

AN AB INITIO STUDY OF HYDROTREATING OF THIIRENE AND THIIIRANE ON MoS_3H_3^+ CATALYTIC SITE

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ABSTRACT. Thiirene and thiirane have been chosen as model molecules representative of products present in crude oil to study the key steps in hydrotreating. The hydrotreating which can be desulfurization, deoxygenation or denitrogenation is the treatment of oil crude products under hydrogen pressure in presence of catalysts. This process leads to hydrogenolysis of carbon-heteroatom bond accompanied by heteroatom elimination. The catalytic site used is based on molybdenum disulfide (MoS_2), which is considered as active phase in the commercial catalysts containing molybdenum atoms. Two steps characterise the desulfurization process: the adsorption and the carbon-sulfur bond cleavage. The thiirene geometry has been destroyed through the cleavage of one of the carbon-sulfur bonds. The calculation results showed that the desulfurization of the thiirene and thiirane do follow a heterolytic process. At the end of process, the reaction pathways are the same with an activation energy which was higher for thiirane than for thiirene. These results confirmed the same catalytic site and molecules obtained in previous works in the EHT method.

KEY WORDS: Adsorption, Bond cleavage, Hydrotreating, Desulfurization, Molybdenum disulfide, Thiirene, Thiirane, Geometry Optimisation, Reaction mechanism, Reaction pathway, Hartree – Fock (HF), SCF, Density Functional Theory (DFT), B_3LYP , Lanl2dz

INTRODUCTION

The theoretical study of the mechanism of desulfurization of the thiirene and the thiirane [1-7] has been made on three vacancies site based on molybdenum disulfide (MoS_2) of MoS_3H_3^+ type [8-13]. For the process of adsorption, the used variable is the distance site–molecule (Mo-S^*), the other part of the system being relaxed completely otherwise. At the time of cleavage of the C-S^* bond, the site-molecule distance continued to vary according to the geometry of the system. The calculations have been carried out with the geometry optimisation of the two molecules and the site with the aim to see the behaviour of these systems in the catalytic desulfurization process on this type of site in conditions close to the reality.

METHODOLOGY

Theory

The methods used for these calculations are the Hartree–Fock and DFT methods [14–16]. In the Hartree–Fock method, the wave function is the function of spin orbitals. The electronic energy of the ground state is obtained by applying the variation theorem. In the Hartree–Fock theory, the energy has the form:

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$$E_{HF} = V + \langle hP \rangle + \frac{1}{2} \langle PJ(P) \rangle - \frac{1}{2} \langle PK(P) \rangle$$

where V is the nuclear repulsion energy, P is the density matrix, $[hP]$ is the one-electron (kinetic plus potential) energy, $\frac{1}{2}[PJ(P)]$ is the classical coulomb repulsion of the electrons, and $-\frac{1}{2}[PK(P)]$ is the exchange energy resulting from quantum (fermion) nature of electrons.

In the DFT method, the energy is a density functional. The hybrid B3LYP functional is used in our works. This functional uses LYP functional for the correlation part and Becke functional with three parameters (B3) for the exchange part. The expression of energy E_{KS} based of Kohn-Sham method is:

$$E_{KS} = V + \langle hP \rangle + \frac{1}{2} \langle PJ(P) \rangle + EX_{[P]} + EC_{[P]}$$

where $EX_{[P]}$ is the exchange functional, and $EC_{[P]}$ is the correlation functional. The basis set used is lanl2dz.

Program calculations

The HF and B3LYP calculations were performed with Gaussian-98W program [17]. The program data are the geometry of systems, their multiplicity and charge. The calculations were carried out in the "Laboratoire de Chimie Théorique et de Spectroscopie Moléculaire (LACTHESMO)" of "Université d'Abomey-Calavi" in Benin Republic.

Adsorption and desulfurization modelling

The adsorption has consisted to arrange the site in a fixed position compared with the molecule. The thiirene is arranged in a perpendicular plane to the plane containing Mo_1 , S_2 and H_3 of the site. An imaginary atom X is put on top of thiirene sulfur atom such as way the angle X-S*-Mo remain constant and equal to 90° in such a way that the dihedral angle X-S*-Mo-S and the distance X-S remain equal to 0° and 1 \AA , respectively, during the approach. It's from 11 \AA , an important distance we considered as infinite that the approach following Mo-S* began.

The desulfurization process consisted, from the optimised adsorptive geometry of $MoS_3H_3^+$ - molecule system to stretch one of the two C-S* bond until the atom sulfur elimination from the molecule and its bending on the catalytic site. During this stretching process of the carbon-sulfur bond, the site-reactant (Mo-S*) distance was the variable of the process.

Preliminary calculations

From initial geometries published in the literature [18], the program treats the information and takes out the optimised geometries for which the distances as well as the direct and dihedral angles between the atoms are calculated.

Optimised geometries of the $MoS_3H_3^+$ site, of thiirene and thiirane related to HF and B3LYP calculations, are given in Tables 1, 2 and 2, respectively.

These preliminary results have been obtained without imposing symmetry to the system and we have noticed a perfect symmetry on thiirene and thiirane molecules. As far as the site $MoS_3H_3^+$ is concerned the calculations with symmetry gave an unfavourable value of energy (-97.7681 Hartrees).

Table 1. Optimised geometry of MoS₃H₃⁺.

Geometry	Calculation	
	HF	B3LYP
<i>Distances (Å)</i>		
Mo ₁ S ₂	2.311	2.310
Mo ₁ S ₃	2.286	2.290
Mo ₁ S ₄	2.268	2.280
S ₂ H ₅	1.359	1.390
S ₃ H ₆	1.359	1.398
S ₄ H ₇	1.352	1.384
<i>Direct angles (°)</i>		
S ₃ Mo ₁ S ₂	101.0	99.5
S ₄ Mo ₁ S ₂	113.3	107.9
H ₅ S ₂ Mo ₁	101.9	99.5
H ₆ S ₃ Mo ₁	103.1	102.0
H ₇ S ₄ Mo ₁	113.7	110.2
<i>Dihedral angles (°)</i>		
S ₄ Mo ₁ S ₂ S ₃	110.1	108.5
H ₅ S ₂ Mo ₁ S ₃	205.4	199.7
H ₆ S ₃ Mo ₁ S ₂	247.1	241.5
H ₇ S ₄ Mo ₁	243.6	238.8
<i>Energy (Hartree)</i>	-97.92625	-99.35079

Table 2. Optimised geometry of thiirene.

