# Theoretical Study of Hydrodesulphurization of 2-Methyltetrahydrothiophene in the Presence of Molybdenum Disulfide

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## Abstract

A theoretical study of the catalytic hydrodesulphurization (HDS) of 2-méthyltetrahydrothiophene (2-MTHT) in the presence of molybdenum disulfide (MoS$_2$) was carried out by the quantum chemical methods HF and DFT, in the LanL2DZ basis set. The catalyst was modeled by a catalytic site with three anionic vacancies of MoS$_3$H$_3^+$ type. The results obtained shown that, in the presence of MoS$_2$ under pressure of hydrogen (H$_2$), the reaction rather led to the formation of 1-pentene, 2-pentene and pentane with

elimination of hydrogen sulfide ($H_2S$), while passing by the intermediary stage of the formation of 1-pentanethiol and 2-pentanethiol. These results are confirmed by experimental data available in the literature. In addition, we proposed the mechanisms of reactions based on the results discussed in this work.

**Keywords**:  Hydrodesulphurization; 2-methyltetrahydrothiophene; molybdenum disulfide; HF; B3LYP; Lanl2DZ

# 1.  Introduction

In petrochemical industry, one of the most important reactions of the entire catalytic hydrotreating process is hydrodesulphurization. It is a reaction allowing the elimination of sulfur atoms from the sulphurated molecules contained in the crude oil residues. Generally, the sulfur atom is eliminated in the form of hydrogen sulfide ($H_2S$) and the molecules are transformed into saturated or unsaturated hydrocarbons. In reality, the reaction is carried out in the presence of catalyst, under pressure of hydrogen ($H_2$) at high temperature [1-5].

Experimentally, the real mechanisms of these reactions are not well elucidated. For instance, two possible pathways of chemical reactions have been proposed in the literature for the production of butane molecule during the hydrodesulphurization of thiophene: one indicates butadiene as intermediate molecule, while the other proposes tetrahydrothiophene as intermediate product [1, 2, 6-10]. Similar observations have been made on the hydrodesulfurization of other molecules such as the substituted or hydrogenated derivatives of thiophene, and tetrahydrothiopyrane [11-16]

Theoretical results evidencing the possibility of these reactions have been also reported on these sulfur molecules. A great deal of issues concern the determination of the nature of the catalytic active sites of the thiophene adsorption as well as of its derivatives, and the entire determination of the mechanisms of these reactions [4, 14 and 17]. In this regard, little is known, especially in the hydrodesulfurization of tetrahydrothiopyrane and 2-methyltetrahydrothiophene (2-MTHT).

In previous work, we have shown that the 2-MTHT is obtained by isomerization of tetrahydrothiopyrane in the presence of molybdenum disulfide ($MoS_2$) when the reaction occurs in the absence of hydrogen [18, 19]. In this work, we carried out the hydrodesulphurization of 2-MTHT at the temperature 570 K, under hydrogen pressure of 70 bars, in the presence of $MoS_2$. These conditions are close to those implemented in industrial setup conditions [1, 21 and 22]. The catalyst is modeled by the catalytic site of Joffre and al. of type $MoS_3H_3^+$ [8], while aiming to elucidate the 2-MTHT hydrodesulphurization mechanism.

# 2.  Material and Methods

## 2.1. Calculation Methods and Drawings of Chemical Systems

Calculations were carried out by HF and DFT methods with the functional B3LYP using program Gaussian-03W [11-19]. The drawings of chemical systems were produced with ChemDraw Ultra 6.0, and GaussView 3.09, and the curves were plotted with Microsoft Office Excel 2007. This work was carried out on a HP Pentium 4 microcomputer at the "Laboratoire de Chimie Théorique et de Spectroscopie Moléculaire" of "Université d'Abomey-Calavi" in Benin.

## 2.2. Reactions Modeling

The adsorption simulation of 2-MTHT on the catalyst consisted on approaching gradually this molecule to the catalytic site $MoS_3H_3^+$ taken into account its optimized geometry until the system reaches its state of lower energy. In this state the adsorption is supposed to be realized (Fig. 1).

**Figure 1:** Drawing of the [MoS$_3$H$_3^+$-(2-MTHT)] complex at adsorption



Then, a first H$_2$ molecule is gradually approached to the resulted [MoS$_3$H$_3^+$-(2-MTHT)] complex at the adsorption. Due to the fact that the 2-MTHT molecule was asymmetrical, the H$_2$ molecule approach was respectively examined on each of two carbon atoms C$^9$ (substituted) and C$^{12}$ (no substituted) which have a chemical bond with sulfur atom S$^8$. Under this condition, the process was led according to two competitive ways: the approaches C9 and C12 as depicted in Fig. 2.

**Figure 2:** The approaching ways of first H$_2$ molecule over [MoS$_3$H$_3^+$-(2-MTHT)] complex



These two approaching ways led to two different intermediary thiols, which were respectively subjected to two types of treatment:

- the approaching of a second H$_2$ molecule, on the one hand (Fig. 3),
- and the stretching of their C-S bond, on the other hand (fig. 4). The stretching of the chemical bonds is a way of simulating the effect of thermal agitation, which occurs under the real experimental conditions of the reaction.

At the end of the process all the system is released evolving into a stable energy state.

The stretching of C-S bond of thiol obtained through H$_2$ approaching C9 was already studied in previous work [7]. Thus, for this intermediary thiol, we will give only the result of the approach of the second H$_2$ molecule.

Theoretical Study of Hydrodesulphurization of 2-
Methyltetrahydrothiophene in the Presence of Molybdenum Disulfide
496

**Figure 3:** Second $H_2$ molecule approaching to intermediary thiol obtained from C9 approaching
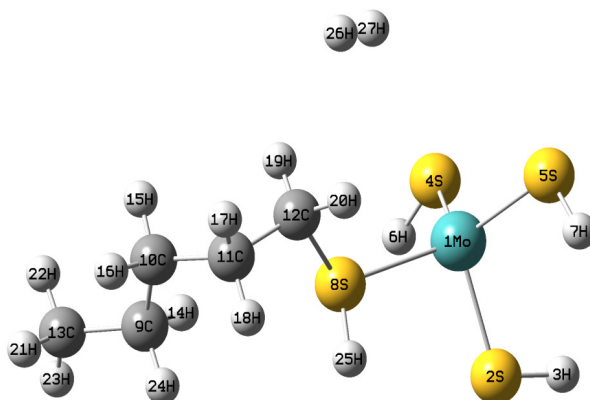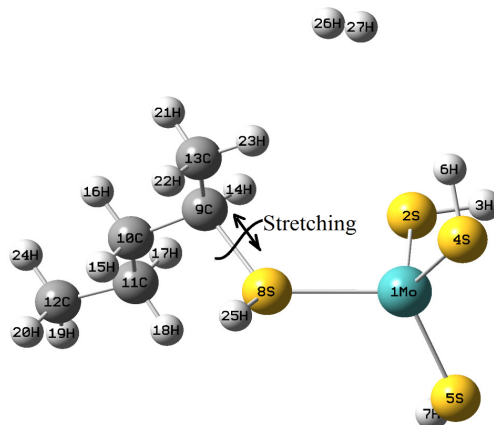


**Figure 4:** Second $H_2$ molecule approaching to intermediary thiol obtained from C12 approaching and geometry of C-S bond stretching



## 3. Results and Discussion
### 3.1. Geometry of 2-MTHT

The calculated geometric parameters of the reactive molecule 2-MTHT are summarized Table 1 and its corresponding conformation is depicted in Fig. 5.

