

THEORETICAL STUDY OF THE CATALYTIC DESULFURIZATION MECHANISM OF THIIREN AND ITS METHYL DERIVATIVE

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ABSTRACT. The desulfurization process of compounds implicates two steps. The first step is the adsorption process on the catalytic site and the second, the breaking of the carbon-heteroatom bond leading to the heteroatom elimination. The adsorption process of thiiren have been studied and published in previous works. The results obtained on MoS_3H_3^+ and MoS_4H_4 have shown that the adsorption of this molecule was very good on the two and three anionic vacancies sites based on molybdenum. In the present study, we have carried out the adsorption according to vertical and horizontal geometries of dihydrothiiren, methylthiiren, and methyl dihydrothiiren, and the desulfurization of all these molecules including thiiren molecule. The results obtained have shown that, the desulfurization of thiiren and its methyl derivate pass through the hydrogenation of the aromatic ring on the two types of catalytic sites.

KEY WORDS: Catalytic site, Adsorption, Desulfurization, Thiiren, Icon program, PSI/77 program, QCPE

INTRODUCTION

In liquid fuels, one finds compounds like thiophene and its derivates. In order to study the hydrodesulfurization mechanism, thiophene is generally chosen as a representative molecule of sulfur compounds [1-7]. The behaviour of thiophene has already been studied on MoS_3H_3^+ and MoS_4H_4 sites modelised by Joffre [8] and so it was logical to use thiiren molecule (Figure 1a) to do the same study and see the behaviour of these two sites in presence of this molecule. Thus a theoretical study of the adsorption of thiiren has been carried out [9] and the results have shown that this molecule is very well adsorbed on the two types of sites according to vertical and horizontal geometries. In the present study we have submitted the dihydrothiiren (Figure 1b), the methylthiiren (Figure 1c) and the methyl dihydrothiiren (Figure 1d) to the same process before proceeding to their desulfurization behaviour in order to propose the sulfur atom elimination mechanism while studying methyl group influence on the thiiren molecule.

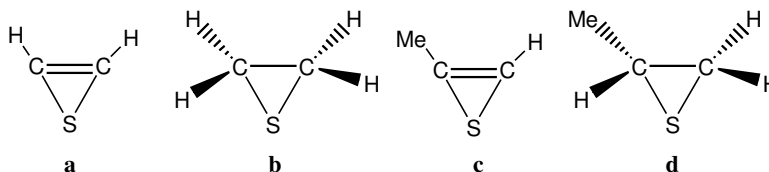


Figure 1. Structural formulas of molecules: a- thiiren; b- dihydrothiiren; c- methyl thiiren; d- methyl dihydrothiiren.

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METHOD AND CALCULATIONS PROGRAMS

EHT method

This method is based on the theory of Roald Hoffmann [10]. Expansion of a molecular orbital as the linear combination of atomic orbitals (LCAO) yields, on minimizing the total energy, the set of Hückel equations

$$\Psi_i = \sum_j c_{ij} \Phi_j \quad (1)$$

$$\sum_{i=1}^n [H_{ij} - ES_{ij}] c_{ij} = 0 \quad j = 1, 2, \dots, n \quad (2)$$

In the process complete secular determinant resulting is treated, all interactions accounted for, and off-diagonal E's retained. The critical choice is the manner of guessing the matrix element H_{ij} . The H_{ii} are chosen as valence state ionization potentials.

$$H_{ii} = -I_i \quad (3)$$

The H_{ij} are calculated by the Wolfsberg-Helmholtz formula [11]

$$H_{ij} = 0.5 \times 1.75 (H_{ii} + H_{jj}) S_{ij} \quad (4)$$

The overlap integrals S_{ij} between atomic orbitals i and j , are calculated taking account the molecule geometry and the AO of its atoms. The AO are of Slater type and expanded in "double zeta" [12] for transition metals.

$$\Phi = R(Zd_1) \times C_1 \times e^{(-Zd_1 r)} + R(Zd_2) \times C_2 \times e^{(-Zd_2 r)} \quad (5)$$

Calculation programs

Program ICON8. The calculation program is ICON 8 provided by the Quantum Chemistry Program Exchange (QCPE 344) written by the Roald Hoffmann group. The program parameters (Table 1) come from the literature [13, 14]. The calculations were carried out in the "Laboratoire de Chimie théorique" at the University of Abomey-Calavi.

