**Research Article**

# Studying on the Addition Reaction Mechanism of Ethylene and Butadiene based on Density Functional Theory

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**Abstract**
Only one-step reaction has been identified for the addition reaction mechanism of ethylene and butadiene based on the first principles calculations. The reactant, product, and transition state (TS) are determined by optimization calculation and confirmed by frequency analysis. The intrinsic reaction coordinate is also calculated to validate the reaction process. Result shows that the whole reaction is an exothermic reaction. The charge distribution is used to understand the novel reaction. In this study, the activation energy of the addition reaction of ethylene and butadiene is 0.83eV, and the heat release of the whole reaction is 2.01eV. The molecular structure, charge distribution and energy of butadiene and ethylene are investigated at the molecular level. The calculated activation energy is helpful for understanding the cyclic addition reaction of butadiene and ethylene, providing theoretical guidance for experiments and deepening people's understanding of this reaction.

**Keywords:** Addition Reaction, Energy Barrier, Intrinsic Reaction Coordinate, Ethylene and Butadiene

## Introduction

Ethylene is a synthetic plastic (PE, PVC), fiber, rubber, ethanol (alcohol) of basic chemical raw materials, also is one of the world's biggest chemical products production, ethylene industry is the core of the petroleum chemical industry, Therefore, ethylene output is also an important measure of national petrochemical labelling. Ethylene has the role of promoting fruit ripening, which is often used as a ripening agent. Butadiene, a colourless faint aromatic gas, anesthetic, especially stimulate the mucous membrane, easy to liquefy, is the main raw material for the production of rubber. Butadiene molecular contains two C=C bonds, which can undergo addition reaction. Cyclohexene is an important organic chemical raw material. It is generally used in the synthesis of pesticides, pharmaceutical intermediates and polymers.

Addition reaction refers to the reaction in which carbon atoms at both ends of the double bond (or triple bond) in organic molecules combine directly with other atoms or groups to form new compounds. The addition reaction of butadiene and ethylene is a typical Diela-Alder reaction [1], which was used as an example in the frontier molecular orbital theory proposed by K.Fukui and the energy-related theory proposed by R.B.Woodward and R.Hoffman [2].

Wu reported that ethylene units into polybutadiene backbones are an approach to synthesize advanced rubber materials, which

has been a research challenge because of distinct polymerization mechanisms of the two monomers [3]. Codimerization of ethylene and butadiene carried out starting with rhodium trichloride trihydrate was also studied by Su [4]. Sautet compared the different low temperature coordination modes of ethylene and butadiene on a platinum (111) face, (110) face and on a palladium (111) face on the basis of extended Hi~ckel calculations [5]. Gul reported acrylonitrile butadiene styrene/ethylene vinyl acetate-based melt blends were prepared using linear low-density polyethylene as modifier [6]. Ma studied the adsorption of cyclohexene and its dehydrogenation intermediates on nAu/Pt (100) (n=0,1,2) surfaces by DFT study [7]. Vandichel investigated the epoxidation reaction of cyclohexene for the catalytic system vanadyl acetylacetonate with tert-butyl hydroperoxide as oxidant with the aim to identify the most active species for epoxidation and to retrieve insight into the most plausible epoxidation mechanism [8].

However, the TS, reaction path and reaction energy barrier about the addition reaction of ethylene and butadiene to form cyclohexene have not been studied based on the first principles calculations. Therefore, based on density functional theory (DFT) calculations, we have conducted an in-depth study on the reaction path of the addition reaction of butadiene and ethylene to generate cyclohexene. The reactant, product, and TS are optimized and the reaction mechanism is analyzed, which will help people to have a deeper understanding of the mechanism of this

addition reaction. It can also provide theoretical guidance for experimental synthesis of cyclohexene.

