

Cycloaddition Reactions Between C₃₀ and Buta-1, 3 -diene An ab Initio Study

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ABSTRACT

Cycloaddition reaction between C₃₀ and buta-1, 3-diene was studied within the framework of AMI (RHF) level. The reaction involving the double bond between two hexagons and a hexagon and a pentagon, as well as the cycloaddition products followed by disrotatory $\sigma_2s + \pi_4s$ electrocyclic ring openings were considered. Thermodynamics parameters and stability energy and transition state are evaluated in three valence isomers.

Keywords: Nano structures of Fullerene, C₃₀; AMI calculations; Cycloadditions

INTRODUCTION

It is known that C₆₀ undergoes various types of cycloaddition reactions, of these [4+2], [3+2], [2+2] and [2+1] are to be mentioned [1-9]. The synthesis and characterizations of the products of cycloadditions of C₆₀ greatly increased the knowledge of fullerene chemistry. In addition, these chemical transformations also provide a very powerful tool for the fullerene functionalization. Almost any functional group can be covalently linked to C₆₀ by the cycloaddition reactions of suitable addends with C₆₀. Some types of the cycloadducts were found to be remarkably stable even at high temperatures [10].

The double bonds between two hexagons in C₆₀ structure are dienophilic, which enable the molecule to undergo a variety of Diels-Alder reactions ([4+2] cycloaddition) [11, 12]. The conditions for cycloadduct formation strongly depend on the reactivity of the diene. Most [4+2] reactions with arc C₆₀ accomplished under thermal conditions, but photochemical reaction have also been reported, and in various additions microwave irradiation can efficiently be used as source of energy [13]. Equimolar amounts of

a cyclopentadiene and C₆₀ react at room temperature to give the monoadduct in comparatively high yield [14, 15].

Fullerene and its derivatives are the most popular structural units in organic chemistry. Collision of fullerene under laser radiation or paralyse cause to preparation of some derivatives of fullerene such as C₅₈, C₃₆, C₃₃, C₃₂, C₄₀, C₂₈, C₂₆, C₂₄ and C₂₀. The C₃₀ is the interesting derivative molecules from C₆₀. The symmetrical structural of the C₃₀ molecules and different position for cycloaddition cause choosing for these calculations. In this calculation cycloaddition reaction on some different position of double bond in C₃₀ with butadiene (fig. 1) carried out and simulated by ab initio calculations. The stability of energy, reaction pathway and transition state and thermodynamics properties for this addition for all situations calculated.

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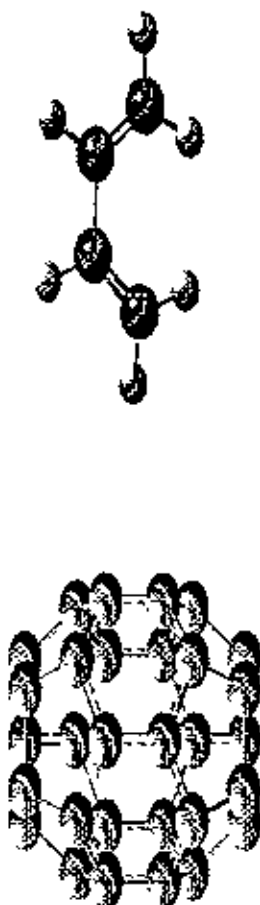


Fig.1. Structures of C_{30} and Buta-1,3-diene.

METHODS

In the present treatise, the geometry optimizations of all the structures leading to energy minima were achieved by using AM1 self-consistent fields molecular orbital (SCF MO) [11] method at the restricted Hartree-Fock (RHF) level [12]. The initial geometry of butadiene and C_{30} structures was excerpted from Gauss View. All these calculations were performed by using Gaussian 98.

C_{30} have three structures and per each of structures to be three valence isomers that we calculated reaction pathway and transition state and intermediate structure in cycloaddition reaction for each different position of double bond in each three valence isomer reaction pathway scanned step by addredundant key words.