Geometry	Calculation	
	HF	B3LYP
<i>Distances (Å)</i>		
S ₁ C ₂	1.982	1.977
S ₁ C ₃	1.982	1.977
C ₂ C ₃	1.260	1.291
C ₂ H ₄	1.059	1.075
C ₃ H ₅	1.059	1.075
<i>Direct angles (°)</i>		
C ₃ S ₁ C ₂	37.7	38.1
H ₄ C ₂ C ₃	156.4	153.6
H ₅ C ₃ C ₂	156.4	153.6
<i>Dihedral angles (°)</i>		
H ₄ C ₂ C ₃ S ₁	180.0	180.0
H ₅ C ₃ C ₂ S ₁	180.0	180.0
<i>Energy (Hartree)</i>	-86.63099	-87.38378

Table 3. Optimised geometry of thiirane.

Geometry	Calculation	
	HF	B3LYP
<i>Distances (Å)</i>		
C ₁ C ₂	1.474	1.491
C ₁ S ₃	1.908	1.929
C ₁ H ₄	1.070	1.085
C ₁ H ₅	1.070	1.085
C ₂ H ₆	1.070	1.085
C ₂ H ₇	1.070	1.085
<i>Direct angles (°)</i>		
S ₃ C ₁ C ₂	67.2	67.2
H ₄ C ₁ C ₂	119.0	118.8
H ₅ C ₁ C ₂	119.0	118.8
H ₆ C ₂ C ₁	119.0	118.8
H ₇ C ₂ C ₁	119.0	118.8
<i>Dihedral angles (°)</i>		
H ₄ C ₁ C ₂ S ₃	105.3	105.5
H ₅ C ₁ C ₂ S ₃	105.3	105.5
H ₆ C ₂ C ₁ S ₃	105.4	105.6
H ₇ C ₂ C ₁ S ₃	105.4	105.6
<i>Energy (Hartree)</i>	-87.88276	-88.67486

RESULTS AND DISCUSSION

Molecule of thiirene

Phase of the adsorption

The approach of the thiirene to the site, in accordance with the previously explained geometry, gave by the HF method the energy curve of Figure 1 corresponding to the part situated to the right of the minimum of the curve. At the minimum of adsorption the energy is $-215.29 \text{ kJ.mol}^{-1}$. The system being relaxed completely, the angles Mo-S-H, S-Mo-S and the lengths of the Mo-S bonds, of the site and the C-S-C angle, the lengths of the C-S and C-C bonds, of the molecule, the charges on molybdenum and carbon atoms, varied. The values of these different parameters are given in Table 4.

On the basis of these results obtained by the HF method, we can note that all along the process the length of the C-C bond did not vary a lot contrary to the C-S bonds that did not vary until the Mo-S distance of 6 Å. From 6 Å, we noticed an elongation of the two C-S bonds. At the minimum of adsorption, these two bonds, that had the same length practically since the departure until 6 Å, have different lengths. Indeed at this step of the process the S₈-C₉ bond is shortened itself of 4.34% while the second S₈-C₁₀ bond lay down itself of 33.28%. The molecule of thiirene that was of symmetry C_{2v} at the departure became C₁. The distortion of this molecule is therefore manifest; the interactive strength presence in the system is at the basis of these results. Of the side of the site until the minimization of the geometry of the system the angles of the interatomic bonds varied in an interval of 7.9, 5.8 and 3.4 degrees for the S₄-M_{o1}-S₅, S₄-M_{o1}-S₂ and S₅-M_{o1}-S₂ angles, respectively. With regard to the angles between the

molybdenum, sulfur and hydrogen atoms one noted a light variation of the infinity until least adsorption point. More precisely the Mo₁-S₂-H₃, Mo₁-S₄-H₆ and Mo₁-S₅-H₇ angles decreased 3.5, 3.8 and 3.7 degrees in relation to the initial angles, respectively. The data of the optimised adsorptive geometry for MoS₃H₃⁺ - thiirene obtained with B₃LYP calculations are listed in Table 5.

Tables 4. Thiirene adsorption data.

	Mo ₁ S ₈ (Å)						
	11	9	7	5	3	2.449	2.0
<i>Angles (°)</i>							
Mo ₁ S ₂ H ₃	109.5	109.4	109.4	109.0	107.8	105.9	98.9
Mo ₁ S ₄ H ₆	111.3	111.3	111.2	110.9	102.5	107.5	110.6
Mo ₁ S ₅ H ₇	111.3	111.3	111.2	110.9	111.0	107.6	109.8
S ₄ Mo ₁ S ₅	109.6	109.7	109.6	109.5	117.4	115.1	111.0
S ₂ Mo ₁ S ₄	107.0	107.0	107.0	106.7	104.2	109.8	112.2
S ₂ Mo ₁ S ₅	107.0	107.0	106.9	106.6	106.9	109.9	112.1
<i>Distances (Å)</i>							
Mo ₁ S ₂	2.277	2.277	2.277	2.279	2.286	2.309	2.336
Mo ₁ S ₄	2.279	2.279	2.279	2.280	2.325	2.314	2.281
Mo ₁ S ₅	2.279	2.279	2.279	2.280	2.293	2.312	2.305
S ₈ C ₉	1.986	1.986	1.986	1.990	2.023	1.900	4.433
S ₈ C ₁₀	1.986	1.986	1.987	1.991	2.011	2.647	4.483
C ₉ C ₁₀	1.258	1.258	1.258	1.257	1.252	1.268	1.204
<i>Charge on atoms (e)</i>							
Mo ₁	0.567	0.569	0.571	0.560	0.328	0.144	0.093
S ₈	-0.103	-0.114	-0.135	-0.138	+0.047	+0.142	+0.286
C ₉	0.052	0.057	0.068	0.084	0.179	-0.011	0.027
C ₁₀	0.052	0.058	0.069	0.085	0.158	0.523	0.026

Table 5. Data of the optimised adsorptive geometry for MoS₃H₃⁺-thiirene system in B₃LYP calculations.

