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An *ab initio* study of the mechanism of the cycloaddition reaction forming bicyclic compounds between vinylidene ($\text{H}_2\text{C}=\text{C}:$) and ethylene

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Abstract: The mechanism of the cycloaddition reaction forming a bicyclic compounds between singlet vinylidene ($\text{H}_2\text{C}=\text{C}:$) and ethylene was investigated using the CCSD(T)/MP2/6-31G* method. From the potential energy profile, it can be predicted that this reaction has one dominant channel. The presented rule of this reaction, a [2+2] cycloaddition reaction between the two reactants occurred forming a four-membered ring carbene (INT1), in which the sp lone electron of the C atom from carbene in INT1 and the π^* unoccupied orbital of ethane form the $\text{sp} \rightarrow \pi^*$ donor–acceptor effect, resulting in the formation of intermediate (INT2). Due to the further sp^3 hybridization of C atom from carbene in INT1, INT2 isomerizes to the bicyclic compound (P2) via the transition state (TS2).

Keywords: vinylidene; reaction mechanism; potential energy surface.

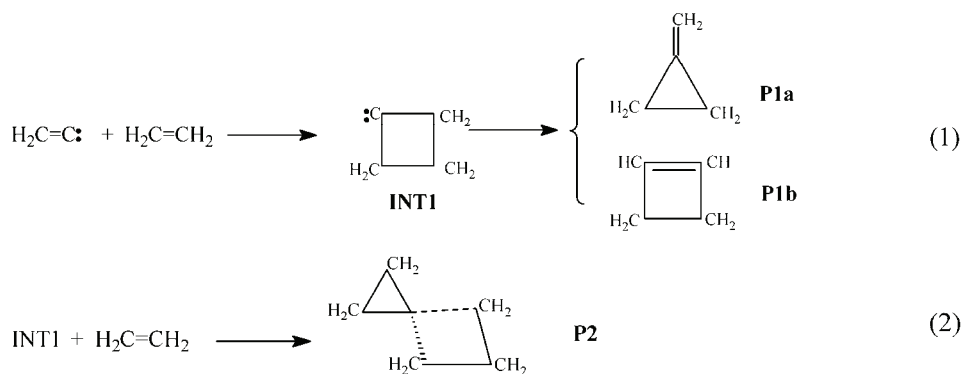
INTRODUCTION

Since unsaturated carbene was recognized as an active intermediate in the 1960s, it has not only attracted much attention from theoretical chemists but has also been practically applied in organic chemistry.^{1,2} For example, it was shown that the cycloaddition reaction of unsaturated carbene can provide a simple and direct way for the synthesis of small-ring, highly strained compounds, as well as those that can hardly be synthesized through conventional ways.² Hitherto, in depth exploration of the rearrangement reaction of alkylidene carbene has been realized,^{3,4} and the insertion reactions of alkylidene carbene have also been studied.^{5,6} Apeloig and Fox performed experimental and theoretical studies on the 3-dimensional selectivity of substitute groups from the products of the vinylidene–olefins addition reactions of alkylidene carbene.^{7,8} In previous papers, the

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mechanism of cycloaddition reaction between alkylidene carbene and asymmetric π -bonded compounds was explored.^{9–12} However, no report on the mechanism of the cycloaddition reactions between alkylidene carbene and symmetric π -bonded compounds, in which bicyclic compounds are formed, was found. It is quite difficult to investigate the mechanisms of these cycloaddition reactions directly by experimental methods due to the high activity of alkylidene carbene; therefore, a theoretical study is more practical. To explore the mechanism of cycloaddition reactions between alkylidene carbene and symmetric π -bonded compounds, in which bicyclic compounds are formed, vinylidene ($\text{H}_2\text{C}=\text{C}:$) and ethylene were selected as model molecules. Its mechanism (considering simultaneous hydrogen transfer) was investigated and analyzed theoretically. The results showed that the cycloaddition reaction has two possible pathways, as follows:



CALCULATION METHOD

MP2/6-31G^{*13} implemented in the Gaussian 98 package was employed to locate all the stationary points along the reaction pathways. Full optimization and vibrational analysis were realized for the stationary points on the reaction profile. Zero-point energy and CCSD (T) corrections were included in the energy calculations. The CCSD(T) method consists of a coupled-cluster calculation with single, double and perturbative triple excitations. Thus, this method could generate more accurate energies than the MP2 method. In order to explicitly establish the relevant species, the intrinsic reaction coordinates (IRC)^{14,15} was also calculated for all the transition states appearing on the potential energy profile.