Table 1. EHT parameters [13].

Atom	H	C	S	Mo
Valence electrons	1	4	6	6
COUL s	-13.6	-21.4	-20.0	-8.5 (5s)
EXP s	1.3	1.625	1.817	1.960
COUL p	-	-11.4	-13.3	-5.8 (5p)
EXP p	-	1.625	1.817	1.900
COUL d	-	-	-	-11.0 (4d)
EXP D1(Zd ₁)	-	-	-	4.540
C ₁	-	-	-	0.58988
EXP D ₂ (Zd ₂)	-	-	-	1.900
C ₂	-	-	-	0.58988

The distances and angles between the atoms in these molecules are taken from [8, 15]: C=C (1.382 Å); C-S (1.839 Å); C-H (1.09 Å); C-C (1.54 Å); Mo-S (2.35 Å); S-S (3.16 Å), for sulfur atoms in the same layer; S-S (2.98 Å), for sulfur atoms in two consecutive layers; S-H (1.34 Å).

Program PSI/77. The construction of the orbital drawings is included for completeness and for the theoretical chemists who would require such details [16]. The primary concern in producing the drawings was the selection of wavefunctions, orbital energies and of a contour level for the surfaces. Ideally, wavefunctions and orbital energies from accurate ab initio molecular orbital calculations would be employed. Since ab initio wavefunctions for complex molecules are rarely recorded in the literature and since we had to treat a large number of systems, it was necessary to use wavefunctions calculated from semiempirical molecular orbital theories. Several of the methods, as Extended Hückel method, produce orbital coefficients and charge distribution in good agreement with ab initio values. The wavefunctions obtained from ICON are introduced in the Jorgensen Program PSI/77 (QCPE 340) with the geometry of the molecule. The result of this operation yields contour levels which give two or three – dimensional orbital maps. The drawings are obtained with the help of a basic program (VISU3D).

RESULTS AND DISCUSSION

Adsorption of molecules

The adsorption of molecules was carried out through the S-atom according to vertical and horizontal geometries. On the three anionic vacancies site, all the molecules are well adsorbed vertically. As for the horizontal adsorption on the same site, only the methylthiiren molecule is well adsorbed (Figure 2-4).

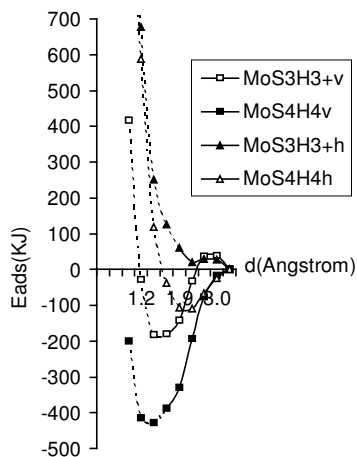


Figure 2. Adsorption of dihydrothiiren.

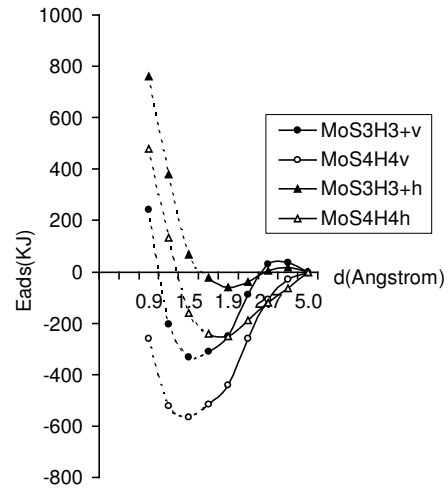


Figure 3. Adsorption of methylthiiren.