## Computational Methods

First principles calculations are performed with the hybrid functional DFT (B3LYP) [9] implemented in the Gaussian 09 program [10, 11]. B3LYP is a gradient-corrected hybrid DFT with exchange-correlation functional in Becke's three-parameter form, which includes a mixture of Hartreee Fock exchange with the Vosko, Wilk and Nusair (VWN) functional III for local correlation and the correlation functional of Lee, Yang, and Parr (LYP) for non-local correlation [12]. The mixed basis set of the 6-31G (d, p) is adopted. Geometry optimization and frequency calculation of all stationary points (reactant, product, and TS) for the addition reaction of ethylene and butadiene are performed at the same theoretical level. Initially, the structures of ethylene and butadiene are optimized respectively. Then, the adsorption site is chosen and putting ethylene and butadiene on the same plane to construct the adsorption complex, which is the reactant of the addition reaction, and cyclohexene as the product of the addition reaction. After the reactant and product are optimized and their energy stability has been confirmed with harmonic frequency analysis, the TS is searched by using the quadratic synchronous transit (QST2) method [13]. The obtained TS is confirmed with TS optimization algorithm and another frequency calculation. All structures are fully optimized to local minima except for the TS that is optimized with the constrained optimization. Vibrational frequencies are used to confirm the minima geometries and the TS. Intrinsic reaction coordinate (IRC) calculation is performed at the same level to confirm the connection of the product and the reactant [14]. Thus, the entire reaction path has been constructed. The activation energy ($E_{activation}$) or energy barrier for reaction is calculated according to the following formula:

$$E_{Activation} = E_{TS} - E_{Reactant} \qquad (1)$$

All calculations are convergent to the default criterion of Gaussian 09 program. The standard self-consistent energy convergence in the calculation is $1.0*10^{-6}$ Hartree. The standard maximum displacement and maximum forceconvergence in the calculation are $1.8*10^{-3}$Å and $4.5*10^{-4}$ Hartree/Bohr, respectively.

## Results and Discussion
### Geometric structure
### Geometric structure of ethylene and butadiene

We built the initial structures of ethylene and butadiene, and obtained stable structures with optimization calculations. The energy stability of them has been confirmed because no imaginary frequency has been found.

Figure 1 (left) is the geometric structure of ethylene. The length of C-C bond is 1.331Å, and the four C-H bonds are 1.088Å. It can be seen from the figure that there are only two different bonds, namely C=C and C-H. Two C atoms are distributed in the center of ethylene, while four H atoms are evenly distributed and symmetrical around it.

Figure 1 (right) is the geometric structure of butadiene. One can find that four C and six H atoms are in the same plane, four C atoms are symmetrically distributed, and there are six H atoms around them. There are three different bonds: C=C, C-C and C-H. There are two C=C bonds and one C-C bond. The length of C-C bond is 1.470Å, the lengths of two C=C bonds are1.339Å. The length of C-H bond is between 1.086Å and 1.091Å.
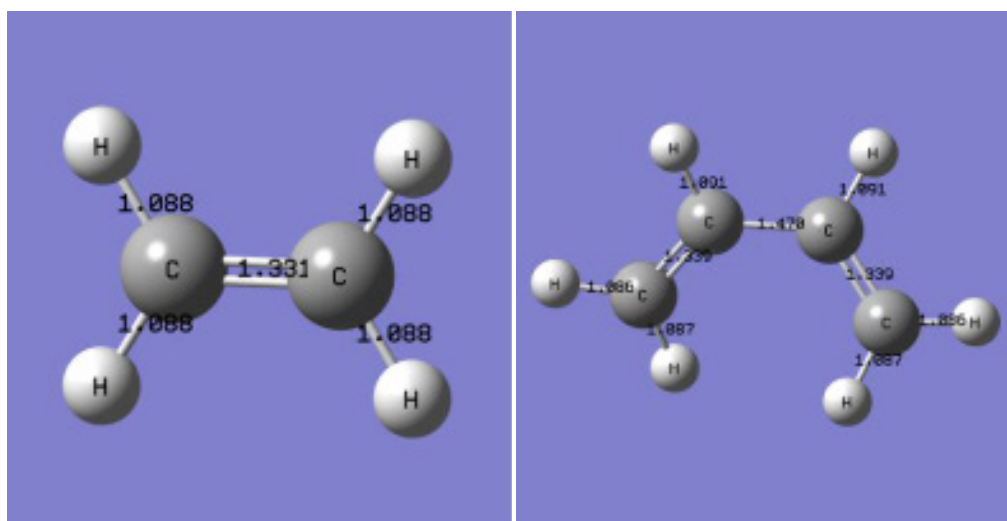