RESULTS AND DISCUSSION

Reaction (1): channels for forming the four-membered ring intermediate (INT1), the H-transfer product (P1b) and the three-membered ring product (P1a)

Theoretical calculations show that the ground state of vinylidene is singlet state. The geometrical parameters of the intermediate (INT1), transition states (TS1a, TS1b) and products (P1a, P1b) which appear in reaction (1) between vinylidene and ethene are given in Fig. 1. The energies are listed in Table I, and

the potential energy surface for the cycloaddition reaction is shown in Fig. 2. The unique imaginary frequencies of the transition states TS1a and TS1b are 525.3 and 684.9 cm^{-1} , and consequently these transition states can be affirmed as real ones. According to the calculations of the IRC of TS1a and TS1b, further optimization for the primary IRC results, TS1a connects INT1 with P1a and TS1b connects INT1 with P1b.

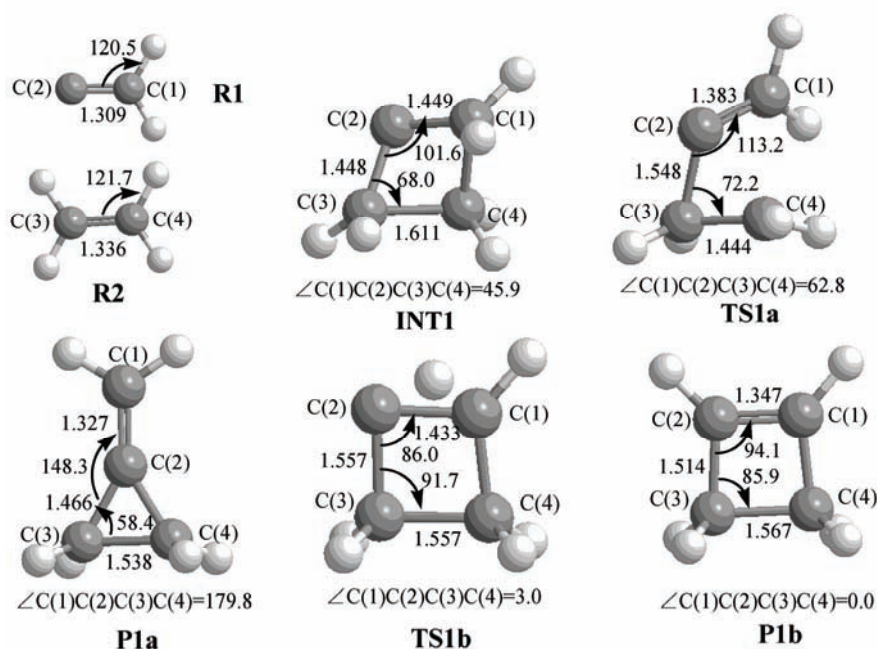


Fig. 1. Optimized MP2/6-31G* geometrical parameters and atomic numbering for the species in the cycloaddition reaction (1), in which the bond lengths and bond angles are given in angstroms and degrees, respectively.

According to Fig. 2, it can be seen that Reaction (1) has two reaction pathways a and b, both of which are composed of two steps, the first step is that the two reactants (R1, R2) form a four-membered ring intermediate (INT1), which is a barrier-free exothermic reaction of 22.9 kJ mol^{-1} ; the second step is that INT1 isomerizes to a three-membered ring product (P1a) and a H-transfer product (P1b) via transition states TS1a and TS1b, with energy barriers of 45.1 and 43.4 kJ mol^{-1} , respectively. As the barrier difference is only 1.7 kJ mol^{-1} , Reactions a and b mutually compete.

Reaction (2): the channel for forming the bicyclic compound (P2)

In Reaction (2), INT1 further reacts with ethylene (R2) to form a bicyclic compound (P2). The geometrical parameters of the intermediate (INT2), transi-

tion state (TS2) and the product (P2) appearing in Reaction (2) are given in Fig. 3. The energies are listed in Table 1 and the potential energy surface for the cycloaddition reaction is shown in Fig. 2. The unique imaginary frequencies of the transition state TS2 is 180.1 cm^{-1} and, consequently, the transition state can be affirmed as a real one. According to the calculations of the IRC of TS2 and further optimization for the primary IRC results, TS2 connects INT2 with P2.