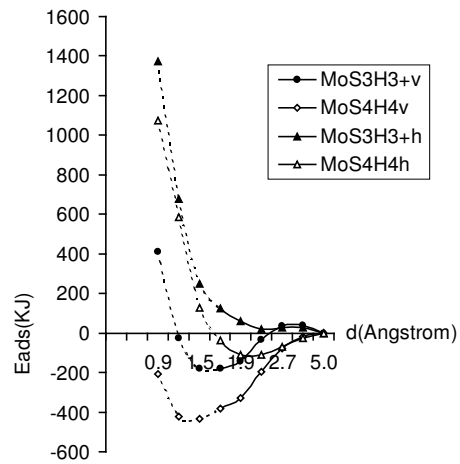


Figure 4. Adsorption of methylidihydrothiiren.

On the curves of the figures, some minima are at weak distances and must not be considered as stable complexes given that the length of the Mo-S bond cannot have such a length. The length of the Mo-S bond is about 2.3 Å, and we have proceeded to study complexes formed by the molecules and the sites, in calculating the bond populations between the two carbon atoms of the aromatic ring (C₁-C₂), on the one hand, and between the S-atom and each of the C_α-atoms, on the other hand. The adsorption energies have been correlated to enthalpies ΔH (Tables 2 and 3).

Table 2. Bond population (p) and "heat" of adsorption of molecules, ΔH, on MoS₃H₃⁺ at 2.3Å.

Molecules	p(C ₁ -S)	p(C ₂ -S)	p(C ₁ -C ₂)	p(Mo-S)	ΔHads
	<i>Vertical adsorption</i>				
Thiiren	0.415	0.415	1.147	0.754	-81.132
Methylthiiren	0.397	0.444	1.145	0.758	-88.958
Dihydrothiiren	0.546	0.546	0.592	0.686	-33.082
Methyldihydrothiiren	0.547	0.547	0.601	0.685	-32.610
	<i>Horizontal adsorption</i>				
Thiiren	0.483	0.482	1.029	0.540	-54.475
Methylthiiren	0.449	0.505	1.136	0.553	-39.917
Dihydrothiiren	0.503	0.490	1.063	0.496	20.846
Methyldihydrothiiren	0.586	0.583	0.678	0.474	19.637

Table 3. Bond population (p) and "heat" of adsorption of molecules, ΔH, on MoS₄H₄ at 2.3Å.

Molecules	p(C ₁ -S)	p(C ₂ -S)	p(C ₁ -C ₂)	p(Mo-S)	ΔHads
	<i>Vertical adsorption</i>				
Thiiren	0.489	0.489	1.150	0.775	-250.407
Methylthiiren	0.491	0.513	1.140	0.774	-260.895
Dihydrothiiren	0.572	0.572	0.613	0.715	-193.395
Methyldihydrothiiren	0.572	0.573	0.622	0.715	-194.310
	<i>Horizontal adsorption</i>				
Thiiren	0.500	0.500	1.165	0.543	-186.165
Methylthiiren	0.488	0.517	1.171	0.548	-188.655
Dihydrothiiren	0.580	0.580	0.657	0.562	-109.758
Methyldihydrothiiren	0.579	0.577	0.666	0.565	-111.646

In studying Tables 2 and 3, it can be seen that on MoS₃H₃⁺ and MoS₄H₄ sites, vertically, and horizontally, the adsorption is proportional to the Mo-S bond population. The positive enthalpies of adsorption given by dihydrothiiren and methyldihydrothiiren on MoS₃H₃⁺ are due to the weak population of the Mo-S bond.

As for the methylation of thiiren, the result describes the destruction of the bond population between the S-atom and the two C_α-atoms. However, we notice that near the C_α-atom substituted, the electronic population is more denser than near the second C_α-atom. All these results obtained are well illustrated by the contours of the molecular orbitals (Figure 5-8).