Frequency calculations have been performed for the all reactants, TSs and products mentioned

above in order to determine their stabilities. Intrinsic reaction coordinates were also calculated to confirm the accuracy of the TSs and their thermodynamic geometry parameters are listed in Table 1.

RESULTS AND DISCUSSION

Presently considered cycloaddition products of C_{30} structures and buta diene are shown in fig. 2.



Fig. 2. Three structures of C_{30} and buta 1,3 diene.

Table 1. Some thermodynamic parameters at T=298.15K, P=1atm for three structure of C₃₀

Kcal/mol	C30-3	C30-2	C30-1
ΔG	-136.424	-430.289	-103.807
ΔH	-151.711	-584.858	-118.654
ΔE	7.626	7.801	5.691
ΔS	-0.851277	-0.051839	-0.050469
C_v	-0.001254	-0.000423	-0.000044
ZPE	8.50325	5.36315	6.73291

In further phase studied cycloaddition reaction at three situations of double bonds in C₃₀₋₁, C₃₀₋₂ and C₃₀₋₃. For example a result of C30-1 is shown in fig. 3 and Table 2.

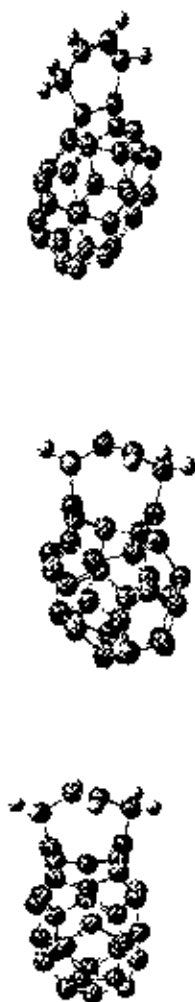


Fig. 3. AM1 optimization geometry structures of product 1, 2 and 3 of the addition of C₄H₆ to the C₃₀₋₁ bonds.

Table 2. Some thermodynamic parameters and Ts at T=298.15K, p=1atm for double bonds between [6, 6] in C₃₀₋₁ structure

Kcal/mol	GS1	TS	GS2
AMI.HF	1.6618	1.71187	1.47129
Freq hf	-1274.2603	-1274.1736	-1274.5133
ZPE	191.61169	197.48158	280.1149
G	-799456.563	-799455.97	-799592.98
H	-799409.296	-799408.53	-799561.88
S	8.1585	8.14836	8.107261
C_v	0.061742	0.96055	0.060488
E	200.012	207.251	287.638

Table 1 shows that the interaction between C₄H₆ and C-C bond in structure 2 is stronger than that between C₄H₆ and C-C bond of structures 1 and 3. The heat of reaction for adding C₄H₆ and C-C bond of structures 1, 2 and 3 in the T= 298k, P= 1atm are -151.711, -584.858 and -118.854 kcal/mol.

So for the three statuses of reactions between C₄H₆ and C-C bond of structure 2 is more exothermic than C-C bond of structure 1 and 3. Among the three structures, structure 2 seems to be the most stable one.

CONCLUSION

There are three status of double bond in structure of C₃₀₋₁, C₃₀₋₂ and C₃₀₋₃ that are completely different from each other. Cycloaddition is selected as a main part of reaction and addition process for single stage is considered. Thermodynamics parameters, stability energy and transition state are evaluated in three structures. The new cycle that produced after cycloaddition reaction was opened and created a new cycle with large size. Three positions of double bond that lead to three products are strongly different. The structure that contain much resonance loop and the most double bond in resonance form was stable than that others, in the other hand these results completely confirmed thermodynamics results that obtained from calculations.

When C₄H₆ is added to the C-C bond of C₃₀ structure, our investigation results show that the reaction mechanism is probably as below:
 Reactants → Transition state 1 (Ts 1) → Closed Isomer → Transition state 2 (Ts 2) → products

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