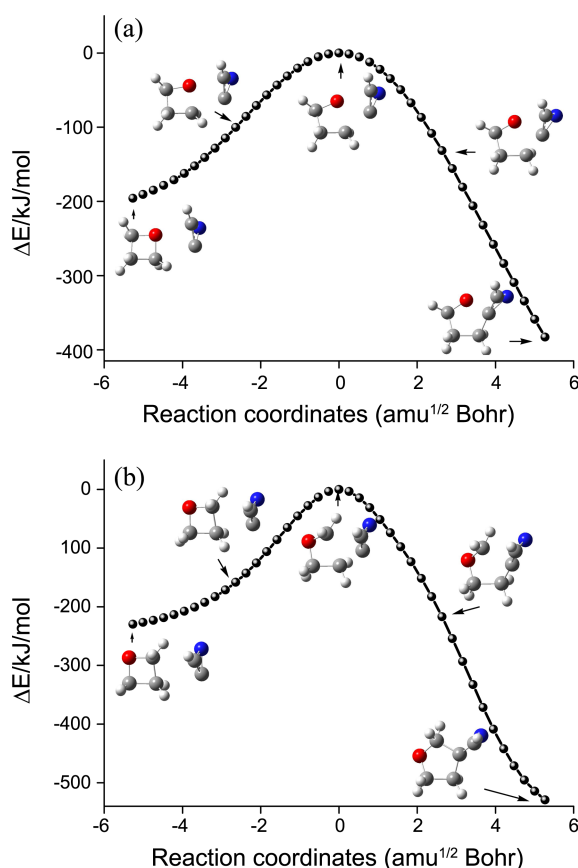


Figure 3. (a) IRC of $^{\circ}1$ TS and geometry evolution. (b) IRC of $^{\circ}1$ TS and geometry evolution.

plus the subsequent ring-opened step at the C-N bond, respectively.

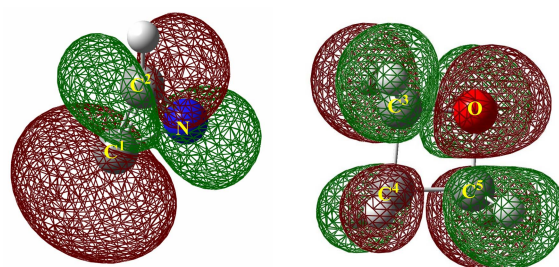


Figure 4. The calculated HOMO orbitals for azacycloprenylidene and epoxypropane.

Pathway (1): Ring-Opened Process to form Carbene product. As mentioned above, the first step of pathway ($^{\circ}1$) is the process of the formation of $^{\circ}IM$. Through the cleavage of the C^1-C^2 bond, the second step of pathway ($^{\circ}1$) is that $^{\circ}IM$ convert to $^{\circ}P1$ via $^{\circ}TS1$, where the barrier is 188.1 kJ/mol. The calculated only imaginary frequency of transition state $^{\circ}TS1$ is $365i\text{ cm}^{-1}$. IRC calculations have also been performed on the basis of the calculated $^{\circ}TS1$ to investigate the interactions between intermediate $^{\circ}IM$ and product $^{\circ}P1$ in the pathway ($^{\circ}1$) process.

As shown in Figure 1, for the angle of C^1NC^2 in $^{\circ}TS1$, it increases continuously 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^1NC^2 .

In $^{\circ}P1$, all the non-hydrogen atoms are located in the same plane approximately. The N atom adopts sp^2 hybridization and the bond length of C^1-N is 1.270 Å, which is shorter than the normal $C=N$ double bond. On the other hand, the distance of $N-C^2$ (1.254 Å) is shorter than the normal $N-C$ single bond. As for the C^2 atom, it has a pair of lone electrons, making the $^{\circ}P1$ exhibit the carbene characters. Meanwhile, as described above, all of the electrons in $^{\circ}IM$ are coupled, making it has relative stability even though there exists ring-tension in $^{\circ}IM$. Therefore, from the thermodynamics viewpoint, $^{\circ}P1$ is not a stable product. Here, the calculated relative energy for $^{\circ}P1$ is -263.5 kJ/mol , which is higher about 86.6 kJ/mol than that of $^{\circ}IM$. Similarly, the calculated relative energy of $^{\circ}C1P1$ (-252.8 kJ/mol) is higher than that of $^{\circ}C1IM$ (-323.0 kJ/mol). Therefore, $^{\circ}C1P1$ is not the most stable species along the pathway ($^{\circ}1$).

Pathway (2): H-Transferred and Ring-Opened Process to form Allene Product. The second step and the third step of pathway ($^{\circ}2$) is the H-transferred process to form spiro intermediate $^{\circ}IM2a$, and the ring-opened process to form allene product $^{\circ}P2$, respectively.