Interatomic distances (Å)		Interatomic angles (°)		Charge on atoms (e)	
Mo ₁ S ₂	2.342	S ₄ Mo ₁ S ₅	111.5	Mo ₁	0.137
Mo ₁ S ₄	2.342	S ₂ Mo ₁ S ₄	113.1	S ₈	0.161
Mo ₁ S ₅	2.286	S ₂ Mo ₁ S ₅	111.6	C ₉	0.090
Mo ₁ S ₈	2.106	Mo ₁ S ₂ H ₃	98.5	C ₁₀	0.091
C ₉ S ₈	4.527	Mo ₁ S ₄ H ₆	98.5		
C ₁₀ S ₈	4.523	Mo ₁ S ₅ H ₇	109.4		
C ₉ C ₁₀	1.227				

The Mo-S lengths in the catalytic site have the same values practically that with the HF method. As for the C-S bonds, they lay down more distinctly that in the HF method. The C-S bond obtained by DFT method using B₃LYP functional is lower than the one obtained by the HF method. With regard to the interatomic angles S-Mo-S, they varied very little. Moreover concerning the angles Mo-S-H, those between the molybdenum, sulphur (2) and hydrogen (3), on the one hand, the molybdenum, sulphur (4) and hydrogen (6), on the other hand, decreased of about 10 and 13 degrees respectively while the Mo₁-S₅-H₇ angle decreased about 2 degrees. Furthermore, the Mulliken analysis of populations of Mo₁ and S₈ shows that in the HF method sulfur atom S₈ is populated more than the molybdenum and in DFT method the two atoms have equal charge.

As far as the level of energy is concerned, the molecular orbital highest occupied (HO) and unoccupied molecular orbital (LUMO) are situated at -0.43742 and -0.33306 Hartrees,

respectively, in the DFT method and at -0.51194 and -0.20358 Hartrees, respectively, in the HF method. This result showed that the gap of the two levels of energy is greater with the HF method than with the DFT method. Furthermore, the distance between the molybdenum atom and the sulfur atom of molecule ($\text{Mo}_1\text{-S}_8$) at the minimum of adsorption with the DFT method (2.106 Å) is lower than the one obtained with the HF method (2.449 Å). The distance obtained with the HF method is close to the Mo-S bond length in the MoS_2 crystal (2.356 Å) [10]. For this reason, the rest of the calculations have been made with HF method.

Phase of the C-S bond cleavage

During the breaking process of one of the C-S bond, some changes happened on the site and on the thiirene molecule. The variations noted on the retained parameters are given in the Table 6. The energy curve of this process corresponding at the left part of the curve between 2.05 and 2.449 Å is given in Figure 1. At the maximum of the curve situated about 2.238 Å, we have the transition state during which the sulfur atom of thiirene is transferred to the molybdenum atom. This reaction pathway point is where the C-S bonds break in the thiirene molecule and where the formation of a new Mo-S bond starts. Beyond this point, the curve decreases very quickly before stabilizing. At this step, the new Mo-S bond reinforce itself and the two formed chemical species (MoS_4H_3^+ and acetylene) become stable. The calculations carried out on these chemical species showed that the sum of the energies of acetylene (-76.79885 Hartrees) and MoS_4H_3^+ (-107.81987 Hartrees) is slightly above the second minimum energy of the curve.

Table 6. Relative data for the thiirene desulphurization on MoS_3H_3^+ .

	Mo_1S_8 (Å)											
	2.505	2.479	2.445	2.434	2.423	2.417	2.404	2.393	2.047	2.047	2.048	
<i>Angles (°)</i>												
$\text{Mo}_1\text{S}_2\text{H}_3$	106.5	106.2	105.9	105.8	105.8	105.7	105.5	105.4	99.2	99.2	99.2	
$\text{Mo}_1\text{S}_4\text{H}_6$	108.1	107.9	107.6	107.5	107.6	107.8	107.9	108.0	108.3	108.5	109.2	
$\text{Mo}_1\text{S}_5\text{H}_7$	108.1	107.7	107.7	107.4	107.5	107.7	107.8	107.9	110.0	109.9	109.7	
$\text{S}_4\text{Mo}_1\text{S}_5$	115.7	115.4	114.9	114.7	113.8	114.2	114.4	114.5	111.3	111.2	111.0	
$\text{S}_2\text{Mo}_1\text{S}_4$	109.0	109.3	110.1	110.5	111.4	110.8	110.3	109.9	112.4	112.3	112.2	
$\text{S}_2\text{Mo}_1\text{S}_5$	108.8	109.1	109.9	110.4	111.4	110.8	110.3	110.0	112.5	112.3	112.1	
<i>Distances (Å)</i>												
Mo_1S_2	2.303	2.305	2.310	2.311	2.313	2.313	2.315	2.316	2.333	2.333	2.333	
Mo_1S_4	2.307	2.308	2.313	2.315	2.312	2.311	2.310	2.308	2.286	2.284	2.281	
Mo_1S_5	2.308	2.312	2.314	2.314	2.316	2.315	2.312	2.311	2.302	2.302	2.302	
S_8C_9	2.200	2.400	2.700	2.900	3.100	3.200	3.300	3.350	3.500	3.700	4.000	
S_8C_{10}	2.003	1.944	1.893	1.902	1.968	2.050	2.148	2.209	3.822	3.966	4.11	
C_9C_{10}	1.245	1.254	1.271	1.279	1.286	1.286	1.282	1.277	1.204	1.204	1.207	
<i>Charge on atoms (e)</i>												
Mo_1	0.168	0.159	0.141	0.131	0.143	0.145	0.146	0.146	0.107	0.107	0.109	
S_8	0.130	0.127	0.147	0.173	0.195	0.208	0.220	0.229	0.273	0.271	0.267	
C_9	0.317	0.437	0.528	0.511	0.508	0.487	0.459	0.441	0.013	0.015	0.020	
C_{10}	0.131	0.045	-0.012	0.001	-0.022	-0.024	-0.024	-0.026	0.033	0.031	0.030	