**Figure 5:** Drawing of the considered conformation of 2-MTHT
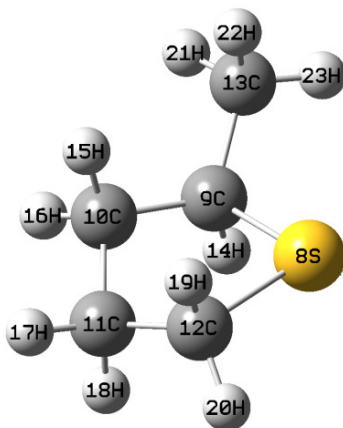
**Table 1:**    Optimized geometric parameters of 2-MTHT

| Lengths (Å) | | | Angles (°) | | | Dihedrals (°) | | |
|---|---|---|---|---|---|---|---|---|
| | HF | DFT | | HF | DFT | | HF | DFT |
| $S^8C^9$ | 1.900 | 1.928 | $C^9S^8C^{12}$ | 93.58 | 93.00 | $S^8C^9C^{10}C^{11}$ | -37.07 | -37.17 |
| $C^9C^{10}$ | 1.538 | 1.548 | $S^8C^9C^{10}$ | 105.02 | 104.75 | $S^8C^{12}C^{11}C^{10}$ | -35.83 | -37.06 |
| $C^{10}C^{11}$ | 1.537 | 1.546 | $C^9C^{10}C^{11}$ | 108.15 | 108.41 | $C^{12}S^8C^9C^{13}$ | 138.04 | -110.29 |
| $C^{11}C^{12}$ | 1.538 | 1.541 | $C^{10}C^{11}C^{12}$ | 107.52 | 107.34 | $C^{11}C^{10}C^9C^{13}$ | -159.53 | 84.44 |
| $C^{12}S^8$ | 1.883 | 1.910 | $C^{11}C^{12}S^8$ | 106.10 | 106.10 | | | |
| $C^9C^{13}$ | 1.529 | 1.538 | $C^{13}C^9S^8$ | 111.49 | 111.06 | | | |
| $C^9H^{14}$ | 1.080 | 1.095 | | | | | | |
| $C^{10}H^{15}$ | 1.085 | 1.098 | | | | | | |
| $C^{11}H^{17}$ | 1.084 | 1.098 | | | | | | |
| $C^{12}H^{19}$ | 1.079 | 1.093 | | | | | | |
| $C^{13}H^{21}$ | 1.086 | 1.100 | | | | | | |

The results of the two calculation methods revealed that the presence of methyl group on $C^9$ atom encumbers this last and caused a light stretching of $C^9$-$S^8$ bond compared to $C^{12}$-$S^8$ bond. The geometric parameters of the catalytic site $MoS_3H_3^+$ have been confirmed in previous reports [8, 20]. All the calculated values of bond lengths and angles are in agreement with the accepted standard values [21, 22]

### 3.2. Adsorption of 2-MTHT on MoS$_2$

The calculated geometric parameters of [(2-MTHT)-$MoS_3H_3^+$] complex at adsorption are given (Table 2).

**Table 2:** Optimized geometric parameters of [(2-MTHT)-$MoS_3H_3^+$] complex at adsorption

| Lengths (Å) | | | Angles (°) | | | Dihedrals (°) | | |
|---|---|---|---|---|---|---|---|---|
| | HF | DFT | | HF | DFT | | HF | DFT |
| $C^9S^8$ | 1.957 | 1.990 | $C^{12}S^8C^9$ | 95.47 | 93.98 | $S^8C^9C^{10}C^{11}$ | -37.96 | -40.01 |
| $C^9C^{10}$ | 1.537 | 1.539 | $S^8C^9C^{10}$ | 101.11 | 101.29 | $C^{10}C^{11}C^{12}S^8$ | -35.96 | -35.26 |
| $C^{10}C^{11}$ | 1.538 | 1.547 | $C^9C^{10}C^{11}$ | 110.17 | 109.88 | $C^{13}C^9S^8C^{12}$ | 137.66 | 140.36 |
| $C^{11}C^{12}$ | 1.537 | 1.540 | $C^{10}C^{11}C^{12}$ | 108.78 | 108.78 | $Mo^1S^8C^9C^{10}$ | 147.11 | 142.99 |
| $C^{12}S^8$ | 1.904 | 1.934 | $C^{11}C^{12}S^8$ | 103.72 | 104.46 | $Mo^1S^8C^{12}C^{11}$ | -122.43 | -116.67 |
| $C^{13}C^9$ | 1.524 | 1.526 | $C^{13}C^9S^8$ | 110.58 | 109.91 | | | |
| $C^9H^{14}$ | 1.077 | 1.094 | $Mo^1S^8C^9$ | 123.22 | 119.44 | | | |
| $C^{10}H^{16}$ | 1.082 | 1.098 | $Mo^1S^8C^{12}$ | 120.97 | 119.00 | | | |
| $C^{11}H^{18}$ | 1.082 | 1.096 | | | | | | |
| $C^{12}H^{20}$ | 1.075 | 1.092 | | | | | | |
| $C^{13}H^{22}$ | 1.081 | 1.095 | | | | | | |
| $Mo^1S^8$ | 2.452 | 2.409 | | | | | | |

At the adsorption, the 2-MTHT molecule practically preserved its initial geometry. However, one observes a light stretching of $C^9S^8$ and $C^{12}S^8$ bonds (approximately from 1 to 3 %) and a light contracting of the $S^8C^9C^{10}$ angle for the two calculation methods. In such situation, these bonds are weakened and can easily break during the later stages of the process. The congestion effect of methyl group on $C^9$ atom explains also the fact that $C^9S^8$ bond is more stretched than $C^{12}S^8$ bond at adsorption. The values 2.452 and 2.409 Å of the $Mo^1S^8$ distance are evidently close to the length value of the Mo–S bond in the crystal MoS$_2$ [23], suggesting that this bond established at the adsorption. Consequently, the adsorption of 2-MTHT on MoS$_2$ would be a chemisorption. This fact is also in agreement with the calculated enthalpies of adsorption ($\Delta H_{ads}$), which values are higher than 100 kJ, mol$^{-1}$ in absolute values [24] (Table 3).

**Table 3:** Adsorption enthalpy of 2-MTHT on $MoS_2$

|  | HF | DFT |
|---|---|---|
| $\Delta H_{ads}$ en kJ / mol | -210.041 | -215.291 |

### 3.3. Addition of First Hydrogen Molecule on 2-MTHT in Presence of MoS$_2$

### 3.3.1. Approach C9: Rupture of $C^9$–$S^8$ Bond of 2-MTHT

During this stage, the $C^9$–$S^8$ bond broke with the approach of a hydrogen molecule ($H^{24}H^{25}$) which was also dislocated. After the dislocation of the hydrogen molecule, both $H^{24}$ and $H^{25}$ atoms established new chemical bonds with $C^9$ and $S^8$ atoms respectively. This new chemical bond establishment was revealed by the variation of the interatomic distances in the system (Table 4). For example, the $H^{24}H^{25}$ interatomic distance calculated in HF, passed from 0.731 Å at the process beginning to 3.325 Å at the end. This observation indicates that the corresponding chemical bond is broken. In addition, the passage of distance $C^9H^{24}$ and $S^8H^{25}$ from 10.000 to 1.088 Å and from 10.08 to 1.346 Å respectively suggest a formation of these bonds at the end of the reaction. Furthermore, the distance between $C^9$ and $S^8$ atoms increases from 1.957 to 3.517 Å, suggesting a rupture of the corresponding bond. Ultimately, there was the hydrogenolysis of the C9–$S^8$ bond and the intermediate product formed is 1-pentanthiol, adsorbed on the catalytic site.