The second step of pathway ($^{\circ}2$) is the hydrogen transfer from C^2 atom to the adjacent N atom, resulting in the conversion of $^{\circ}IM$ into $^{\circ}IM2a$ via $^{\circ}OTS2a$. IRC calculations have been performed on the basis of the calculated $^{\circ}OTS2a$ and $^{\circ}OTS2b$ in the pathway ($^{\circ}2$) process. Here, the calculated barrier is 278.9 kJ/mol and the imaginary frequency of $^{\circ}OTS2a$ is $1321i\text{ cm}^{-1}$. In details, as shown in Figure 1, the distance of C^2-H^1 in $^{\circ}OTS2a$ has been elongated to 1.266 Å, and the distance of $N-H^1$ reaches to 1.201 Å, indicating that

the H¹ atom can transfer from C² atom to N atom.

Like ^oIM, ^oIM2a is also a spiro intermediate. However, its bond between C² and N atoms is a single bond, whereas it is a double bond in ^oIM. Therefore, there are two unpaired electrons in C² atom. In other words, ^oIM2a possesses carbene characters, which is active and can convert into a more stable configuration.

The third step of pathway (^o2) is the ring-opened process to form allene product ^oP2. Through the cleavage of the C¹-N bond, ^oIM2a converts into ^oP2 via ^oTS2b, where the barrier is 54.3 kJ/mol. The calculated one imaginary frequency of transition state ^oTS2b is 410i cm⁻¹. As shown in Figure 1, the bond distance of C¹-N in ^oTS2b elongates and the angle of C¹C²N increases along with the reaction process, implying the breakage of the three-membered ring involving C¹C²N.

In ^oP2, the bond length of C¹-C² is 1.321 Å, which falls in the range of the intermediate between C=C and C≡C bond lengths. Similarly, the bond length of C²-N (1.246 Å) is in the middle of C=N and C≡N bonds. The three atoms, C¹, C², and N atoms, are almost in the same line (angle of C¹C²N is 168.7°). Therefore, ^oP2 has the typical structural feature of allene. Like ^oIM, all of the electrons in ^oP2 are coupled as well. There is a three-membered ring in ^oIM, and allene in ^oP2, both of those two structures are unstable factors for a compound. Therefore, ^oIM and ^oP2 should have similar stability. Along the reaction profiles of pathway (^o1) and (^o2), ^oIM is the most stable species, which is exothermic with the value of 350.1 kJ/mol compared with those of the reactants. The energy of ^oIM is merely lower by 3.0 kJ/mol than that of ^oP2, which illustrates the similar stability of ^oIM and ^oP2. Similarly, ^cIM and ^cP2 also have similar stability. Somewhat different with reaction profile of pathways (^o1) and (^o2), the ^cP2, instead of ^cP1, is the most stable species along the pathways (^c1) and (^c2).

Conclusions

In this study, the reaction mechanism between azacyclopropenylidene and epoxypropane has been systematically investigated employing the MP2/6-311+G* level of theory. It is found that there are four pathways named (^o1), (^o2), (^c1), and (^c2) to form four ultimate products ^oP1, ^oP2, ^cP1 and ^cP2, respectively. For the reaction of azacyclopropenylidene insertion into O-C bond in epoxypropane, the first step of the reaction is the formation of the common intermediate ^oIM. The barrier height of the rate-determining step in reaction pathways (^o1) and (^o2) are 203.0 and 278.9 kJ/mol, respectively. It's more difficult for azacyclopropenylidene to insert into C-C bond in epoxypropane than into O-C bond. Therefore, the reaction pathway (^o1) is the most favorable channel from the kinetic viewpoint. On the other hand, the overall trend of stabilized energies of products is: ^cP2 (-364.2 kJ/mol) > ^oP2 (-347.1 kJ/mol) > ^oP1 (-263.5 kJ/mol) > ^cP1 (-252.8 kJ/mol). Therefore, the most favorable product ^cP2 should be confirmed from the thermodynamical viewpoint.

Acknowledgments. This work is supported by NSFC (21003082, 21303093), the project of Shandong Province Higher Educational Science and Technology Program (J13LM06), and the State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (KF2013-05).