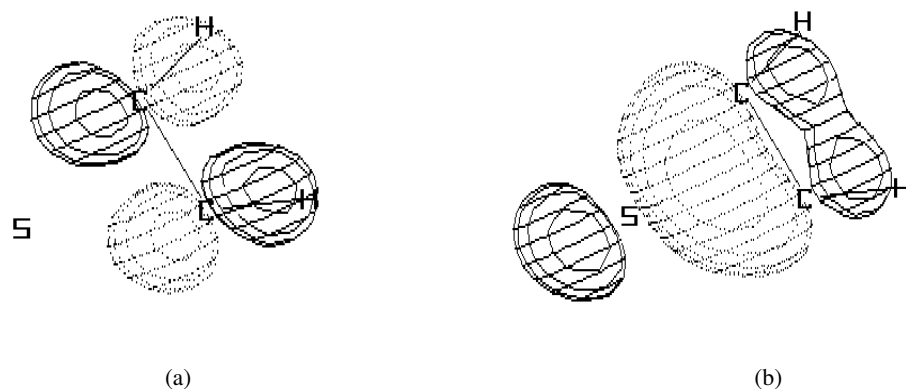


Figure 5. Molecular orbitals of thiiren: a- LUMO (-8.5224 eV); b- HOMO (-11.2933 eV).

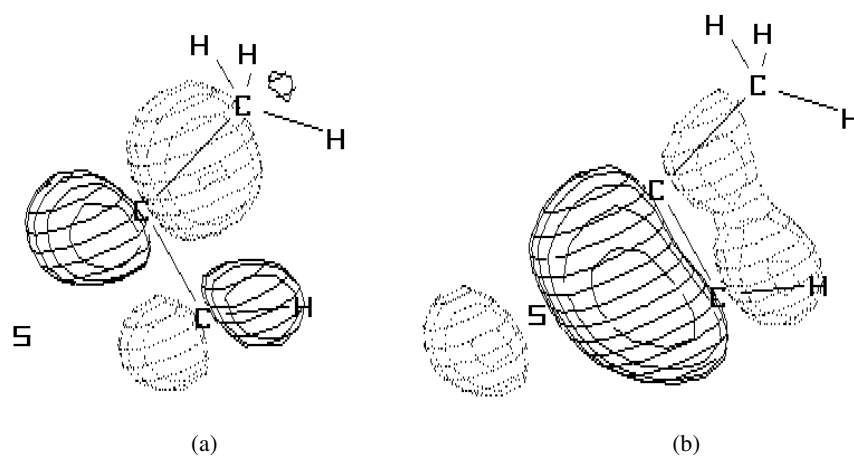


Figure 6. Molecular orbitals of methylthiiren: a- LUMO (-7.7952 eV); b- HOMO (-10.9373 eV).