**Table 4:** Calculated and standard values of interatomic distances during the hydrogenolysis of $C^9$-$S^8$ bond of 2-MTHT by approach C9

| Distances (Å) | Initial State | | Transition State | | Final State | | Standard Values [21, 22] | Observations |
|---|---|---|---|---|---|---|---|---|
|  | HF | DFT | HF | DFT | HF | DFT |  |  |
| $H^{24}$-$H^{25}$ | 0.731 | 0.743 | 0.742 | 0.785 | 3.325 | 3.271 | 0.73(H-H) | Rupture H-H |
| $C^9$-$H^{24}$ | 10.00 | 10.00 | 1.450 | 1.380 | 1.088 | 1.102 | 1.09(C-H) | Formation C-H |
| $S^8$-$H^{25}$ | 10.08 | 9.69 | 4.978 | 4.841 | 1.346 | 1.377 | 1.35(S-H) | Formation S-H |
| $C^9$-$S^8$ | 1.957 | 1.990 | 2.976 | 2.785 | 3.517 | 3.498 | 1.89(C-S) | Rupture C-S |

### 3.3.2. Approach C12: Rupture of $C^{12}$-$S^8$ Bond of 2-MTHT

In this case, there was the hydrogenolysis of $C^{12}$–$S^8$ bond during the approach of a hydrogen molecule ($H^{24}H^{25}$) which was also dislocated. The reaction product was 2-pentanthiol. Indeed, after the dislocation of the hydrogen molecule, both $H^{24}$ and $H^{25}$ atoms established new bonds with $C^{12}$ and $S^8$ atoms respectively. This was revealed by the variation of the interatomic distances in the system (Table 5). For example, according to the HF results, the distance $H^{24}H^{25}$ passed from 0.731 Å at the process beginning to 5.816 Å at the end. This variation suggests that the corresponding bond is broken. In addition, the passage of distances $C^{12}H^{24}$ and $S^8H^{25}$ from 10.000 to 1.084 Å and from 10.07 to 1.347 Å respectively indicates the formation of these bonds at the end of reaction. The distance between atoms $C^{12}$ and $S^8$ increases from 1.904 to 4.756 Å, suggesting a rupture of the $S^8$-$C^{12}$ bond.

**Table 5:** Calculated and standard values of interatomic distances during the hydrogenolysis of $C^{12}$-$S^8$ bond of 2-MTHT by approach C12

| Distances (Å) | Initial State | | Transition State | | Final State | | Standard Values [21, 22] | Observations |
|---|---|---|---|---|---|---|---|---|
|  | HF | DFT | HF | DFT | HF | DFT |  |  |
| $H^{24}$-$H^{25}$ | 0.731 | 0.743 | 0.817 | 0.828 | 5.816 | 5.831 | 0.73(H-H) | Rupture H-H |
| $C^{12}$-$H^{24}$ | 10.00 | 10.00 | 1.200 | 1.250 | 1.084 | 1.098 | 1.09(C-H) | Formation C-H |
| $S^8$-$H^{25}$ | 10.07 | 9.67 | 2.656 | 2.693 | 1.347 | 1.378 | 1.35(S-H) | Formation S-H |
| $C^{12}$-$S^8$ | 1.904 | 1.990 | 1.914 | 1.980 | 4.756 | 3.956 | 1.79(C-S) | Rupture C-S |
| $C^9$-$S^8$ | 1.957 | 1.990 | 1.965 | 1.994 | 2.002 | 2.009 | 1.79 (C-S) | Stretching C-S |

We also observe that the length of $C^9$-$S^8$ bond is larger than the accepted standard value because the thiol is still adsorbed on catalyst. In this condition, the stretched bond is weakened and can break during the later step of the process. So the second rupture C-S could be facilitated.

### 3.4. Addition of Second $H_2$ Molecule on the Intermediary Thiols

### 3.4.1. Addition of a $H_2$ Molecule on 1-Pentanthiol

The 1-pentanthiol is the intermediary product through the approach of $C^9$ by the first $H_2$ molecule on the adsorbate. Gradually, we have approached this second hydrogen from the 1-pentanthiol, which is also adsorbed over the catalyst at the end of the first stage. During the approach, we have observed the rupture of $C^{12}$-$S^8$ bond and the formation of $C^{12}$-$H^{26}$ and $S^8$-$H^{27}$ bonds. Indeed, at the end of the process, the distances $C^{12}H^{26}$ and $S^8H^{27}$ are 1.084 Å and 1.345 Å in HF and then 1.098 Å and 1.376 Å in DFT (Table 6). The values bond lengths and angles show that the reaction products are n-pentane ($C_5H_{12}$) and hydrogen sulfide ($H_2S$). These values are in agreement with the expected standard values [21, 22].

The same products are obtained in the case of the tetrahydrothiopyran hydrodesulphurization [7]. These results are in agreement with the experimental data [1, 25].

**Table 6:** Calculated and standard values of interatomic distances during the hydrogenolysis of $C^{12}$-$S^8$ bond of 1-pentanthiol

| Distances (Å) | Initial State | | Transition State | | Final State | | Standard Values [21, 22] | Observations |
|---|---|---|---|---|---|---|---|---|
| | HF | DFT | HF | DFT | HF | DFT | | |
| $H^{26}$-$H^{27}$ | 0.731 | 0.745 | 0.732 | 0.746 | 3.015 | 2.733 | 0.73 (H-H) | Rupture H-H |
| $C^{12}$-$H^{26}$ | 10.00 | 5.00 | 4.020 | 4.404 | 1.084 | 1.098 | 1.09 (C-H) | Formation C-H |
| $S^8$-$H^{27}$ | 10.40 | 4.925 | 4.017 | 3.638 | 1.345 | 1.376 | 1.35 (S-H) | Formation S-H |
| $C^{12}$-$S^8$ | 1.935 | 1.956 | 1.947 | 1.969 | 4.031 | 3.807 | 1.79 (C-S) | Rupture C-S |

The reaction path (Fig. 6) shows the geometrical structure of the two transition states TS1 (II) and TS2 (IV) among other things. The first transition state (II) shows the rupture of $C^9$-$S^8$ bond, a light stretching of $H^{24}$-$H^{25}$ bond and $C^9$-$H^{24}$ bond which is being formed. It is this transition state which evolves to give the 1-pentanthiol (III) after the total dislocation of $H^{24}$-$H^{25}$ and migration of $H^{25}$ to $S^8$ (Table 4).