**Figure 1:** Optimized ethylene and butadiene

## Geometric structure of reactant and product

Figure 2 (left) is the geometric structure of reactant which is composed by ethylene and butadiene. In this reactant, the length of three C=C bond is 1.326Å, one C-C bond is 1.548Å, and C-H bond is 1.098 Å. We obtained stable structure of cyclohexene with optimization calculation by the same base set, as shown in Figure 2 (right). They are stable in terms of energy because no imaginary frequency is found for them.

Cyclohexene consists of 6 carbon atoms forming a carbon ring structure composed of one C=C bond and five C-C bonds. As can be seen from Figure 2, the length of C=C bond is 1.337 Å. The length of two C-C bonds adjacent to C=C bond is 1.510Åwhile the rest of three C-C bonds is 1.535~1.537 Å.
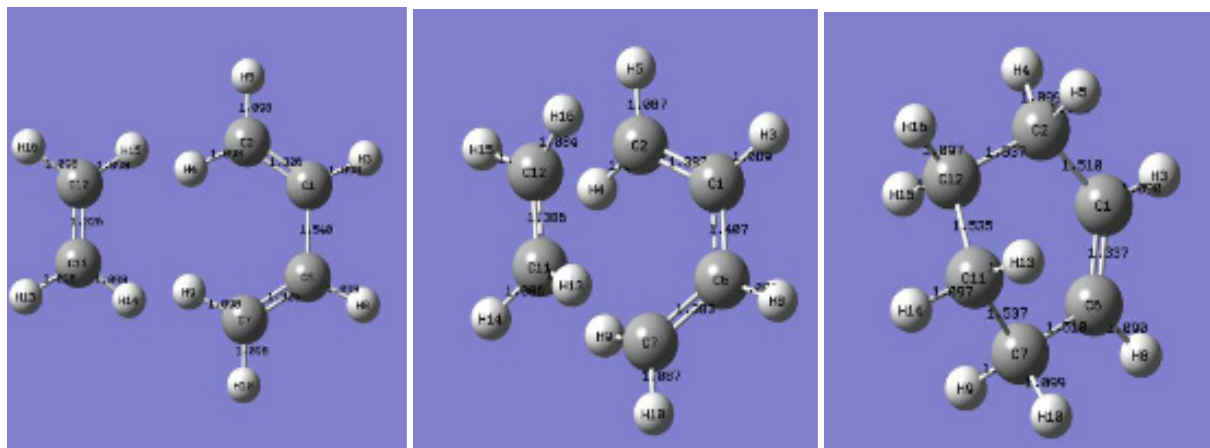


**Figure 2:** Geometric structures of reactant, TS and product

## Addition reaction of ethylene and butadiene
### Reaction path of cyclization addition reaction

Using the obtained geometrical structure composed of ethylene and butadiene as reactant and corresponding cyclohexene as product, we searched the TS connecting the reactant and product by using the quadratic synchronous transit (QST2) method. The obtained TS is confirmed again using TS optimization and frequency calculation. The imaginary frequency is up to -525.79 cm$^{-1}$. All structures are fully optimized to local minima except for the TS that is optimized via constrained optimization. We then studied the addition reaction process using the reaction path by using the algorithm intrinsic reaction coordinate (IRC) to clarify the correlation among the reactant, TS, and the product. The reactant and the final product of the reaction are optimized again and then compared with the previous ones, in which the same structure was found, respectively.