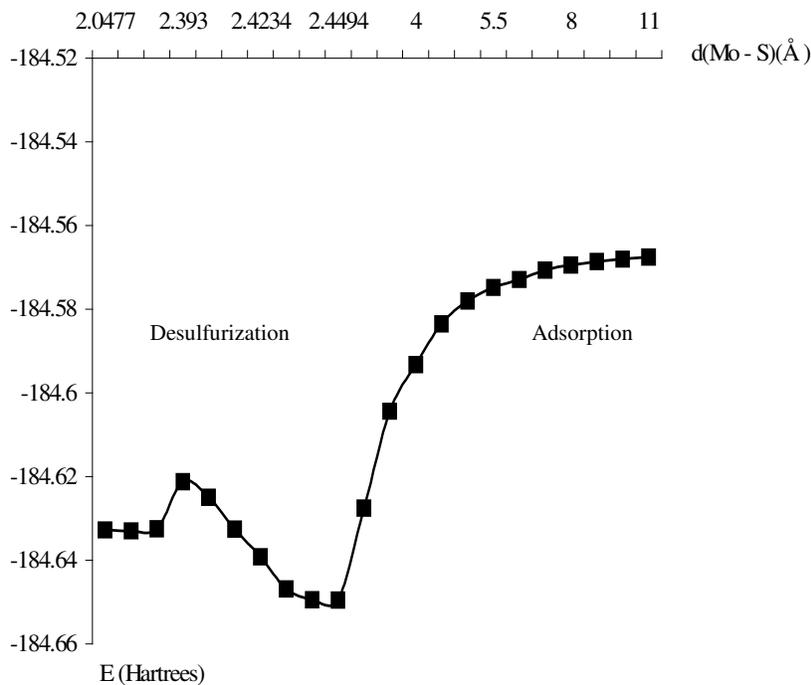


Figure 1. Reaction pathway for the thiirene desulfurization on MoH_3S_3^+ .

The two C-S bonds of thiirene do not break simultaneously during the process of desulfurization. Indeed, the one on which one pulls breaks before the other. At this stage, the carbon-carbon double bond (C=C) of initial length 1.258 Å shorten by 0.054 Å to give at the end of the desulfurization of the thiirene a carbon-carbon bond of length 1.204 Å, a value that corresponds well to the length of a triple C≡C bond in the acetylenic hydrocarbons [18, 19]. In the complex MoS_4H_3^+ , the charge carried by the absorbed sulfur atom is different from those carried by the three other atoms of sulfur of the MoS_3H_3^+ site because of the presence of hydrogen on these atoms of sulfur. In the same way, the length of the new Mo-S* bond is different from those of the three other Mo-S bond of the site for the same reason. From the only site, we made to adsorb an atom of sulfur with the aim of to get the complex formed at the end of thiirene desulfurization. Between the formed species and the one calculated, we noted a light difference at the level of the distribution of the charges with regard to the heavy atoms but on the other hand, the length of the Mo-S* bond is the same. The plot of the value of charges on S, C₁, C₂ and Mo as function of Mo-S distance has been made (Figure 2).

At the Mo_1S_8 distance of 2.393 Å where the C-S bonds cleavage seems to occur the charge on the sulfur atom (S₈) is positive which on carbon atom (C₉) is positive and which on the second carbon atom (C₁₀) is negative. This distribution of the charge obtained with RHF method has not varied when using UHF calculations (Figure 2).

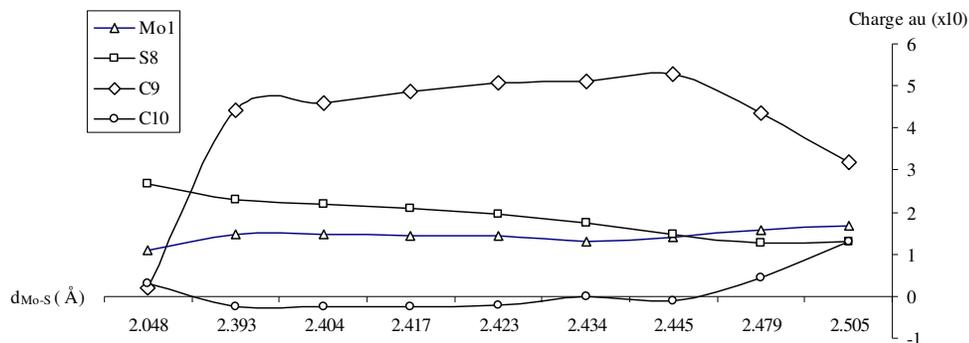
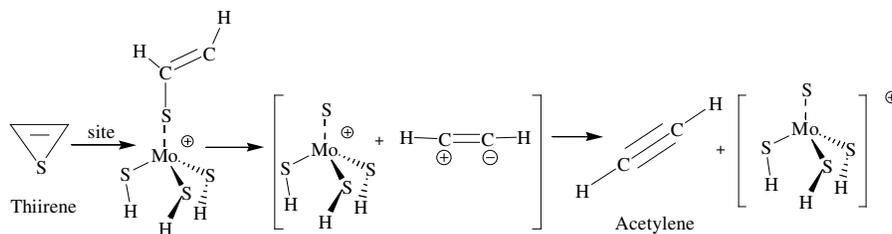


Figure 2. Distribution of the charge during thiirene desulfurization on some atoms.