The structure of second transition state (IV) also shows a stretching of $C^{12}$-$S^8$ bond, while the $H^{26}H^{27}$ distance remains unchanged. Here the $H_2$ molecule dislocation seems to be done simultaneously with the formations of $C^{12}$-$H^{26}$ and $S^8$-$H^{27}$ bonds (Table 6).
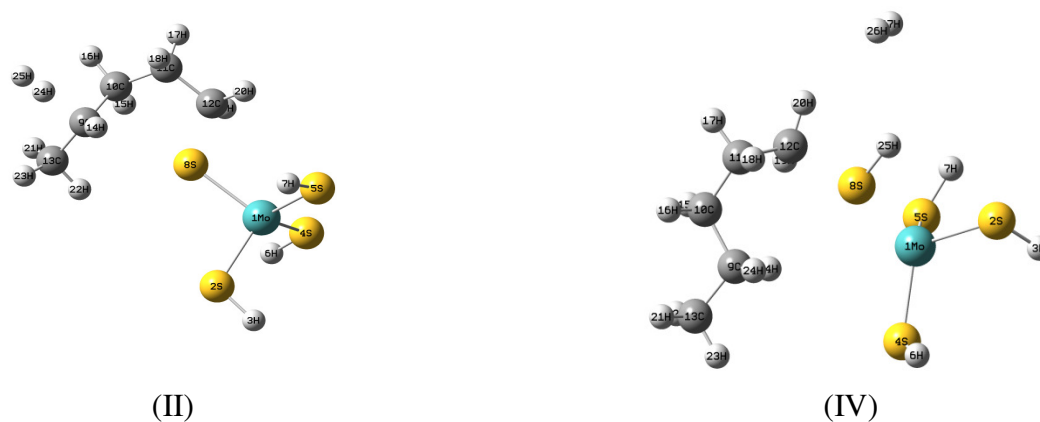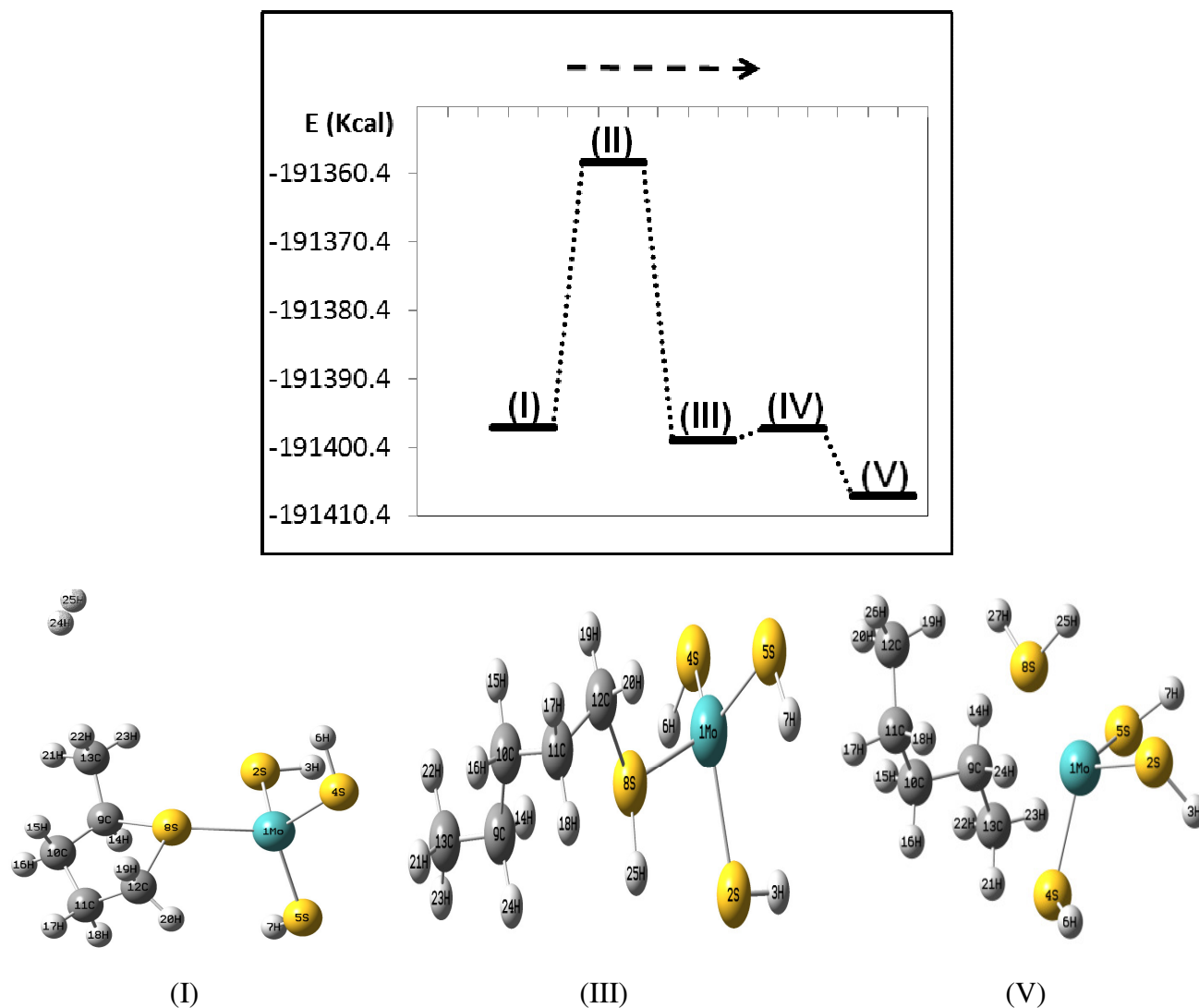
**Figure 6:** Path of hydrodesulphurization of 2-MTHT on the catalytic site $MoS_3H_3^+$ by the approach C9: Hydrogenolysis of $C^9$-$S^8$ and $C^{12}$-$S^8$ bonds leading to n-pentane



(II)                        (IV)

**Figure 6:** Path of hydrodesulphurization of 2-MTHT on the catalytic site $MoS_3H_3^+$ by the approach C9: Hydrogenolysis of $C^9$-$S^8$ and $C^{12}$-$S^8$ bonds leading to n-pentane - continued



With the aim of determining the nature of the rupture of $C^9$–$S^8$ and $C^{12}$–$S^8$ bonds, we resorted to the analysis of population of Mulliken. This analysis made from the DFT results suggests that these two chemical bond ruptures are heterolytic. Indeed, for the $C^9$–$S^8$ bond, we observe an increase of the negative charge on the $S^8$ atom, from 0.107 u.a, at the beginning of the process, to -0.126 u.a, at the transition state. Moreover, the $C^9$ atom loses electronic charges, which passes from -0.227 u.a to -0.106 u.a. at the same time. In addition, the electronic charge of $S^8$ and $C^{12}$ atoms passed from 0.031u.a to 0.041 u.a and from -0.539 u.a to-0.552 u.a from the beginning to the transition state, respectively.

The variation of geometric parameters of the system and the analysis of population of Mulliken allowed us to propose a probable mechanism of hydrodesulphurization of 2-MTHT leading to pentane (Fig. 7).

**Figure 7:** Hydrodesulphurization of 2-MTHT on the catalytic site $MoS_3H_3^+$ by the approach C9 leading to pentane: (a) Reaction scheme; (b) Probable mechanism



(a)



(b)
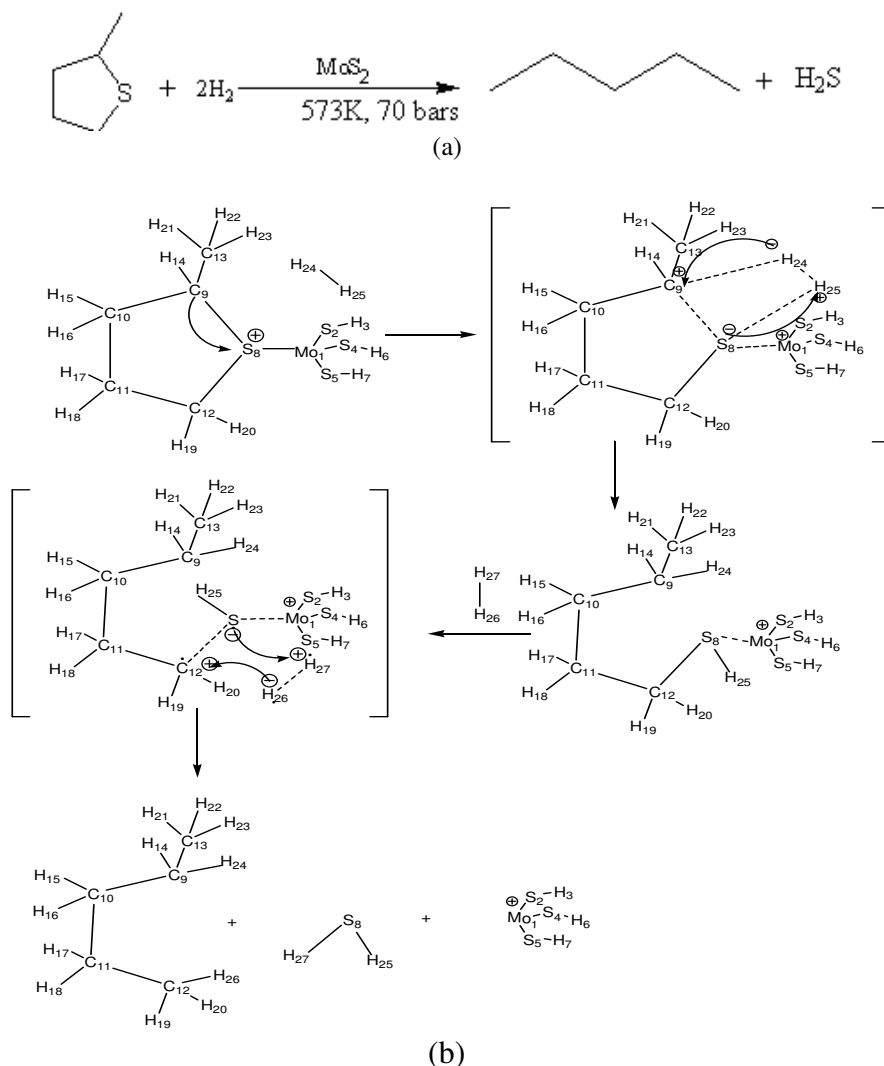
### 3.4.2. Addition of $H_2$ Molecule on 2-Pentanthiol