Figure 2 (middle)shows the obtained TS corresponding to reactant and product. The obtained reaction path (IRC) of the cyclization addition reaction of ethylene and butadiene to generate cyclohexene is shown in Figure 3. It is worth noting that the last structures of both reactant and product ends have not really reached to the optimized reactant and product, because the value of the imaginary is difficult to reach to the tolerance limits when the potential energy surface in the ranges of the two ends are very flat. Fortunately, we have obtained both the reactant and the product, which are same as those we have optimized above when we performed the optimizations using the last structures of the two ends on the reaction path as initial structures. The energy of reactant and product is -234.5744 Hartree and -234.64829 Hartree (1Hatree=27.21eV), respectively. The most stable cyclohexene configuration is generally lower than the complex configuration. Thus, the energy of the product is lower than that of the reactant, and the whole reaction process is exothermic.
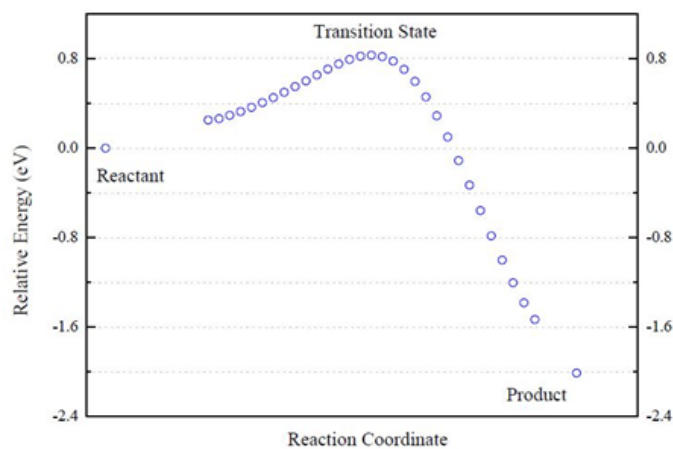


As can be seen from IRC diagram, as the reaction progresses, the energy of the system gradually increases. In order to facilitate comparison, we set the energy of the reactant as zero. Both the TS and the product are the energy relative to the reactant, so they are relative energy. When calculating the reaction path, we set Max Point to 30, and the energy of the TS reaches the maximum (-234.5438966 Hatree), and the relative energy is 0.83014eV. Therefore, the activation energy of the reaction is 0.83014eV, and the energy of the product is -2.00948eV. Thus, the addition reaction is exothermic and the heat released is -2.00948eV. In conclusion, as long as the activation energy of 0.83014 eV is overcome, the cyclization addition reaction can proceed smoothly. This addition reaction first absorbs 0.83014eV energy to reach the saddle point, then releases 2.83962eV energy, and finally produces cyclohexene, the product of this reaction.

As the reaction goes on, the total energy of the system also increases with the increase in C=C distance. The total energy peaks when the C=C distance (12-C and 11-C) of ethylene, (1-C and 2-C; 6-C and 7-C) of butadiene increase to above 1.383Å. Meanwhile, C=C breaks to form C-C. The new bond (1-C and 6-C) becomes C=C, and the new C-C bonds (12-C and 2-C) and (11-C and 7-C) form. Then the total energy of the system gradually decreases thereafter. When the length of C-C bonds (12-C and 2-C, 11-C and 7-C) reaches 1.537Å, and the length of C-C bond (11-C and 12-C) reaches 1.535Å, the energy of the system is minimum and a stable product is formed.

