



Theoretical Study of the Hydrogenation of Cyclopentene without Catalyst and in the Presence of Molybdenum Disulfide

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Abstract

A study Hartree Fock of the hydrogenation of cyclopentene was carried out at the temperature of 298.15 Kelvin, under atmospheric pressure, without catalyst, on the one hand, and in the presence of molybdenum disulfide, catalyst of hydrotreating modeled by a catalytic site of MoS_3H_3^+ type, on the other hand. The results of calculations showed that, without catalyst, the hydrogenation of the molecule leads to the dislocation of its carbon skeleton by giving propane and acetylene. In the presence of molybdenum disulfide used as catalyst, one observes a simple reaction of addition on the cycle. The product of reaction is then cyclopentane. This result highlights the double hydrogenating and selective character of catalyst.

Keywords: cyclopentene, cyclopentane, hydrogenation, hydrotreating catalyst, cyclic carbon skeleton, atomic rearrangement, Hartree Fock, LanL2DZ base set, disulphur of molybdenum, propane, acetylene, MoS_3H_3^+ site.

Introduction

Cyclopentene (C_5H_8) is a cyclic olefin, normally being able to undergo a reaction of addition such as hydrogenation. In the presence of a catalyst of hydrotreating having a good hydrogenating activity and under adapted experimental conditions of temperature and pressure, the hydrogenation of such a molecule should occur without rearrangement of its carbon skeleton^{1,2}. The disturbances related to the secondary reactions possibly being able to intervene during the process of hydrogenation are then avoided. In practice, such a reaction is used as criterion of evaluation of the hydrogenating activity of catalysts of hydrotreating^{3,4}. Moreover, the selectivity of such catalysts in hydrodesulphurization compared to the hydrogenation of olefins must be controlled and if possible improved in order to limit the loss of octane number of gasoline⁵.

With an aim of appreciating hydrogenating character of molybdenum disulfide MoS_2 (usual catalyst of hydrotreating), we carried out the modeling of the hydrogenation of cyclopentene, at the temperature of 298.15 Kelvin and under the atmospheric pressure, without catalyst, on the one hand, and in presence of catalyst, on the other hand.

Material and Methods

Calculation methods and drawings of chemical systems: The calculations were performed using the program Gaussian-03W, by quantum methods HF, in the basis

Lanl2DZ. Data obtained are geometry, multiplicity and charge of studied systems⁶⁻⁹.

The drawings of chemical systems studied were produced with ChemDraw Ultra 6.0, Chem3D Ultra 6.0 and Gauss View 3.09. The work was done in the "Laboratoire de Chimie Théorique et de Spectroscopie Moléculaire" of "Université d'Abomey-Calavi" in Republic of Benin, on a HP Pentium 4 microcomputer.

Reaction Modeling: Hydrogenation is an addition reaction of hydrogen molecule (H_2) on an unsaturated reactive molecule¹. The modeling of the hydrogenation of cyclopentene without catalyst was carried out by progressive approach of the two reactive molecules (H_2 and C_5H_8). The approach consisted in decreasing distance H^{14}C^3 between the C^3 atom of cyclopentene and the H^{14} atom of hydrogen molecule until that the system reaches its lowest energy state, figure-1a.

The reaction in the presence of molybdenum sulfide was modeled in a same way, but in two stages: the adsorption of cyclopentene molecule on the catalyst (MoS_2) modeled by the catalytic site MoS_3H_3^+ , and simultaneous approach of two hydrogen molecules of the complex formed by cyclopentene and catalyst with the stage of adsorption. During the adsorption stage, the coordinates of reaction is the Mo^{14}C^3 distance and during hydrogenation stage, they are H^{21}C^3 and H^{23}C^4 distances, figure-1b.