TABLE I. Zero point energy ($ZPE / \text{a. u.}$), total energies ($E_T / \text{a. u.}$) and relative energies ($E_R / \text{kJ}\cdot\text{mol}^{-1}$) for the species from various theoretical methods (${}^a E_T = E(\text{Species}) + ZPE$, ${}^b E_R = E_T - E_{(R1+R2)}$, ${}^A E_T = E_T - E_{(\text{INT1}+\text{R2})}$, ${}^B E_R = E_T - E_{(\text{INT1}+\text{R2})}$)

Reaction	Species	ZPE	MP2/6-31G*		CCSD(T)//MP2/6-31G*	
			${}^a E_T$	${}^b E_R$	${}^A E_T$	${}^B E_R$
Reaction (1)	R1+R2	0.07620	-155.19440	0.0	-155.27029	0.0
	INT1	0.08701	-155.21863	-63.62	-155.27902	-22.9
	TS1a (INT1-P1a)	0.08502	-155.20073	-16.62	-155.26185	22.2
	P1a	0.08726	-155.30944	-302.04	-155.36961	-260.8
	TS1b (INT1-P1b)	0.08372	-155.19920	-12.60	-155.26250	20.5
	P1b	0.08838	-155.32180	-334.49	-155.38185	-292.9
Reaction (2)	INT1+R2	0.13905	-233.45162	0.0	-233.54891	0.0
	INT2	0.13961	-233.45378	-5.7	-233.55087	-5.1
	TS2 (INT2-P2)	0.14093	-233.45086	-2.0	-233.54875	0.4
	P2	0.14823	-233.59602	-379.1	-233.68358	-353.6

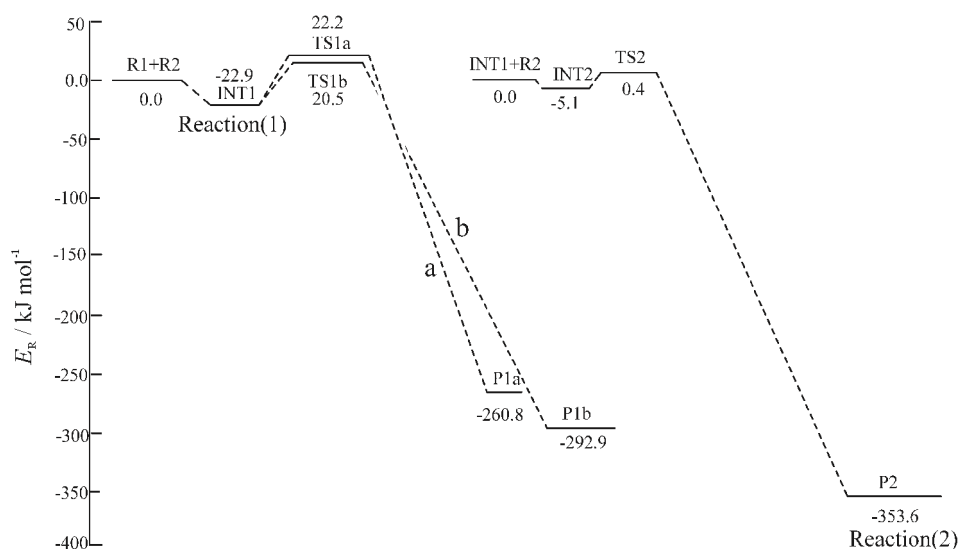


Fig. 2. The potential energy surface for the cycloaddition reactions of vinylidene and ethylene at the CCSD(T)//MP2/6-31G* level.

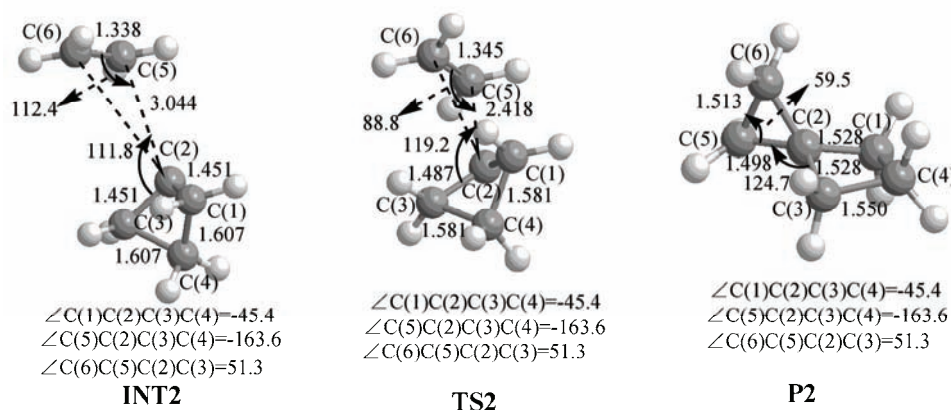
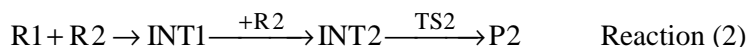