This type of distribution cannot occur if the reaction mechanism is not of heterolytic type. After this step, the two carbon atoms acquire the same charge in the acetylene molecule formed. The probable mechanism of the reaction proposed for the desulfurization of the thiirene molecule is given in Scheme I.



Scheme I. Probable mechanism for the thiirene desulfurization on MoS_3H_3^+ .

Molecule of thiirane

Phase of the adsorption

The adsorption energy curve is given in Figure 2. When the molecule evolves toward the site, the energy of the system decreases until a minimum situated at 2.535 Å, minimum from which the energy of the system start to grow. At a difference about 5%, this minimum corresponds to the experimental value of the length of Mo-S bond in the molybdenum disulphide MoS_2 . The adsorption energy is $-204.80 \text{ kJ}\cdot\text{mol}^{-1}$. The parameters retained for the study of the site and thiirane behaviour are the same that those used previously for the study of the same site and the thiirene in the context of the thiirene adsorption. These parameters (Table 7) also varied during the thiirane adsorption.

The data of the optimised adsorptive geometry for MoS_3H_3^+ - thiirane obtained with B_3LYP calculations are listed in Table 8.

Table 7. Thiirane adsorption data.

	Mo ₁ S ₈ (Å)						
	11	9	7	5	3	2.535	2.3
<i>Angles (°)</i>							
Mo ₁ S ₂ H ₃	109.5	109.5	109.3	109.0	109.3	109.0	108.2
Mo ₁ S ₄ H ₆	111.3	111.3	111.2	110.9	102.7	103.3	103.1
Mo ₁ S ₅ H ₇	111.3	111.3	111.2	110.9	111.0	110.1	110.0
<i>Distances (Å)</i>							
S ₄ Mo ₁ S ₅	109.6	109.6	109.6	109.5	116.5	120.1	121.2
S ₂ Mo ₁ S ₄	111.3	107.0	106.9	106.7	103.3	105.4	106.5
S ₂ Mo ₁ S ₅	107.0	107.0	106.9	106.6	106.7	107.6	108.4
<i>Distances (Å)</i>							
Mo ₁ S ₂	2.276	2.277	2.277	2.279	2.293	2.308	2.317
Mo ₁ S ₄	2.279	2.279	2.279	2.280	2.316	2.321	2.329
Mo ₁ S ₅	2.279	2.279	2.280	2.282	2.291	2.298	2.304
<i>Charge on atoms (e)</i>							
S ₈ C ₉	1.911	1.911	1.913	1.918	1.962	1.996	2.045
S ₈ C ₁₀	1.910	1.911	1.913	1.918	1.961	1.992	2.038
C ₉ C ₁₀	1.472	1.472	1.471	1.470	1.455	1.447	1.436
<i>Charge on atoms (e)</i>							
Mo ₁	0.568	0.569	0.572	0.566	0.376	0.227	0.190
S ₈	-0.040	-0.053	-0.077	-0.109	0.023	0.073	0.036
C ₉	0.021	0.028	0.038	0.066	0.182	0.244	0.289
C ₁₀	0.019	0.025	0.040	0.066	0.181	0.243	0.285

Table 8. Data of the optimised adsorptive geometry for MoS₃H₃⁺ - thiirane system in B3LYP calculations.

Interatomic distances (Å)		Interatomic angles (°)		Charge on atoms (e)	
Mo ₁ S ₂	2.304	S ₄ Mo ₁ S ₅	116.6	Mo ₁	0.111
Mo ₁ S ₄	2.322	S ₂ Mo ₁ S ₄	105.7	S ₈	0.144
Mo ₁ S ₅	2.297	S ₂ Mo ₁ S ₅	108.8	C ₉	0.205
Mo ₁ S ₈	2.461	Mo ₁ S ₂ H ₃	107.6	C ₁₀	0.203
C ₉ S ₈	2.039	Mo ₁ S ₄ H ₆	101.0		
C ₁₀ S ₈	2.043	Mo ₁ S ₅ H ₇	107.6		
C ₉ C ₁₀	1.457				

At the minimum of adsorption, the lengths of the Mo-S bonds of the site have equal values practically with the two methods HF and DFT. It is some in the same way of the carbon-carbon bond in the thiirene where the lengths are the same order of magnitude. Between the Mo-S* distance (sulfur atom belonging to thiirane) calculated by HF and DFT methods, the gap is about 0.07 Å, value that shows that at this level also the two methods give practically the same results. With regard to the interatomic angles, one notes for the same angles a gap of 2.2 to 3.5 degrees. As far as population analysis is concerned, the charge carried by the molybdenum atom decreased half when HF method is substituted by DFT method. At the level of the adsorbed sulfur atom the tendency is reversed especially as the charge carried by this atom in the setting of the DFT method doubled in relation to the one related to the HF method. Of the side of the two atoms of carbon for which the results show a certain symmetry between them with the B₃LYP calculation, the charge carried by carbon atoms decreased of about 0.04 a.u. in relation to the one obtained by the method HF at least adsorption point.

In the fundamental state, the level of energy of the system is -10.42815 Hartrees while the molecular orbital highest occupied (HO) and unoccupied molecular orbital (LUMO) are situated at -0.38881 and -0.30250 Hartrees, respectively.

Phase of the C-S cleavage

The calculation of the breaking process of the C-S bond in the thiirane has been performed and the energy curve is shown in Figure 2. We notice in the beginning of this process a continuous growth of the energy of the system until the value -185.809 Hartrees, value from which the energy begins to decrease as far as stabilizing. At the maximum of the curve, the transfer of the sulfur atom of the thiirane occurs follow-up of the optimisation of the geometry of the two chemical species formed at the end of the process of desulfurization. The data which varied during this thiirane desulfurization process are listed in the Table 9.