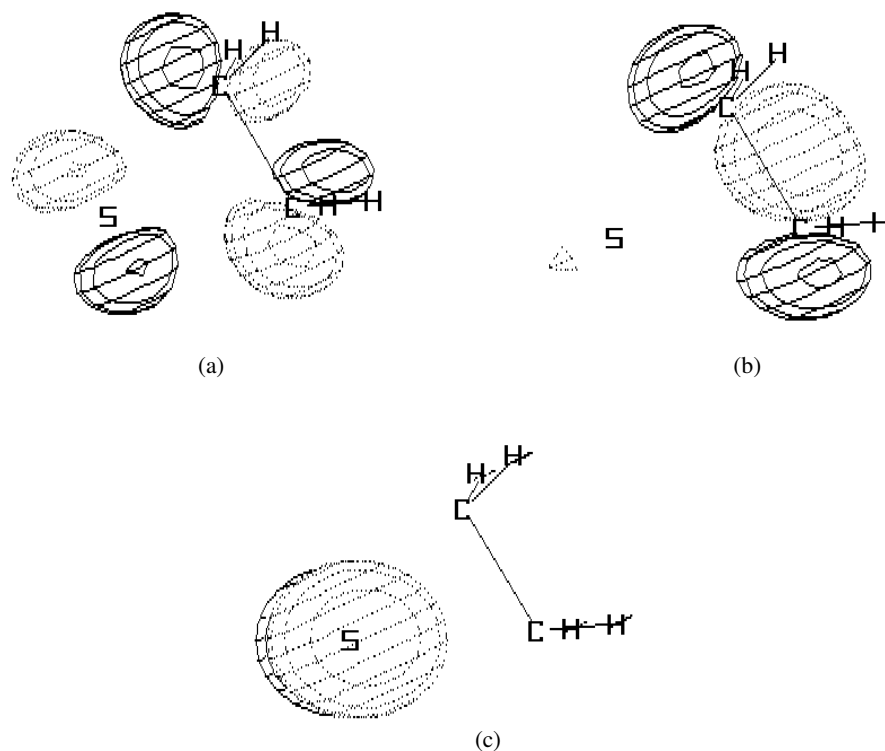
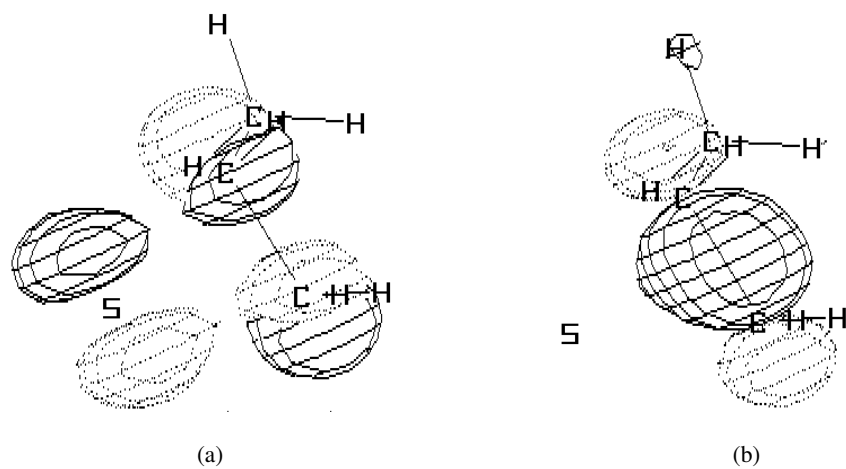


Figure 7. Molecular orbitals of dihydrothiiren: a- LUMO (-6.6012 eV); b- HOMO (-12.7978 eV); c- OM underneath of the HOMO (-12.8991 eV).



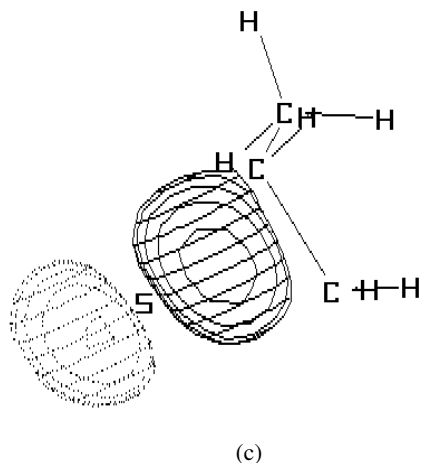


Figure 8. Molecular orbitals of methylthiiren: a- LUMO (-6.5781 eV); b- HOMO (-12.5226 eV); c- OM underneath of the HOMO (-12.7965 eV).