## Charge analysis

We calculated the Hirshfeld charges for reactant, TS and product of the addition reaction of ethylene and butadiene, and the results are shown in Figure 4. Table 1 lists each atom charges. One can find that all C atoms are negatively charged and H atoms are positively charged. As the reaction progresses, the charge of 2-C and 7-C atoms near to ethylene in butadiene increases, reaching their maximum charge at the saddle point, and then gradually decreases. It was shown that the charge attraction of C atoms (2-C and 7-C) in butadiene and H atoms (13-H and 16-H) in ethylene promoted the reaction.
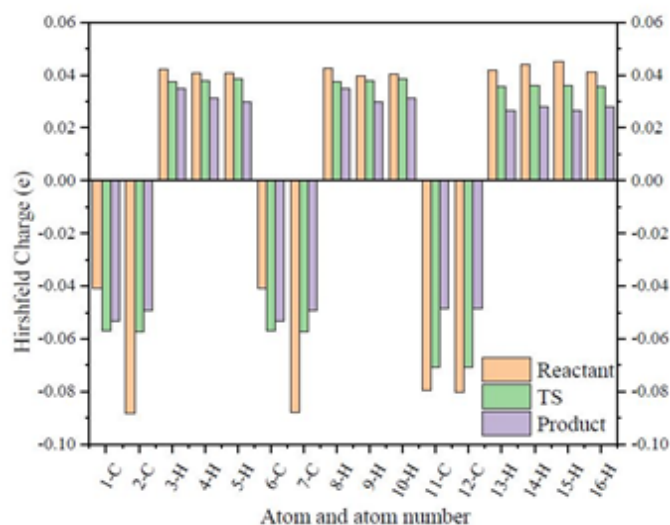


**Figure 4:** The Hirshfeld charges for reactant, TS and product of the addition reaction

**Table 1: Each atom charges in reactant, TS and product of the addition reaction**

| Atom | Reactant | TS | Product |
|------|----------|-----|---------|
| 1-C | -0.0408616875 | -0.0569083349 | -0.0531786904 |
| 2-C | -0.0884282225 | -0.0574409716 | -0.0491419752 |
| 3-H | 0.0421699251 | 0.0372900504 | 0.0349435528 |
| 4-H | 0.0407763630 | 0.0376494274 | 0.0313732398 |
| 5-H | 0.0406293505 | 0.0384217735 | 0.0299666151 |
| 6-C | -0.0407844490 | -0.0569204949 | -0.0531711009 |
| 7-C | -0.0877578878 | -0.0574312833 | -0.0491375007 |
| 9-H | 0.0396327415 | 0.0376512249 | 0.0299600942 |
| 10-H | 0.0402902564 | 0.0384210525 | 0.0313942812 |
| 11-C | -0.0796287049 | -0.0705928255 | -0.0486416634 |
| 12-C | -0.0803709040 | -0.0705929957 | -0.0486431845 |
| 13-H | 0.0417853656 | 0.0355099620 | 0.0267049724 |
| 14-H | 0.0441093333 | 0.0360721779 | 0.0279635145 |
| 15-H | 0.0450477460 | 0.0360585920 | 0.0267047942 |
| 16-H | 0.0410113996 | 0.0355147947 | 0.0279668371 |