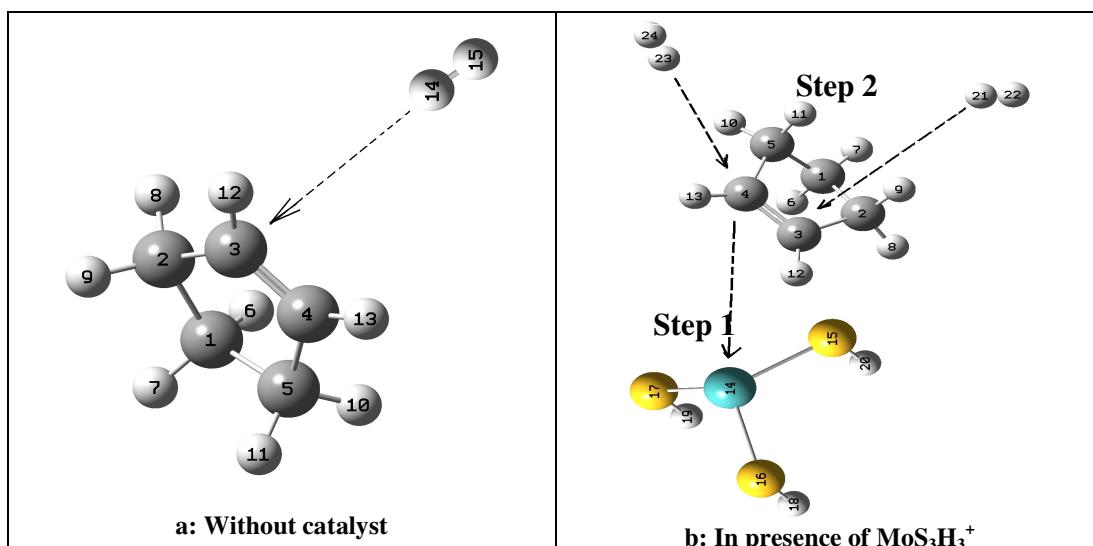


Figure - 1
Modeling of hydrogenation of cyclopentene

Results and Discussion

Reaction without catalyst: One hydrogen molecule was gradually brought closer to a molecule of cyclopentene. Beginning at the end of reaction, while passing by an intermediate state (IS)¹⁰, the geometrical parameters (interatomic distances and angles), the atomic charges and the energy of the formed chemical system, varied according to the coordinate of reaction H^{14}C^3 .

The curve of figure-2 represents the variation of the energy of the system according to the coordinate of reaction. It shows that the system is more stable at the end of the reaction than at the beginning. This observation is well in agreement with the computed values of the enthalpy ($\Delta\text{Hr} = -626,463 \text{ kJ/mol}$) and of the free energy ($\Delta\text{Gr} = -600,494 \text{ kJ/mol}$) of the reaction. The negative signs of these energies indicate respectively that the reaction is exothermic and thermodynamically favorable.

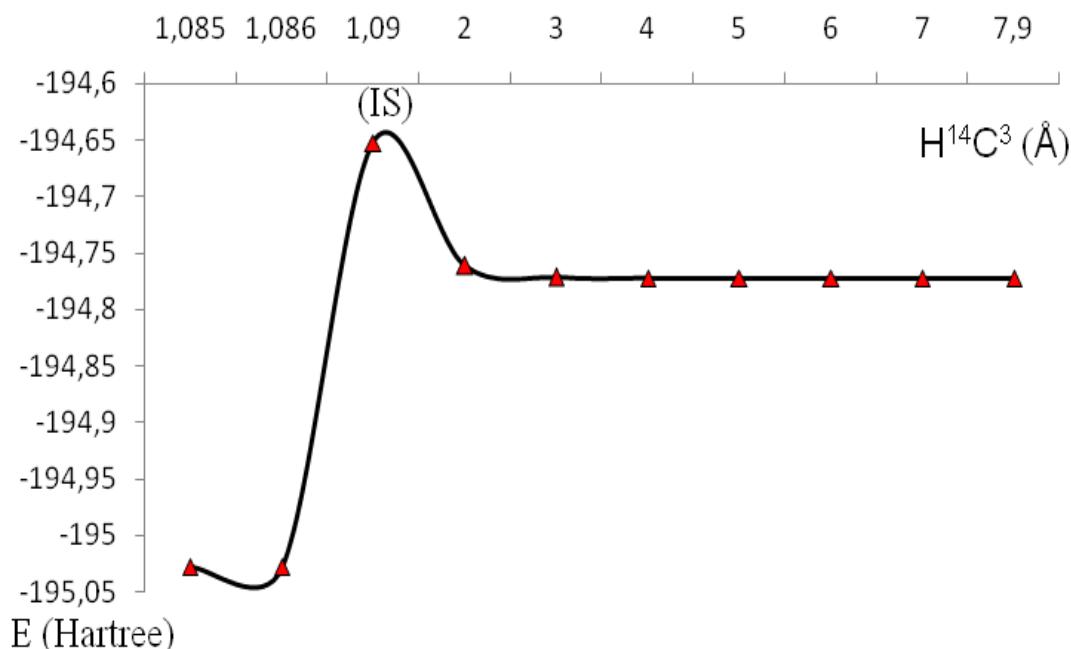


Figure – 2
Path of the cyclopentene hydrogenation without catalyst

Table - 1
Interatomic distances and angles calculated during hydrogenation without catalyst