For example, the good adsorption of the thiiren or methylthiiren molecule is due to its high-occupied molecular orbital (HOMO) which is of p_z symmetry with an important electronic density near the S-atom and the two C_α -atoms (Figure 5b, 6b). As for the dihydrothiiren and methylthiiren, the HOMO's are dominated by the orbitals p_x of the two C_α -atoms (Figure 7b, 8b). Therefore the electronic density is very important along the $C_\alpha-C_\alpha$ bond. The molecular orbital which is underneath each HOMO of these two hydrogenated molecules (Figure 7c, 8c), has the same symmetry as the HOMO of thiiren and its methyl derivate. It can be concluded that the hydrogenation of thiiren and its methyl derivate lead to the movement on the molecular orbital of p_z -type centred on the S-atom underneath the HOMO characterized by a strong percentage (~80%) of p_x -orbital contribution. For each hydrogenated molecule, the difference between the energy of HOMO and the energy of the OM underneath the HOMO is very weak (0.101 and 0.274 eV, for dihydrothiiren and for methylthiiren, respectively). This is why the transformation with respect to the molecular orbitals has been possible, on the one hand, and that the adsorption of dihydrothiiren and methylthiiren is weak in comparison with thiiren and methylthiiren molecules, on the other hand.

Desulfurization of molecules

The desulfurization reaction was based on the model proposed by Joffre [8]. This model consists of fixing distance between molybdenum atom and heteroatom of the molecule and to stretch the other part of the molecule until the breaking of the C-heteroatom bond.

When the curve presents a maximum, it can be concluded that the bond breaks at this point and the activation energy can then be estimated. The results obtained are represented by graphs of energy according to the C_α -heteroatom distance in Å (Figure 9, 10).

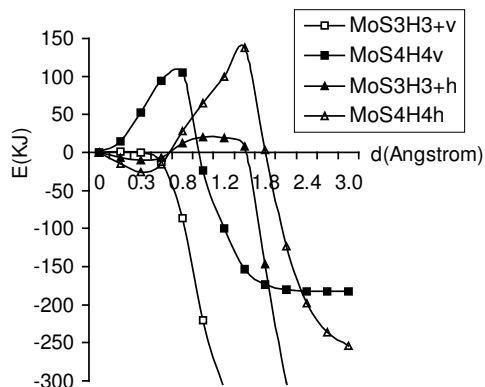


Figure 9. Desulfurization of dihydrothiiren.

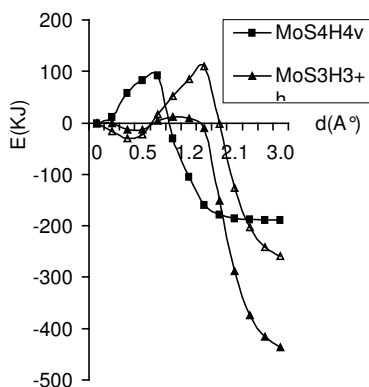


Figure 10. Desulfurization of methyl dihydrothiiren.

This process applied to thiiren and methylthiiren have not given Gaussian curves. The dihydrothiiren is desulfurised on the two kinds of sites but in the flat position, the desulfurization is too fast (Figure 9). As for the methyl dihydrothiiren, in the vertical position, the desulfurization has not been possible on MoS_3H_3^+ , in comparison with MoS_4H_4 site. However in a flat position, the breaking of the C-S bond is easier on the three vacancy sites than on the two vacancy sites (Figure 10, Table 4).

It appears that [17], a reorganization can occur inside the complex formed by the molecule and the site after the adsorption's step, and this minimizes the energy of the whole system. This probably explains the desulfurization of the molecule according to a horizontal geometry rather than a vertical geometry on the MoS_3H_3^+ site.

Table 4. Activation energy of molecules.

Molecules	Sites			
	MoS_3H_3^+		MoS_4H_4	
	Vertical	Vertical	Vertical	Vertical
Thiiren	-	-	-	-
Dihydrothiiren	1.43	30.26	105.04	162.65
Methylthiiren	-	-	-	-
Methyldihydrothiiren	-	25.27	93.40	140.58

CONCLUSION

In this study, we note that the desulfurization of thiiren and its monomethylened derivative must pass through a hydrogenated species. The hypothesis according to which a reorganization can occur inside the complex formed by the substrate adsorbed and the site before the heteroatom elimination process has been confirmed. The presence of a methyl group on the ring of the thiiren molecule has strongly modified the electronic structure of this molecule, and thus influences the contours plots of the molecular orbitals of thiiren and the methylthiiren.

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