On the basis of the data in the Table 9, the length of the C-C bond varied during the process before stabilizing around 1.453 Å value. This value of the length of carbon-carbon bond is not precisely the one related to the C=C double bond (1.34(5) Å) [18]. This length of the C=C double bond is located nevertheless between 1.34(5) Å and 1.54 Å, length of the simple C-C bond [20]. The same data of the table show that the adsorbed sulfur atom is closer to the molybdenum atom on which it is fixed than the three other atoms of sulfur. The presence of hydrogen atom on each of the three sulfur atoms belonging to the site and its absence on the adsorbed sulfur atom explain this result. The total energy of the system at the end of the process is equal to the sum of energies of ethylene (-78.01179 Hartrees) and of MoS_4H_3^+ (-107.81987 Hartrees).

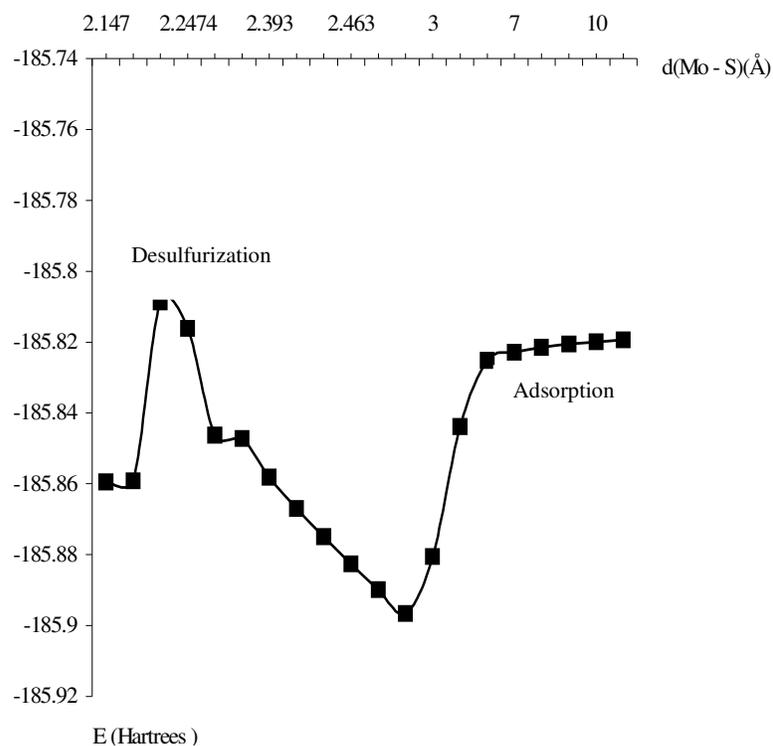


Figure 3. Reaction pathway for the thiirane desulfurization on MoH_3S_3^+ .

As far as the thiirane molecule is concerned when the C-S bond is on the point to break itself at Mo₁S₈ distance of 2.238 Å, the sulfur atom of the thiirane molecule (S₈) acquires a negative charge and carbon atom positive charge in RHF and UHF methods (Figure 4).

Table 9. Relative data for the thiirane desulfurization on MoS₃H₃⁺.

	Mo ₁ S ₈ (Å)											
	2.493	2.463	2.434	2.410	2.393	2.370	2.295	2.285	2.260	2.238	2.147	2.147
<i>Angles (°)</i>												
Mo ₁ S ₂ H ₃	108.5	108.4	108.1	107.8	107.5	106.8	101.7	101.3	100.6	100.2	107.7	107.7
Mo ₁ S ₄ H ₆	103.1	103.0	103.0	103.0	103.0	102.9	116.5	117.2	115.1	109.0	7.8	3.1
Mo ₁ S ₅ H ₇	109.8	109.9	109.8	109.8	110.0	110.5	111.6	111.3	111.3	111.6	109.2	109.2
S ₄ Mo ₁ S ₅	119.5	119.6	119.6	119.7	119.8	119.7	119.4	119.5	118.9	116.5	97.6	96.4
S ₂ Mo ₁ S ₄	105.4	105.7	105.9	106.2	106.6	107.3	111.6	111.7	112.0	112.4	107.6	107.0
S ₂ Mo ₁ S ₅	108.1	108.4	108.9	109.4	109.6	109.7	119.5	118.5	118.6	120.1	104.7	104.6
<i>Distances (Å)</i>												
Mo ₁ S ₂	2.314	2.318	2.322	2.326	2.328	2.327	2.327	2.329	2.335	2.341	2.348	2.348
Mo ₁ S ₄	2.326	2.329	2.332	2.334	2.334	2.332	2.604	2.640	2.687	2.754	5.764	5.731
Mo ₁ S ₄	2.300	2.301	2.303	2.305	2.304	2.303	2.299	2.301	2.307	2.314	2.346	2.346
Mo ₁ S ₅												
S ₈ C ₉	2.296	2.496	2.696	2.896	3.096	3.296	3.496	3.696	3.896	4.096	4.196	4.296
S ₈ C ₁₀	2.023	2.041	2.058	2.082	2.136	2.253	2.257	2.285	2.787	3.067	4.044	4.154
C ₉ C ₁₀	1.435	1.434	1.435	1.439	1.441	1.435	1.615	1.595	1.550	1.512	1.453	1.453
<i>Charge on atoms (e)</i>												
Mo ₁	0.205	0.199	0.191	0.187	0.188	0.187	0.240	0.242	0.221	0.193	0.487	0.487
S ₈	0.031	0.033	0.052	0.081	0.113	0.145	0.119	0.054	-0.023	-0.080	-0.365	-0.361
C ₉	0.414	0.507	0.572	0.604	0.596	0.543	0.139	0.134	0.115	0.089	0.250	0.249
C ₁₀	0.170	0.111	0.060	0.022	0.005	0.005	0.116	0.207	0.342	0.463	0.248	0.246