The 2-pentanthiol is the intermediary product obtained by approaching the first $H_2$ molecule on the $C^{12}$ adsorbate. This compound, which is still adsorbed over the catalyst at the end of first stage, reacts with the second hydrogen molecule. During this last approach, we observed the rupture of $C^9$-$S^8$ bond and the formation of $C^9$-$H^{26}$ and $S^8$-$H^{27}$ bonds. Indeed, at the end of the process, the distances HF of $C^9H^{26}$ and $S^8H^{27}$ are 1.093 Å and 1.348 Å (Table 7). The values of bond lengths and angles show that the reaction products are also n-pentane ($C_5H_{12}$) and hydrogen sulfide ($H_2S$) and are in agreement with the standard values [1, 26].

**Table 7:** Calculated and standard values of interatomic distances during the hydrogenolysis of $C^9$-$S^8$ bond of 2-pentanthiol

| Distances (Å) | Initial State | | Transition State | | Final State | | Standard Values [21, 22] | Observations |
|---|---|---|---|---|---|---|---|---|
| | HF | DFT | HF | DFT | HF | DFT | | |
| $H^{26}$-$H^{27}$ | 0.731 | 0.744 | 0.732 | 0.745 | 2.278 | 1.728 | 0.73(H-H) | Rupture H-H |
| $C^9$-$H^{26}$ | 10.00 | 10.00 | 4.400 | 3.000 | 1.093 | 1.116 | 1.09(C-H) | Formation C-H |
| $S^8$-$H^{27}$ | 10.08 | 10.22 | 4.051 | 3.614 | 1.348 | 1.391 | 1.35(S-H) | Formation S-H |
| $S^8$-$H^{25}$ | 1.347 | 1.378 | 1.346 | 1.376 | 1.346 | 1.375 | 1.35(S-H) | Formation S-H |
| $C^9$-$S^8$ | 2.002 | 2.012 | 2.001 | 2.018 | 4.077 | 3.766 | 1.79(C-S) | Rupture C-S |

The reaction path (Fig. 8) shows the geometrical structure of the two transition states TS1 (II) and TS2 (IV) among other things. The first transition state (II) shows a light stretching of three bonds $C^9$-$S^8$, $H^{24}$-$H^{25}$ and $C^{12}$-$S^8$ with a $C^{12}$-$H^{24}$ bond being formed. This transition state evolved to give the formation of the 2-pentanthiol (III) after the total dislocation of $H^{24}$-$H^{25}$, the rupture of $C^{12}$-$S^8$ bond and migration of $H^{25}$ to $S^8$ (Table 5).

The stretching and the rupture of $C^9$-$S^8$ bond, as well as the formations of $C^9$-$H^{26}$ and $S^8$-$H^{27}$bonds seem to be carried out simultaneously with the rupture of $H^{26}$-$H^{27}$bond when the system passes from the transition state TS2 (IV) to the final state (Table 7).

**Figure 8:** Reaction path of hydrodesulphurization of 2-MTHT on the catalytic site $MoS_3H_3^+$ by the approach C12: Hydrogenolysis of $C^{12}$-$S^8$ and $C^9$-$S^8$ bonds leading to n-pentane
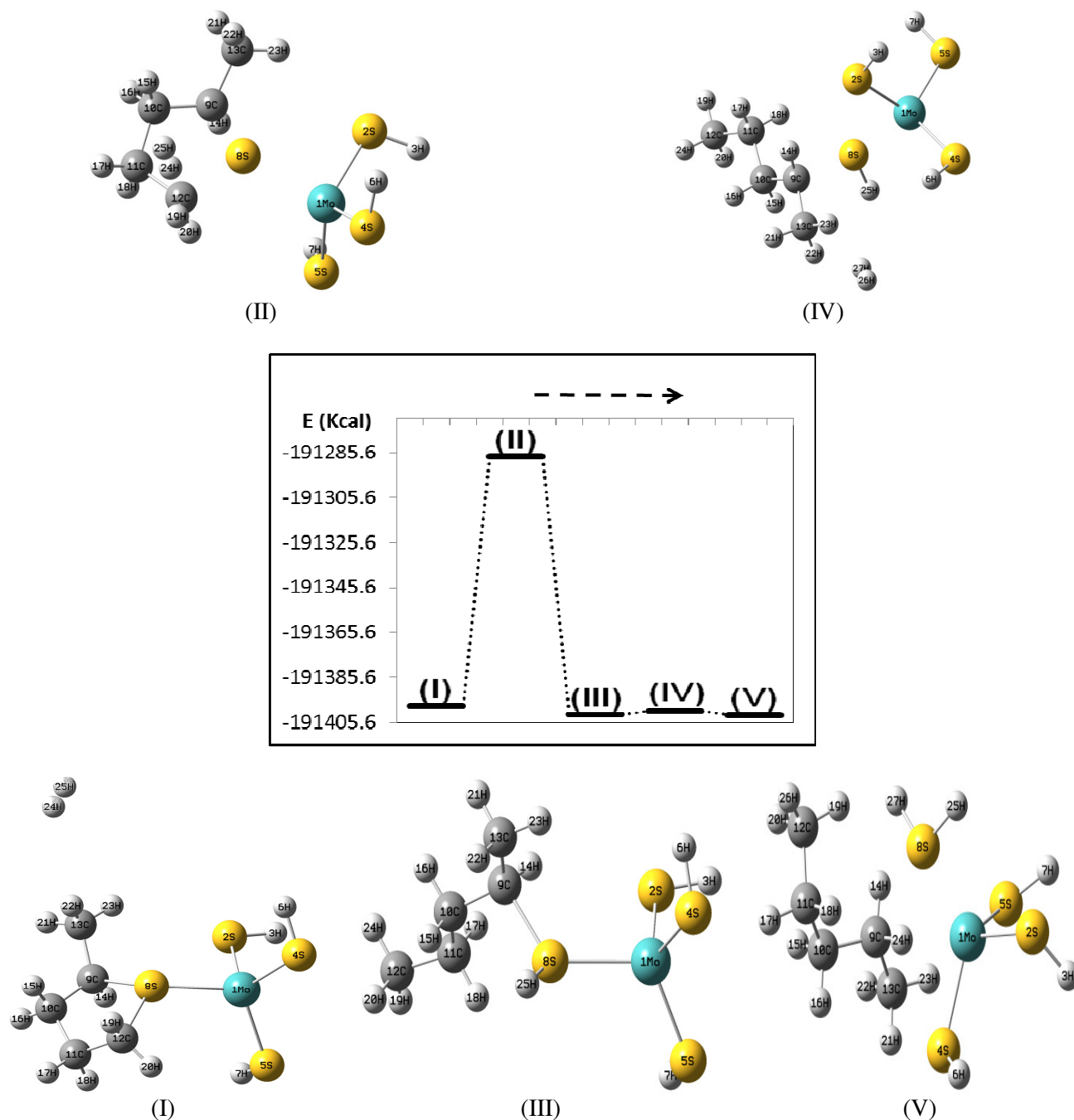
In this case, the analysis of Mulliken population showed that the two ruptures $C^9$–$S^8$ and $C^{12}$–$S^8$ are also heterolytic. Indeed, during the first stage, for the $C^{12}$–$S^8$ bond, we observed a reduction of the negative charge on the $S^8$ atom, from 0.107 u.a at the beginning of the process, to 0.162 u.a at the transition state. Moreover, the $C^{12}$ atom gains electronic charges which passes from -0.541 u.a to -0.690 u.a. In addition, during the second stage, the electronic charge of $S^8$ and $C^9$ atoms passed from -0.014 u.a to -0.019 u.a and from -0.267 u.a to-0.258 u.a from the beginning to the transition state, respectively.