References

1. João, B. P.; Da, S.; Mozart, N. R. *Int. J. Quantum. Chem.* **1992**, 2, 215.
2. Francisco, J. A.; Richardson, S. L. *J. Chem. Phys.* **1994**, 9, 7707.
3. Botschwina, P.; Horn, M.; Seeger, S.; Flugge, J. *Mol. Phys.* **1993**, 1, 191.
4. Botschwina, P.; Schulz, B.; Horn, M.; Matuschewski, M. *Chem. Phys.* **1995**, 190, 345.
5. Suzuki, S.; Yamamoto, H.; Ohishi, M.; Kaifu, N.; Ishikawa, S.; Hirahara, Y.; Takano, S. *Astrophys. J.* **1992**, 392, 551.
6. Matthews, H. E.; Irvine, W.; Freiberg, P.; Brown, R. D.; Godfrey, P. D. *Nature* **1984**, 310, 125.
7. Aoki, K.; Ikuta, S.; Murakami, A. *Chem. Phys. Lett.* **1993**, 3, 211.
8. Aoki, K.; Ikuta, S.; Nomura, O. *J. Chem. Phys.* **1993**, 9, 7661.
9. Irvine, W. M. *Adv. Space Res.* **1995**, 3, 35.
10. Lee, B. *Chem. Phys. Lett.* **1998**, 1-2, 171.
11. Saito, S.; Kawaguchi, K.; Yamamoto, S.; Ohishi, M.; Suzuki, H.; Kaifu, N. *Astrophys. J.* **1987**, 317, L115.
12. Bell, M. B.; Avery, L. W.; Feldman, A. *Astrophys. J.* **1993**, 417, L37.
13. Yamamoto, S.; Saito, S.; Kawaguchi, K.; Kaifu, N.; Suzuki, H.; Ohishi, M. *Astrophys. J.* **1987**, 317, L119.
14. Kim, K.; Lee, B.; Lee, S. *Chem. Phys. Lett.* **1998**, 297, 65.
15. Lee, S. *Chem. Phys. Lett.* **1997**, 1-2, 69.
16. Ohishi, M.; Kaifu, N.; Kawaguchi, K.; Murakami, A.; Saito, S.; Yamamoto, S.; Ishikawa, S. I.; Fujita, Y.; Shiratori, Y.; Irvine, W. M. *Astrophys. J.* **1989**, 345, L83.
17. Bell, M. B.; Feldman, P. A.; Travers, M. J.; McCarthy, M. C.; Gottlieb, C. A.; Thaddeus, P. *Astrophys. J.* **1997**, 483, L61.
18. McGonagle, D.; Irvine, W. M. *Astron. Astrophys.* **1996**, 310, 970.
19. McCarthy, M. C.; Gottlieb, C. A.; Cooksy, A. L.; Thaddeus, P. *J. Chem. Phys.* **1995**, 18, 7779.
20. Goldberg, N.; Fiedler, A.; Schwarz, H. *J. Phys. Chem.* **1995**, 42, 15327.
21. Aoki, K.; Ikuta, S.; Nomura, O. *J. Chem. Phys.* **1993**, 5, 3809.
22. Sun, F.; Kosterev, A.; Scott, G.; Litosh, V.; Curl, R. F. *J. Chem. Phys.* **1998**, 20, 8851.
23. Hung, P. Y.; Sun, F.; Hunt, N. T.; Burns, L. A.; Curl, R. F. *J. Chem. Phys.* **2001**, 20, 9331.
24. Rice, J. E.; Schaefer, H. F. *J. Chem. Phys.* **1987**, 12, 7051.
25. Seidl, E. T.; Schaefer, H. F. *J. Chem. Phys.* **1992**, 6, 4449.
26. Sung-Woo, P.; Sungyul, L. *Bull. Korean Chem. Soc.* **2002**, 11, 1553.
27. Natalia, I.; Xinchuan, H.; Timothy, J. L. *J. Chem. Phys.* **2011**, 135, 244310.
28. Kassae, M. Z.; Musavi, S. M.; Jalalimanesh, N. *J. Theor. Comput. Chem.* **2008**, 3, 367.
29. Kassae, M. Z.; Ghambarian, M.; Musavi, S. M. *Heteroatom Chem.* **2008**, 4, 377.
30. Jacek, K. *J. Phys. Chem. A* **2003**, 107, 4717.
31. Maier, G.; Reisenauer, H. P.; Rademacher, K. *Chem. Eur. J.* **1998**, 10, 1957.
32. Maier, G.; Bothur, A.; Eckwert, J.; Reisenauer, H. P. *Chem. Eur. J.* **1998**, 10, 1964.
33. Balucani, N.; Alagia, L.; Cartechini, M.; Casavecchia, P.; Volpi, G. G.; Sato, K.; Takayanagi, T.; Kurosaki, Y. *J. Am. Chem. Soc.* **2000**, 18, 4443.

34. Nimlos, M. R.; Davico, G.; Geise, C. M.; Wenthold, P. G.; Lineberger, W. C.; Blanksby, S. J.; Hadad, C. M.; Petersson, G. A.; Ellison, G. B. *J. Chem. Phys.* **2002**, *9*, 4323.
35. Frisch, M. J. *et al.*, Gaussian 98; Gaussian Inc.: Pittsburgh, PA, 1998.
36. Thaddeus, P.; Gottlieb, C. A.; Mollaaghababa, R.; Vrtilek, J. M. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 2125.
-