As shown in Figure 5, for reactant composed by ethylene and butadiene, the HOMO and LUMO are completely located on the butadiene, with the Eg (energy gap) of 5.64eV. The hybridization is mainly p-p hybridization to form the π bond, which is the phase overlap. We also examine the HOMO and LUMO for product and find that the HOMO and LUMO mainly locate on 1-C, 2C and 6-Catoms, while the HUMO locate on a small part on 5-H and 9-H atoms. And the hybridization is mainly p-p hybridization to form the π bond, and the hybridization is also s-sand s-p hybridization. Eg generally refers to the energy difference between the valence (HOMO) and the conduction levels (LUMO) in insulators and semiconductors. Therefore, the Egis one of the most important factors in determining the electrical conductivity of the materials. The Eg of system is increased from 5.64 eV to 7.28 eV, implying that the electrical conductance of the product system is decreased. It also shows that the product is more chemically stable than the reactant.
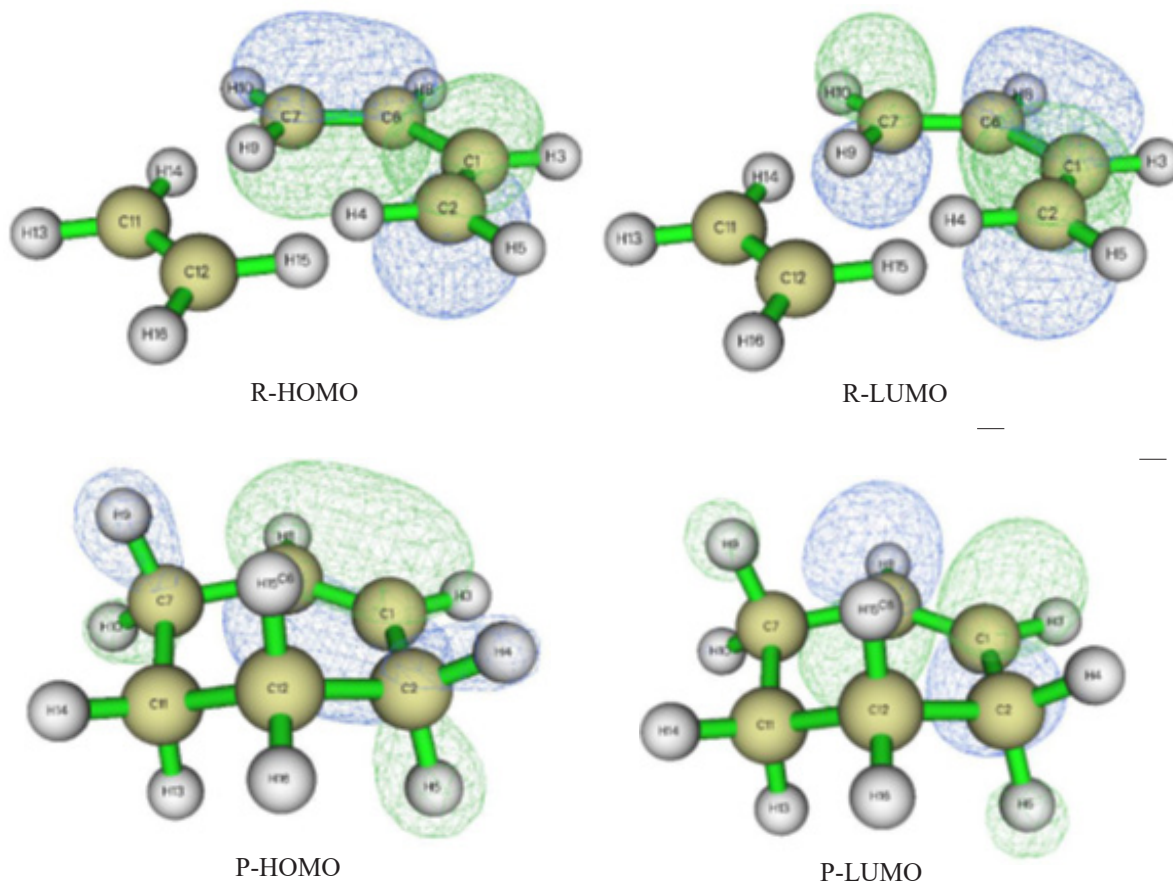


R-HOMO

R-LUMO

P-HOMO

P-LUMO

**Figure 5:** The HOMO and LUMO of reactant (R) and product (P).

## Conclusion

In summary, we identified the reaction path for addition reaction mechanism of ethylene and butadiene based on the first principles calculations. The cyclic addition reaction is completed with only one step. The energy barrier of the reaction is 0.083 eV, implicating that cyclohexene can be easily synthesized through addition reaction of ethylene and butadiene under appropriate conditions. The ethylene and butadiene can react to form cyclohexene by overcoming a 0.083 eV barrier. The cyclohexene molecule is obtained with an only one-step reaction. The IRC demonstrates that the whole process of the addition reaction is exothermic with 2.00 eV of reaction energy. The reaction is supported by the wonderful charge distribution. The reaction shows close relationship with the charge distribution of the C atoms near to ethylene in butadiene that promoted the reaction. The calculated activation energy is helpful for understanding the cyclic addition reaction of butadiene and ethylene, providing theoretical guidance for experiments and deepening people's understanding of this reaction.

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