The variation of geometric parameters of the system and the analysis of Mulliken population allowed us to propose a second probable mechanism of hydrodesulphurization of 2-MTHT leading to pentane (Fig 9).

**Figure 9:**   Probable mechanism hydrodesulphurization of 2-MTHT on the catalytic site $MoS_3H_3^+$ by the approach C12 leading to pentane
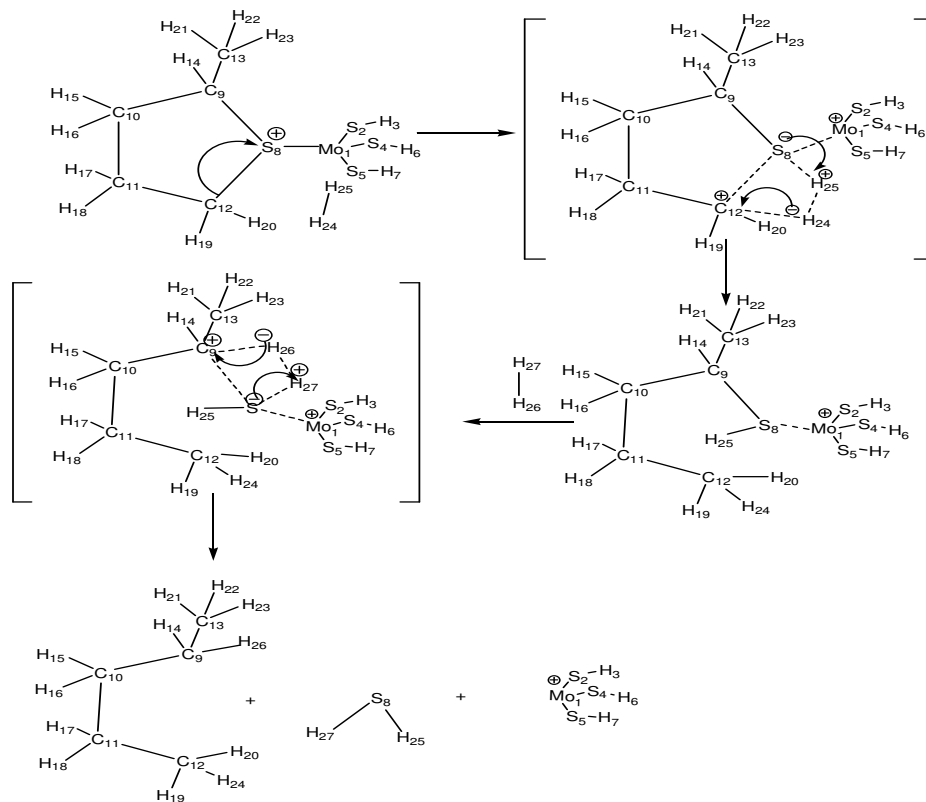


## 3.5. Desulphurization of 2-Pentanthiol without Addition of Second $H_2$ Molecule

The modeling of this reaction consisted in stretching of the $C^9$–$S^8$ bond of 2-pentanthiol formed at the end of the approach C12, until its rupture (Fig. 4). During this bond stretching, certain interatomic distances varied by giving place to formation or rupture of certain chemical bonds. The Table 8 summarizes the calculated and standard values [21-24] of these interatomic distances at the beginning, the transition state and the end of reaction.

At the end of the process the $C^{10}$-$H^{15}$ bond also breaks and the $S^8$-$H^{15}$ is formed. At the same time, the distance $C^9C^{10}$ decreases from 1.531 Å at the process beginning to 1.343 Å at the end. This last observation means that the simple $C^9$-$C^{10}$ bond transfers to double $C^9$=$C^{10}$ bond. The reaction product is then (E) pent-2-ene ($C_5H_{10}$) with a formation of hydrogen sulfide ($H_2S$). The calculated values of angles and dihedrals confirm this conclusion well. The transition state of this transformation has a structure in which $C^9$-$S^8$ and $C^{10}$-$H^{15}$ bonds are already broken, but the distance between the atoms $S^8$ and $H^{15}$ is still 3.196 Å (Table 8).

**Table 8:** Calculated and standard values of interatomic geometric parameters during the stretching of $C^9$-$S^8$ bond of 2-pentanthiol

| Geometric parameters (HF) | Initial State | Transition State | Final State | Standard Values [21, 22] | Observations |
|---|---|---|---|---|---|
| Distances (Å) | | | | | |
| $C^9C^{10}$ | 1.531 | 1.506 | 1.343 | 1.33 (C=C) | Formation C=C |
| $C^{10}H^{15}$ | 1.085 | 1.385 | 2.275 | 1.09 (C-H) | Rupture C-H |
| $S^8H^{15}$ | 3.013 | 3.196 | 1.379 | 1.35 (S-H) | Formation S-H |
| $C^9S^8$ | 2.002 | 2.302 | 3.581 | 1.79 (C-S) | Rupture C-S |
| | | | | | |
| Angles (°) | | | | | |
| $C^9C^{10} C^{11}$ | 115.67 | 117.75 | 125.45 | 120 (sp$^2$) | - |
| $C^{10}C^9 C^{13}$ | 115.30 | 119.64 | 125.34 | 120 (sp$^2$) | - |
| | | | | | |
| Dihedrals (°) | | | | | |
| $C^{11}C^{10}C^9 C^{13}$ | 173.01 | 177.14 | 186.97 | 180 | Configuration Trans (or E) |
| $C^{11}C^{10}C^9 H^{14}$ | 42.42 | 31.70 | 2.54 | 0 | |

The model developed here wants to take into account the thermal agitation in the reaction medium. It can be broken up into two stages:

- rupture of $C^{12}$-$S^8$ bond by the approach C12 of one $H_2$ molecule
- rupture of $C^9$-$S^8$ bond by its stretching.

The path of this last process is given (Fig. 10) and shows the geometrical structure of the two transition states TS1 (II) and TS2 (IV) among other things. The first transition state (II) has been already discussed in the previous section above.