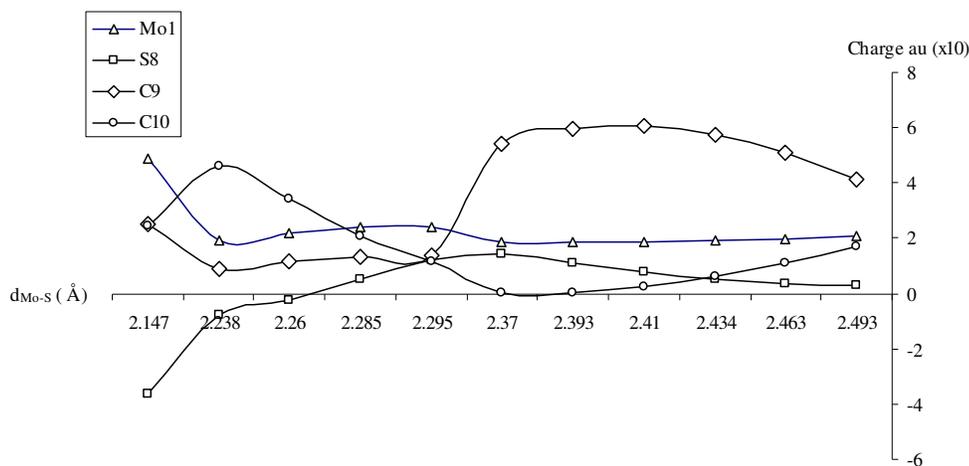
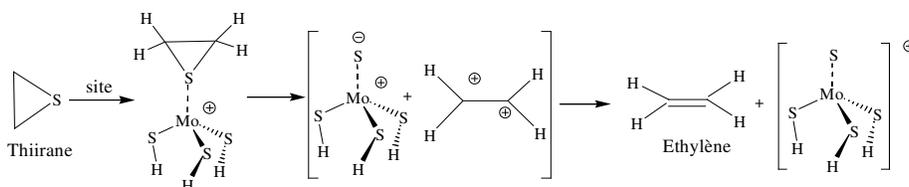


Figure 4. Distribution of the charge during thiirane desulfurization on some atoms.

This type of the distribution of the charge seems to indicate that during the desulfurization process the probable mechanism which occurs is of heterolytic type, which is represented in the Scheme II.



Scheme II. Probable mechanism for the thiirane desulphurization on MoS_3H_3^+ .

Comparative study of the results

The processes of desulfurization of thiirene and thiirane present the energy curves of the Figures 1 and 2. At the adsorption step, although the heteroatom is the same, the $\text{Mo-S}_{(\text{substrate})}$ bond distance is not the same for thiirene and thiirane. The values are 2.44 Å and 2.535 Å, with regard to the HF method, and 2.106 Å and 2.461 Å, with regard to the B3LYP method, for thiirene and thiirane, respectively. In the optimised adsorption geometry, in the HF calculation, the geometry of thiirene is not conserved because of the cleavage of one of the two C-S bonds ($\text{C}_{10}\text{-S}_8 = 2.647$ Å) (Figure 3), while on the side of thiirane, the symmetry is maintained more or less with a light symmetrical stretch of its C-S bonds (Figure 4). So in the thiirene molecule, the C-C bond lays down of 0.79% and of 1.70% in the thiirane molecule.

With regard to the analysis of population, the molybdenum atom and the one of the sulfur of the reactive molecules, carry equal positive charge in thiirene molecule and the different charge in the thiirane molecule ($\text{Charge}_{(\text{Mo})} = 3 \text{ Charge}_{(\text{S}^*)}$). At the end of the reaction it is to say the step where our calculations permitted to reach with thiirane molecule, the adsorbed sulfur atom and the molybdenum atom carry opposite sign charge, the negative charge being from the side of the element the more electronegative element which is here sulfur, whereas in the thiirene we noted the positive charge presence on the two atoms what permitted to affirm that the nature of the bond established between the sulfur atom of the reactive molecule and the molybdenum is not the same with the two molecules. It explains itself by the fact that the thiirane adsorbs itself chemically in its molecular state while the geometry of the thiirene breaks near the site. The thiirene adsorption energy is slightly higher than that of thiirane. That is understandable by the spatial clutter effect, the thiirane molecule occupying a bigger volume than the thiirene in the space. When one observes the state of transition on the two reaction paths, the calculations gave the results that attest the biggest stability of the thiirane in relation to the thiirene whose instability comes once of more than being bet in evidence. Indeed the useful energy to break the only C-S bond that remains in the thiirene cannot be equal to the one that it is necessary to break two C-S bonds in the molecule of the thiirane.

While studying the interaction of MoS_2 with hydrogen (H_2), Sierraalta and Ruette [19], from the exploitation of the topological properties of the density of the Laplacien of spin ($-\nabla^2_{(\text{spin})}$) [11, 18], showed that the interatomic angles Mo-S-H, of the site varies and confirms the results obtained in our works.

The acetylene molecule formed at the end of thiirene desulfurization has geometry in conformity with the experimental data. The C-C and C-H bonds have for experimental lengths 1.204 Å and 1.058 Å whereas our calculations gave 1.204 Å and 1.056 Å. The experimental value of H-C-C angle is 180° while the values obtained from our calculations vary between 176° and 177° , values close to the experimental data.

The geometry of ethylene product at the end of thiirene desulfurization has some geometric parameters globally equal to the experimental data. Is it about the C-H bond of which the theoretical length is 1.07 Å and the experimental value is 1.07 Å and the angles C-C-H or

H-C-C whose theoretical value is 120° and the experimental value is 120° . Only the length of C-C bond of which the value is 1.453 \AA is not in conformity with the geometry of this molecule in which the experimental value of this bond is 1.35 \AA , either a gap of 0.1 \AA . When the optimised data of the C_2H_4 molecule are pulled from the set of the optimised system and that the optimisation of this molecule is thrown, the length of the C=C bond calculated is 1.334 \AA , value close to the experimental data. It is therefore very likely that in the real conditions of the hydrosulfurization that such an optimisation occurs after the desulfurization step.