Calculated parameters	Initial state	Intermediate state	Final state
<i>Distances (Å)</i>			
C ¹ C ⁵	1.556	4.964	7.397
C ⁴ C ⁵	1.519	1.419	1.202
C ³ C ⁴	1.333	1.413	4.094
C ⁵ H ¹¹	1.087	4.859	8.473
C ¹ H ¹¹	2.204	1.097	1.085
C ² H ⁹	1.087	2.702	2.174
C ³ H ⁹	2.156	1.076	1.086
C ² H ¹⁵	9.737	2.702	1.086
C ³ H ¹⁴	10.00	1.090	1.086
H ¹⁴ H ¹⁵	0.732	0.820	2.494
<i>Angles (°)</i>			
H ¹³ C ⁴ C ⁵	122.640	118.955	179.955
H ¹⁰ C ⁵ C ⁴	112.399	110.709	179.971

The computed values of geometrical parameters of the studied chemical system are presented in table-1, with various stages of the process.

These results reveal that during the process, the system underwent important rearrangements. Interatomic distances knew significant variations, from the beginning at the end of the process: C¹C⁵ passes from 1.556 Å to 7.397 Å, C³C⁴ from 1.333 Å to 4.094 Å, C⁵H¹¹ from 1.087 Å to 8.473 Å, C²H⁹ from 1.087 Å to 2.174 Å and H¹⁴H¹⁵ from 0.732 Å to 2.494 Å. All these important increases in interatomic distances indicate the rupture of the corresponding chemical bonds. In

particular, the ruptures of C¹C⁵ and C³C⁴ bonds indicate that the cyclic molecule of cyclopentene is dislocated to give two aliphatic molecules, figure-3.

In addition, new chemical bonds were formed as the variations of the following interatomic distances indicate it: C¹H¹¹ passes from 2.204 Å to 1.085 Å, C³H⁹ from 2.156 Å to 1.086 Å, C²H¹⁵ from 9.737 Å to 1.086 Å and C³H¹⁴ from 10.00 Å to 1.086 Å.

The hybridization state of C³ atom passed from sp² to sp³. This allows the formation of new chemical bonds between the C³ atom and the H¹⁴ and H⁹ atoms. The C⁴ and C⁵ atoms passed from the sp² and sp³ hybridization states to sp respectively. That results in the transformation of simple covalent bond C⁴-C⁵ into a triple bond C⁴≡C⁵, figure-3.

According to what precedes, the two reactive molecules were dislocated during the reaction to give two products of reaction: propane and acetylene, figure-3c.

The computed values of the geometrical parameters of these products are close to the standard and experimental values published in the literature for these parameters ¹¹⁻¹².

Reaction in the presence of catalyst: The modeling of the reaction was carried out while approaching simultaneously and uniformly two hydrogen molecules H²¹H²² and H²³H²⁴ of the complex formed by cyclopentene and the catalytic site MoS₃H₃⁺ with adsorption, figure-4a.