The structure of TS2 (IV) shows a shortening of $C^9$-$C^{10}$ bond caused by the ruptures of $C^{10}$-$H^{15}$ and $C^9$-$S^8$ bonds. The formation of double $C^9$=$C^{10}$ would be simultaneous with the formation of $S^8$-$H^{15}$ (Table 8).
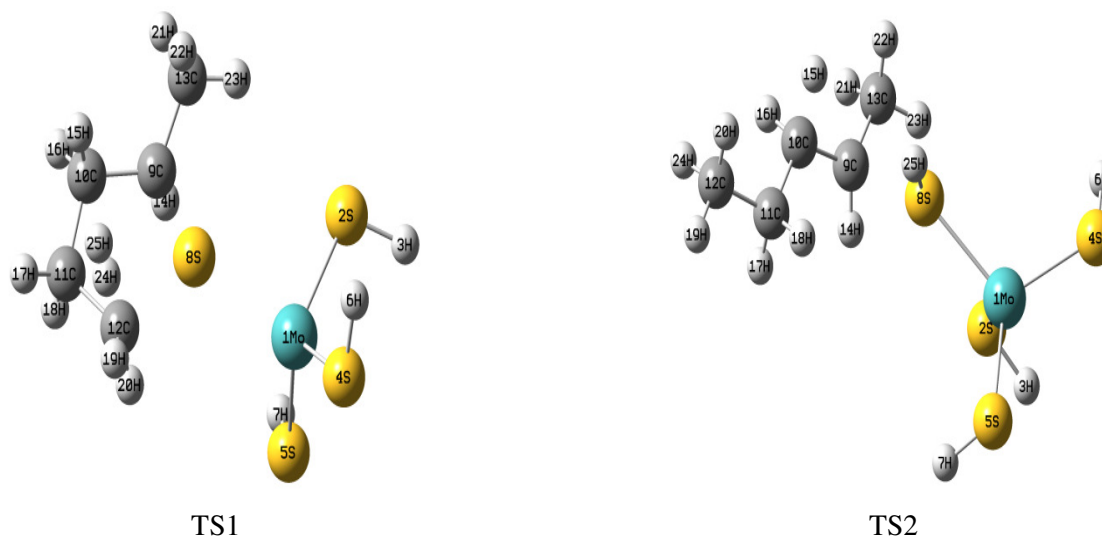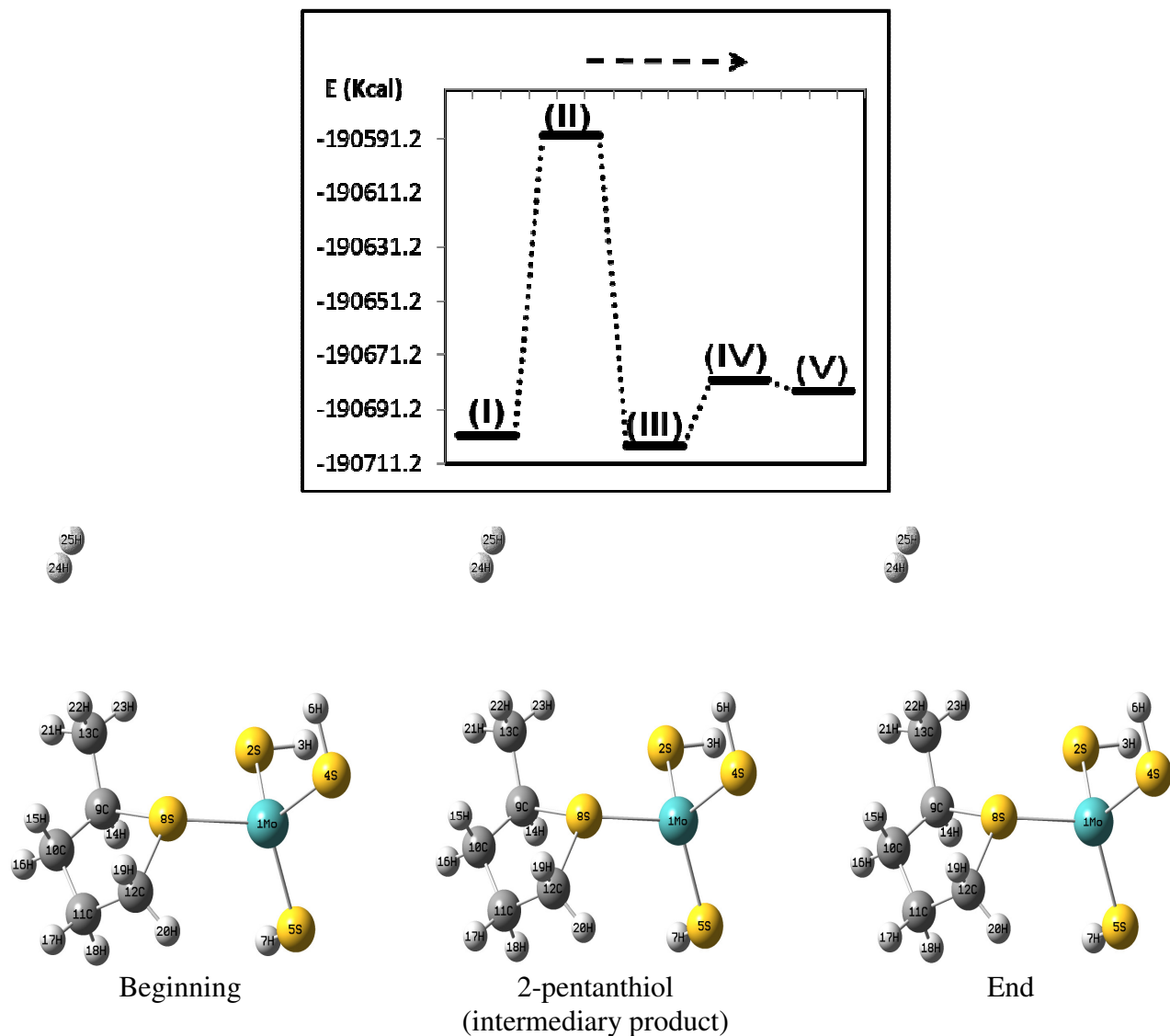
**Figure 10:** Reaction path of hydrodesulphurization of 2-MTHT on the catalytic site MoS$_3$H$_3$$^+$ by the approach C12: Hydrogenolysis of $C^{12}$-$S^8$ and $C^9$-$S^8$ bonds leading to pent-2-ene



TS1                                                  TS2

**Figure 10:** Reaction path of hydrodesulphurization of 2-MTHT on the catalytic site $MoS_3H_3^+$ by the approach C12: Hydrogenolysis of $C^{12}$-$S^8$ and $C^9$-$S^8$ bonds leading to pent-2-ene - continued



Beginning        2-pentanthiol
(intermediary product)        End

The analysis of Mulliken population was also carried out in this case. The results suggest that these two ruptures are heterolytic. On the basis of all these, a probable mechanism of hydrodesulphurization of 2-MTHT by the approach C12 leading to the formation of (E) pent-2-ene was proposed (Fig. 11).

**Figure 11:** Hydrodesulphurization of 2-MTHT on the catalytic site $MoS_3H_3^+$ by the approach C12 leading to pent-2-ene: (a) Reaction scheme; (b) Probable mechanism
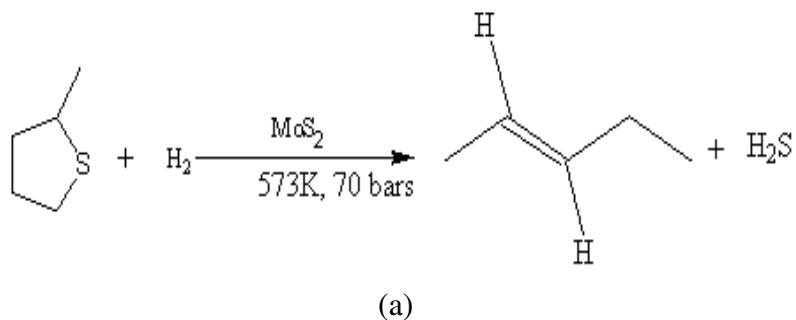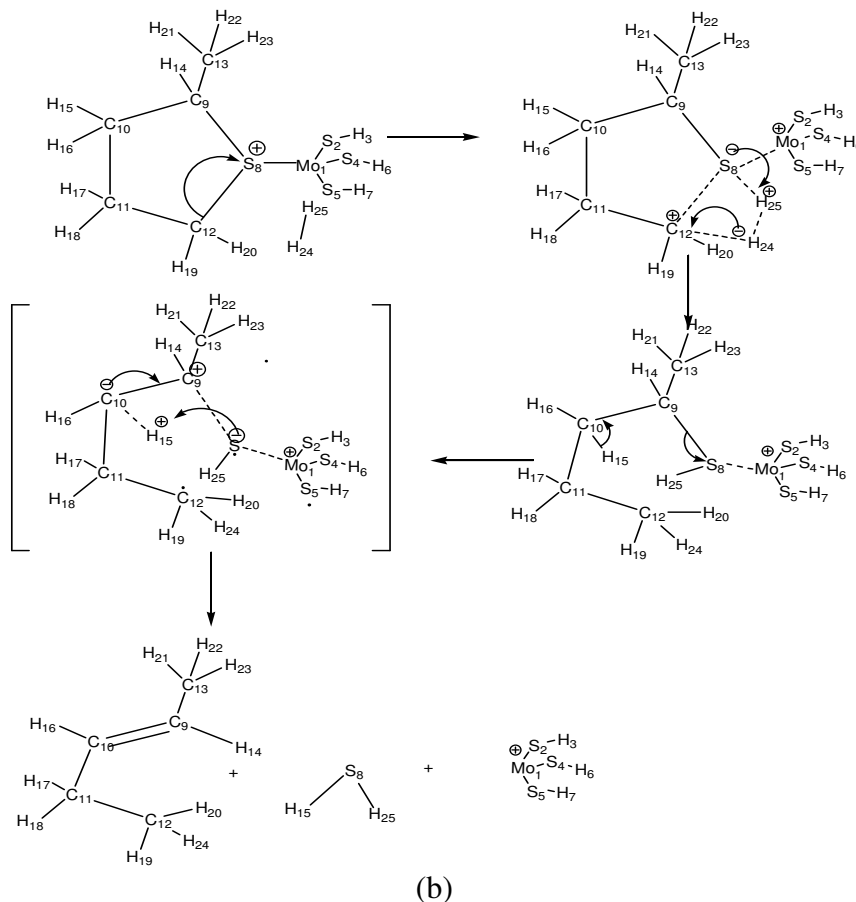