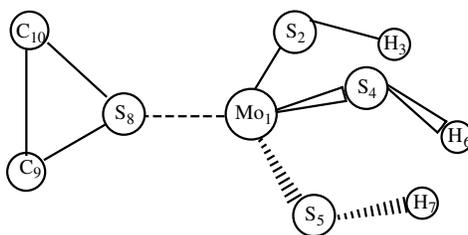


Figure 5. Optimised geometry of the MoS_3H_3^+ - thiirene system.

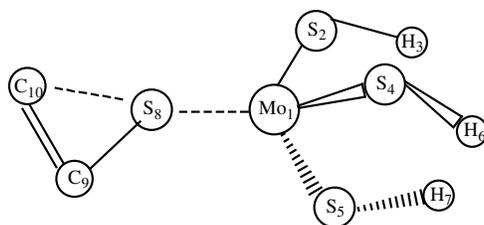


Figure 6. Optimised geometry of the MoS_3H_3^+ - thiirane system.

CONCLUSION

By the SCF-HF method the study of the adsorption and the desulfurization of thiirene and thiirane has been made on the three vacancies site based on molybdenum disulphide (MoS_2) of MoS_3H_3^+ type. The geometries of the site and the two cyclic molecules have been optimised before their implication in these processes. For these two molecules the reaction pathways look alike themselves and the results showed that the hydrogenation of the thiirene consolidated the cycle what explains the relative difficulty of desulfurization of the thiirane in relation to the molecule of the thiirene. At the minimum of adsorption the distances molybdenum-sulfur (Mo-S) are the same order of magnitude that the length of the Mo-S bond. The hydrocarbons produced after the elimination of sulfur do not have all geometry known of these molecules. Indeed, if the geometry of the acetylene coming from the desulfurization of the thiirene is in conformity with the one that one especially knows this molecule with regard to the length of the triple $\text{C}\equiv\text{C}$ bond, it is not the case of the ethylene product after the desulfurization of thiirane because the length of the $\text{C}=\text{C}$ double bond is experimentally slightly different from the one known. This result is understandable by the fact that geometry obtained theoretically of the ethylene is located on a frequency from which the passage to another frequency corresponding

to the best geometry seems to be difficult especially as the observed geometry is located on a minimum.

The B₃LYP calculation that takes into account the electronic correlation gave less interesting results in the process of adsorption than those obtained with the Hartree–Fock calculation because the distances Mo–S at the minimum of adsorption is weak in relation to the length of the Mo–S bond insofar as the adsorption of the molecules is of chemical type.

In total, by the SCF–HF method, the behaviour of the thiirene molecule and its hydrogenous derivative, the thiirane, in the context of the adsorption and the desulphurization, has been better investigated as the MoS₃H₃⁺ site that has been relaxed completely during the whole process.

REFERENCES

1. Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1977**, 99, 4842.
2. Krantz, A.; Laureni, J. *Berichte der Bunsen-Gesellschaft* **1978**, 82, 13.
3. Torres, M.; Safarik, I.; Clement, A.; Berti, J.E. et Strausz, O.P. *Nouv. J. Chim.* **1979**, 3, 365.
4. Hess, B.; Andes, J.; Schaad, L.; Ewig Carl, S. *J. Am. Chem. Soc.* **1980**, 102, 2507.
5. Gosavi Ratnakar, K.; Strausz Otto, P. *Can. J. Chem. Soc.* **1983**, 61, 2596.
6. Hassner, A. *Chemistry of Heterocyclic Compounds*, Vol. 42: *Small Ring Heterocycles*. Part 1: *Aziridines, Azirines, Thiirane, Thiirene*, John Wiley and Sons: New York; **1983**.
7. Hess, B.; Andes, J.; Schadd, L.J.; Caroky, P. *Pure Applied Chem.* **1983**, 55, 253.
8. Mensah, J.B.; Atohou, Y.G.S.; Olatunji, L.O. *Bull. Chem. Soc. Ethiop.* **2003**, 17, 75.
9. Raybaud, P.; Hafner, J.; Kress, G.; Toulhoat, H.; *Surface Sci.* **1998**, 497, 237.
10. Byskov, Line S.; Horskov Je, N.S.K.; Clausen, Bjerne S.; Henrik, T. *J. Catal.* **1999**, 157, 109.
11. Anibal, Sierraalta; Fernando, Ruette; Erik, Machado *Int. J. Quant. Chem.* **1998**, 70, 113.
12. Gate, B.C. *Catalytic Chemistry*, Wiley: New York; **1992**.
13. Topsoe, H.; Clausen, B.S.; Massoth, F.E.; in: *Catalysis: Science and Technology*, Vol. 11, Boudart, T.M.; Anderson, J.A. (Eds.); Springer: Berlin; **1996**; p 1.
14. Hay, P.J.; Wadt, W.R. *J. Chem. Phys.* **1985**, 82, 470.
15. Becke, A.D. *J. Chem. Phys.* **1993**, 98, 5648.
16. Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev.* **1980**, B37, 785.
17. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Zakrzewski, V.G.; Montgomery, J.A.; Stratmann, R.E.; Burant, J.C.; Dapprich, S.; Millam, J. M.; Daniels, A.D.; Kudin, K.N.; Strain, M.C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P.Y.; Cui, Q.; Morokuma, K.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Cioslowski, J.; Ortiz, J.V.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P.M.W.; Johnson, B.G.; Chen, W.; Wong, M.W.; Andres, J.L.; Head-Gordon, M.; Replogle, E.S.; Pople, J.A.; *Gaussian 98 (Revision A.1)*, Gaussian Inc.: Pittsburgh PA; **1998**.
18. Clark, D.T. *Theor. Chim. Acta* **1969**, 15, 225.
19. Sierraalta, A.; Ruette, F. *J. Mol. Catal. A. Chem.* **1996**, 109, 227.
20. Bader, R.F.W. *Atoms in Molecules: A Quantum Theory*, Clarendon Press: Oxford; **1990**.