Fig. 3. Optimized MP2/6-31G* geometrical parameters and atomic numbering for INT2, TS2 and P2 in the cycloaddition reaction (2), in which the bond lengths and bond angles are given in angstroms and degrees, respectively.

According to Fig. 2, it can be seen that the reaction pathway of reaction (2), based on the two reactants (R1, R2) forming the intermediate (INT1), involves INT1 further reacting with ethylene (R2) to form the intermediate INT2, which is also a barrier-free exothermic reaction of 5.1 kJ mol^{-1} . In the next step, the intermediate (INT2) isomerizes to the bicyclic compound (P2) via a transition state (TS2), with an energy barrier of 5.5 kJ mol^{-1} . Comparing reaction (2) with reaction (1), two reactions mutually compete for INT1 but because $\text{INT1} \rightarrow \text{P1a}$ and $\text{INT1} \rightarrow \text{P1b}$ have to climb over barriers of 45.1 and 43.4 kJ mol^{-1} , respectively, while $\text{INT1} + \text{R2} \rightarrow \text{INT2}$ can directly reduce the system energy by 5.1 kJ mol^{-1} , reaction (2) is the dominant reaction pathway.

Theoretical analysis and explanation of the dominant reaction pathway

According to the above analysis, the dominant reaction pathway of the cycloaddition reaction between singlet state vinylidene and ethylene as follows:



The frontier molecular orbitals of R1, R2 and INT1 in these reactions are shown in Fig. 4. According to Fig. 4, the mechanism of the reaction can be explained with the schematic frontier molecular orbitals diagrams (Figs. 5 and 6) and Figs. 1 and 3. According to Figs. 1 and 5, when the vinylidene (R1) interacts with ethane (R2), due to the two π orbital in the reactants; a [2+2] cycloaddition reaction occurs, forming the four-membered ring carbene (INT1). In INT1, because of the unsaturated character of the C(2) atom from carbene, INT1 reacts further with ethylene (R2) to form the bicyclic compound (P2). The mechanism of the reaction can be explained by Figs. 3 and 6 as: INT1 initially interacts with ethane (R2), the sp lone electron of C(2) in INT1 and the π^* unoccupied orbital

of ethene forming a $sp \rightarrow \pi^*$ donor–acceptor effect, resulting in the formation of the intermediate INT2; as the reaction proceeds, the C(2)–C(5) bond (INT2: 3.044 Å; TS2: 2.418 Å; P2: 1.498 Å) gradually shortens after the transition state (TS2) due to further sp^3 hybridization of the C(2) atom from carbene in INT1. Finally, INT2 isomerizes to the bicyclic compound P2.

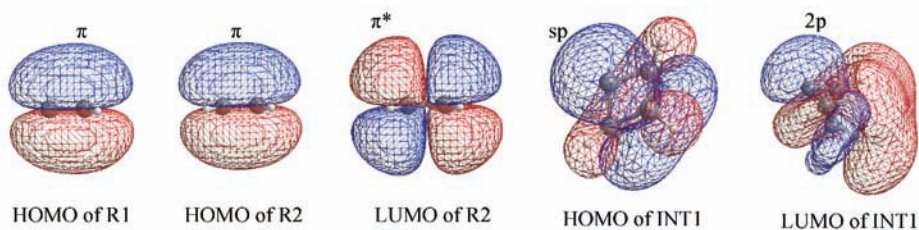


Fig. 4. The frontier molecular orbitals of R1, R2 and INT1.

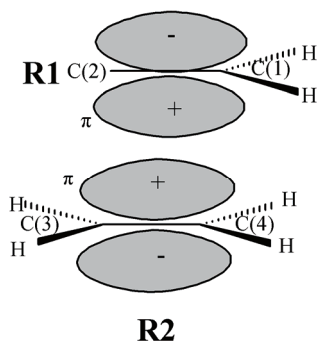


Fig. 5. A schematic interaction diagram for the frontier orbitals of $H_2C=C:$ (R1) and $H_2C=CH_2$ (R2).