(a)

Theoretical Study of Hydrodesulphurization of 2-
Methyltetrahydrothiophene in the Presence of Molybdenum Disulfide
506

**Figure 11:** Hydrodesulphurization of 2-MTHT on the catalytic site $MoS_3H_3^+$ by the approach C12 leading to pent-2-ene: (a) Reaction scheme; (b) Probable mechanism - continued



(b)

## 3.6. Energetic Study of Hydrodesulphurization Paths of 2-MTHT on the Catalytic Site $MoS_3H_3^+$

Table 9 summarizes the values of the thermodynamic and kinetic parameters such as enthalpies ($\Delta H$), free energies ($\Delta G$) and activation energies (Ea) calculated by HF method for the various transformations, which take place during the catalytic hydrodesulphurization of 2-MTHT on the site $MoS_3H_3^+$.

**Table 9:** Energy data of hydrodesulphurization of 2-MTHT on the catalytic site $MoS_3H_3^+$

| Reactions | 2-MTHT + H$_2$ | | H$_2$ + 1-pentanthiol | H$_2$ + 2-pentanthiol | Stretching of C$^9$–S$^8$ bond of 2-pentanthiol |
|---|---|---|---|---|---|
| | **Approach C9** | **Approach C12** | | | |
| Ea (kcal) | 38.694 | 110.684 | 1,626 | 1,787 | 24.368 |
| $\Delta H$ (kcal) | - 1.815 | -4.153 | -8.205 | -0.099 | 20.216 |
| $\Delta G$ (kcal) | 12,301 | -0.756 | 8,901 | 5,128 | 17.285 |
| Products | 1-Pentanthiol | 2-Pentanthiol | Pentane | Pentane | Pent-2-ene |

All the transformations are exoenergetic ($\Delta H < 0$) except the formation of pent-2-ene ($\Delta H > 0$). The free enthalpies values of transformations are almost positive. This suggests that those transformations are not spontaneous. It is certainly for this reason that, in the crude oil industry, the hydrodesulphurization is carried out with high temperature and strong dihydrogene pressure.

The analysis of the different values of activation energy allows us to make the following important deductions.

- The values of activation energies of the first reaction stages are the highest (38.694 and 110.684 kcal) and reveals that the first ruptures of C-S bond, which produce 1-pentanthiol and 2-pentanthiol would be the stages limiting of the hydrodesulphurization of the 2-MTHT in presence of disulfide molybdenum (Table 9).
- The activation energies of the process passing by 1-pentanthiol (38.694 and 1.626 kcal) are smaller than those of the process passing by the 2-pentanthiol (110.684 and 1.787 kcal). At the stage of the first approach of a $H_2$ molecule, the approach C9 would be the fastest. This could be explained by the fact that the $C^9$-$S^8$ bond is longer than the $C^{12}$-$S^8$ bond and thus weaker. In addition, the presence of the methyl group on $C^9$ carbon allows the formation of the best stable carbocation (secondary) after the heterolytic rupture of $C^9$-$S^8$ bond.
- The values of activation energies (1.787 and 24.368 kcal) indicate that the passage from 2-pentanthiol to (E) pent-2-ene is more difficult than the passage to pentane. In this case, the hydrodesulphurization of the 2-MTHT would lead to pentane more than pent-2-ene. This result is perfectly in agreement with the experimental data [1, 25]
- For the whole of the processes, the pentane formation is the most kinetically favored, because activation energies of the transformations leading to it (1.626 and 1.787 kcal) are smaller than that leading to pent-2-ene formation (24.368 kcal).

In previous work [6, 7], we showed that under similar conditions, the 1-pentanthiol leads to pentane and pent-1-ene. So, we propose here a recapitulative scheme of the process of hydrodesulphurization of 2-MTHT in presence of molybdenum disulfide (Fig. 12).

**Figure 12:**     Recapitulative scheme of the process of hydrodesulphurization of 2-MTHT on $MoS_2$
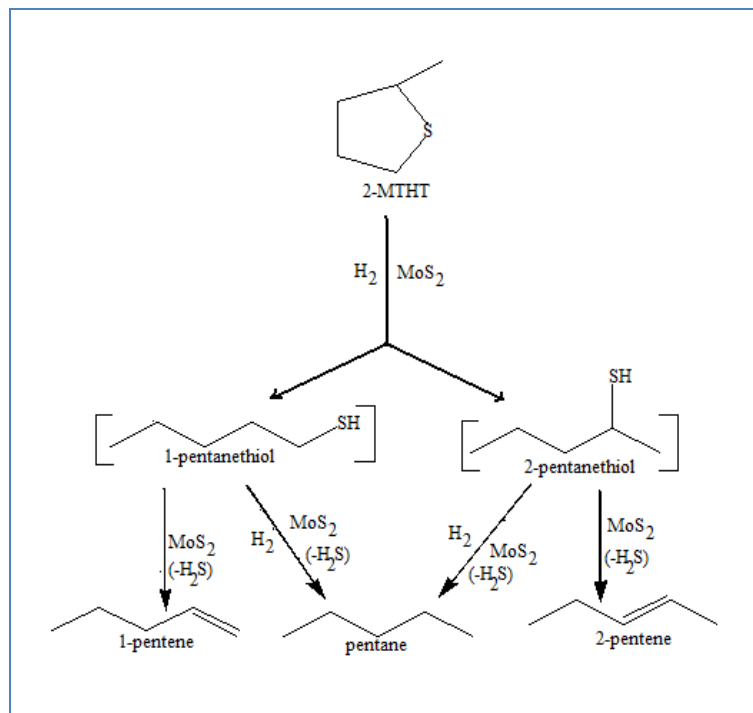


The molecule of the 2-MTHT under the hydrogen pressure undergoes a first rupture C-S which leads to pentan-1-thiol and pentan-2-thiol. The two intermediary thiols can be desulphurized, while leading to pentane and two isomers of pentene (pent-1-ene and pent-2-ene). The reaction occurs in presence of disulfide of molybdenum to a high temperature.

## 4. Conclusion

The model used shows that the hydrodesulphurization of 2-MTHT passes by two reactional intermediaries: 1-pentanthiol and 2-pentanhiol, which continue the process by giving a mixture of hydrocarbons (pent-1-ene, pent-2-ene and pentane) in accordance with the experimental results. All the reactions are exoenergetic. The majoritary product of the reaction is pentane, because it is kinetically the most favored. On the whole of the process, all the ruptures of C-S bonds observed seem to be heterolytic.

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