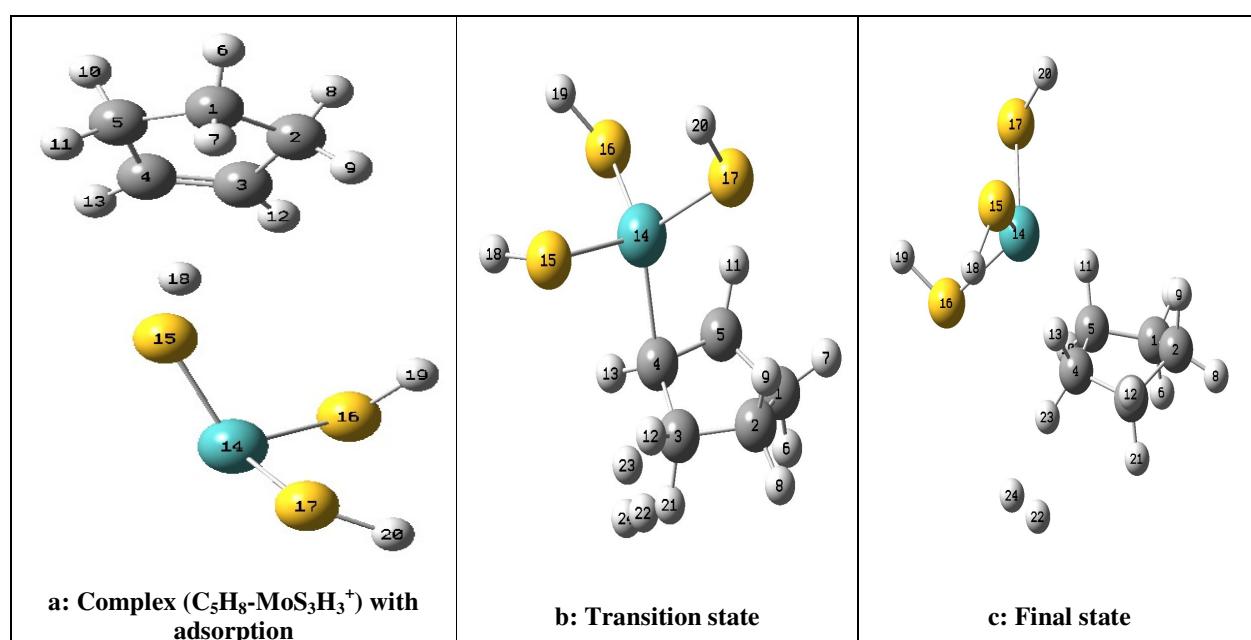


Figure – 4
Drawings of the chemical system with various stages of reaction

Beginning at the end of the reaction while passing by the transition state (TS), the geometrical parameters, the atomic charges and the energy of the chemical system, varied according to the coordinate of reaction $H^{23}C^4$ (or $H^{21}C^3$). The transition state (TS) of the reaction was determined by QST2 process. It was obtained at distance $H^{23}C^4$ equal to 2.030 Å and characterized by only one vibration of negative frequency (- 649.834 cm⁻¹) among all its modes of vibration.

The curve of figure-5, presents the variations of the energy of the system according to the reaction coordinate $H^{23}C^4$. In this case the reaction is also exothermic ($\Delta H_r = -25,803$ kJ/mol) and thermodynamically favorable ($\Delta G_r = -3,109$ kJ/mol).

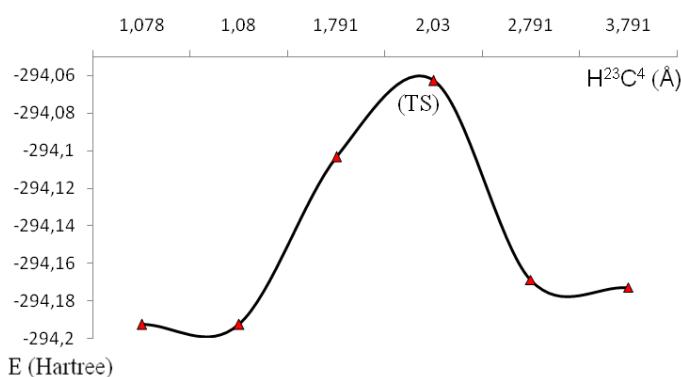


Figure-5
Path of the cyclopentene hydrogenation on catalytic site
 $MoS_3H_3^+$

The interatomic distances and angles calculated with various stages of the process are given in table-2. These results show that during the process, certain chemical bonds broke; others

changed and of new chemical bonds also made themselves, table-2.

Indeed, distance C^3C^4 passes from 1.344 Å to 1.555 Å, angles $H^{13}C^4C^3$ and $H^{12}C^3C^4$ pass from 124.841° to 106.295° and from 124.661° to 112.388° respectively. Bond C=C is thus transformed into a bond C–C and the C^3 and C^4 atoms pass from the hybridization sp^2 to sp^3 .

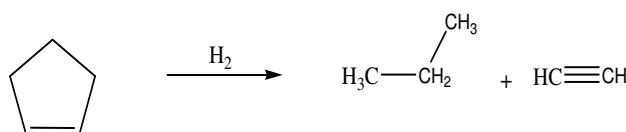
Distances $H^{21}H^{22}$ and $H^{23}H^{24}$ pass from 0.732 Å to 4.181 Å and 3.194 Å respectively, $H^{21}C^3$ and $H^{23}C^4$ pass from 10.00 Å to 1.082 Å and 1.078 Å respectively and $H^{22}H^{24}$ pass from 4.986 Å to 0.732 Å. It results from these variations of interatomic distances that the two hydrogen molecules were dislocated and new chemical bonds, like $H^{21}C^3$, $H^{23}C^4$ and $H^{22}H^{24}$, were formed. Distance $H^{22}H^{24}$ obtained at the end of the reaction indicates that it was formed a new hydrogen molecule with hydrogen atoms coming from the two initial hydrogen molecules, figure-4c.