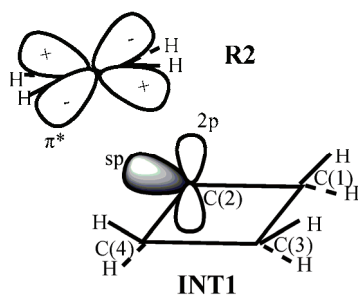


Fig. 6. A schematic interaction diagram for the frontier orbitals of INT1 and $H_2C=CH_2$ (R2).

CONCLUSIONS

From the potential energy profile of the cycloaddition reaction between singlet vinylidene ($H_2C=C:$) and ethane, forming a bicyclic compound, it can be predicted that this reaction has one dominant channel. The dominant channel of this reaction consists of three steps: *i*) the two reactants first form a four-membered ring carbene (INT1) through a barrier-free exothermic reaction of 22.9 kJ mol^{-1} ;

ii) the four-membered ring carbene INT1 further reacts with ethane (R2) to form an intermediate (INT2) through a barrier-free exothermic reaction of 5.1 kJ mol⁻¹;
iii) INT2 isomerizes to a bicyclic compound (P2) *via* a transition state (TS2) with an energy barrier of 5.5 kJ mol⁻¹.

ИЗВОД

AB INITIO ПРОУЧАВАЊЕ МЕХАНИЗМА РЕАКЦИЈЕ ЦИКЛОАДИЦИЈЕ КОЈОМ
НАСТАЈЕ БИЦИКЛИЧНО ЈЕДИЊЕЊЕ ВИНИЛИДЕНА (H₂C=C:) И ЕТИЛЕНА

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Механизам реакције циклоадиције којом настаје бициклично једињење синглетног винилидена (H₂C=C:) и етилена испитиван је коришћењем CCSD(T)MP2/6-31G* методе. На основу профила потенцијалне енергије може да се предвиди да ова реакција има један доминантан пут. Приказани реакциони пут, [2+2] реакција циклоадиције између два реактанта, која се одиграва стварањем четворочланог карбенског прстена (INT1), у којем неспарени sp електрон C атома из карбена у INT1 и π* непопуњена орбитала етана остварују sp→π* донор–акцептор ефекат, што резултује настајањем интермедијара (INT2). Због даље sp³ хибридизације C атома из карбена у INT1, INT2 се изомеризује у бициклично једињење (P2) преко прелазног стања (TS2).

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REFERENCES

1. P. Stang, *Acc. Chem. Res.* **15** (1982) 348
2. P. Stang, *Chem. Rev.* **78** (1978) 384
3. R. Krishnan, M. J. Frisch, J. A. Pople, *Chem. Phys. Lett.* **79** (1981) 408
4. M. J. Frisch, R. Krishnan, J. A. Pople, *Chem. Phys. Lett.* **81** (1981) 421
5. D. J. Wardrop, W. Zhang, *Tetrahedron Lett.* **43** (2002) 5389
6. K. S. Feldman, A. L. Perkins, *Tetrahedron Lett.* **42** (2001) 6031
7. Y. Apeloig, M. Karni, P. J. Stang, D. P. Fox, *J. Am. Chem. Soc.* **105** (1983) 4781
8. D. P. Fox, P. J. Stang, Y. Apeloig, M. Karni, *J. Am. Chem. Soc.* **108** (1986) 750
9. X. H. Lu, Y. X. Wang, *J. Phys. Chem. A* **107** (2003) 7885
10. X. H. Lu, W. R. Wu, H. B. Yu, X. L. Yang, Y. H. Xu, *J. Mol. Struct. (Theochem.)* **755** (2005) 39
11. X. H. Lu, H. B. Yu, W. R. Wu, Y. H. Xu, *Int. J. Quantum Chem.* **107** (2007) 451
12. X. H. Lu, P. P. Xiang, W. R. Wu, X. Che, *J. Mol. Struct. (Theochem.)* **853** (2008) 82
13. L. A. Curtis, K. Raghavachari, J. A. Pople, *J. Chem. Phys.* **98** (1993) 1293
14. K. Fukui, *J. Chem. Phys.* **74** (1970) 4161
15. K. Ishida, K. Morokuma, A. Komornicki, *J. Chem. Phys.* **66** (1977) 2153.