From all that proceeds, it comes out that the product of the cyclopentene hydrogenation in the presence of molybdenum sulfide (represented by the catalytic site $MoS_3H_3^+$) is cyclopentane. The computed values of the geometrical parameters of the obtained product are close to the values standards and experimental published in the literature on cyclopentane¹².

Influence catalyst on the reaction: Without catalyst, the reaction of hydrogenation of cyclopentene gives Propane and Acetylene. During the reaction, the two reactive molecules (C_5H_8 and H_2) are dislocated with atomic rearrangements. Only one hydrogen molecule reacts with the cyclopentene molecule, scheme-1.

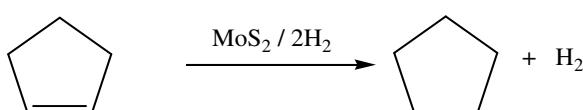
Table – 2
Interatomic distances and angles calculated during hydrogenation in presence of MoS_2 catalyst

Calculated parameters	Initial state	Transition state	Final state
Distances (Å)			
C^3C^4	1.383	1.536	1.555
$H^{21}H^{22}$	0.732	1.359	4.181
$H^{23}H^{24}$	0.732	0.851	3.194
$H^{21}C^3$	10.00	1.131	1.082
$H^{23}C^4$	10.00	2.030	1.078
$H^{22}H^{24}$	5.704	0.863	0.732
Angles (°)			
$H^{13}C^4C^3$	120.736	118.635	106.295
$H^{12}C^3C^4$	123.705	114.307	112.388



Scheme – 1
Scheme of cyclopentene hydrogenation without catalyst

In the presence of catalyst, the product of the reaction is cyclopentane. The carbon skeleton of the cyclopentene molecule remains cyclic during the reaction, which implies two hydrogen molecules for one molecule of cyclopentene, scheme 2. There was no rearrangement of the atoms of cyclopentene molecule. The reaction, was only a simple addition of two hydrogen atoms on the cyclopentene molecule, on the level of its unsaturated chemical bond $C=C$.



Scheme – 2
Scheme of cyclopentene hydrogenation in presence of MoS_2 catalyst

In addition, the system obtained at the end of the reaction in the presence of catalyst, is more stable than that obtained at the conclusion of the reaction without catalyst. It is what energies of the system at the end of the reaction reveal: E (with catalyst) = -294,193 Hartree < E (without catalyst) = -195,028 Hartree. Also, the energy barrier observed during the reaction without catalyst (322,852 kJ/mol) is definitely higher than that presented by the reaction in the presence of catalyst (154,146 kJ/mol) (Figures 2 and 5). Thus, among the two studied reactions, the reaction carried out in the presence of catalyst is easiest, which is quite right since, on the one hand, a reaction is all the more fast as its energy of activation is weaker, and on the other hand, the main role of a catalyst is to accelerate or support a chemical reaction¹³⁻¹⁴.

The reaction in the presence of molybdenum disulfide being produced without rearrangement of the carbon skeleton of the cyclopentene molecule, one can say that the molybdenum disulfide is a catalyst which has a good hydrogenating activity. This conclusion is in agreement with experimental results published in the literature³.

Conclusion

The hydrogenation of cyclopentene, modeled at the temperature of 298.15 Kelvin, under atmospheric pressure, without catalyst, on the one hand, and in the presence of molybdenum disulfide, on the other hand, gives various products of reaction of one case to the other. Without catalyst, the addition of the hydrogen molecule was accompanied by a fragmentation of the cyclopentene molecule; the products of the reaction are propane and acetylene. In the presence of molybdenum disulfide used as

catalyst, the reaction is a simple addition of hydrogen atoms on cyclopentene. The product of reaction is then cyclopentane. The reaction uses two hydrogen molecules and regenerates one at the end. The hydrogen molecule regenerated is made of two atoms coming from the two hydrogen molecules put in reaction.

This result highlights the hydrogenating, accelerating and selective characters of the MoS_2 catalyst. The same study will be continued and extended to other catalysts such as disulfide of tungsten WS_2 and chloride aluminum $AlCl_3$, to deduce more widened conclusions.

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