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A Quantum–Chemical Study of Site Modeling for the Adsorption and Desulfurization of Thiophene

J. JOFFRE, P. GENESTE, AND D. A. LERNER

Laboratoire de Chimie Organique Physique Appliquée (UA 418), Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34075 Montpellier Cedex, France

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The active site of MoS_2 is modeled to obtain information on the initial steps of thiophene hydrodesulfurization. The model consists of a $MoS_3H_3^+$ cluster with three anionic vacancies. Quantum-chemical extended Hückel theory studies were carried out on the adsorption and desulfurization steps for different geometries of the complex between the site and thiophene. The calculations show that the vertical adsorption of the S atom of thiophene on the Mo atom of the model catalyst is favored over any horizontal adsorption. In every case adsorption weakens the C–S thiophene bonds. Desulfurization by straight rupture of these bonds to form a C_4H_4 radical leads to a moderate activation barrier. This theoretical approach to the problem, initially based on available data, leads to conclusions which are in good agreement with experimental results.

INTRODUCTION

Understanding the catalytic hydrodesulfurization (HDS) of thiophene and derivatives is an ongoing challenge for experimental and theoretical chemists. These compounds are considered to be among the best models from which to obtain information about the kinetics and mechanisms involved in the different steps of HDS. The state of the art in this field is reviewed in some recent articles (*1–3*).

In spite of an extensive body of results, a clear picture of the basic processes occurring, especially in the initial steps, has yet to emerge. The need for progress in this direction is dictated, aside from purely scientific motives, by ecological and economic reasons. As a result a good deal of work is being done in this area.

In our own laboratory, we have been interested in the kinetics of HDS in the determination of intermediates (*4–6*). However, these studies have their limits: for instance, a failure to detect a compound does not indicate that it is not an intermediate in the reaction path. As quantum chemistry presents the possibility of analyzing a particular step, theoretical study seems necessary to complement our research.

Molybdenum disulfide is generally thought to be the active component of HDS catalysts and is itself a well-studied catalyst (*7, 8*). In a previous paper (*9*) we defined several sites generated from the MoS_2 structure and having one, two, or three anionic vacancies. The results for adsorption on sites with one and two vacancies point clearly to vertical adsorption being the preferred geometry for thiophene. In the case of the site with three vacancies, interaction energies are stronger, but the energetic gaps between horizontal and vertical adsorptions are much lower. Furthermore Tanaka and Okuhara (*8*) provided experimental evidence showing that isomerization occurs on sites with two degrees of coordinative unsaturation while the sites with three vacancies promote hydrogenation. Hence it is necessary to look in a more detailed way at the interaction of thiophene with three coordinate sites, considering configurations that do not have any symmetry elements (an important factor as pointed out by one referee).

METHODS

To design our model, which can be con-

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sidered as lying among the single proton model (*10*), the sulfurized chain oxide molybdenum structure (*11*), and the Co–Mo–S cluster (*12*), we started with the well-known layer structure of MoS_2 (*13*). In this compound the outer sulfur layer forms a basal plane and the crystal can be easily cleaved between the adjacent sulfur layers. The unit cell of a layer is composed of a trigonal prismatic unit with a central Mo^{4+} ion and S^{2-} ions on the six summits (Fig. 1a).

There are two ways to remove three sulfur atoms in order to form a site with three degrees of coordinative unsaturation. If they are taken away from the same basal plane, a C_{3v} site (Fig. 1b), which we designate as site 1, is obtained. If sulfurs are removed from two different basal planes of a unit cell, an asymmetric site (Fig. 1c) designated site 2, is formed. These sites could be more easily visualized on a crystal corner. To these $(MoS_3)^{2-}$ tetrahedra three protons are added in order to obtain a moderately charged cluster $(MoS_3H_3)^+$ in which molybdenum is formally a Mo^{4+} ion.

To study the adsorption and desulfurization of the thiophene molecule, we performed quantum chemistry calculations using the extended Hückel theory (EHT) (*14*). This method is widely used in chemisorption and reactivity studies (*15*). The ICON version 8.0 program was employed with the usual empirical parameters (*16*) and a standard geometry for thiophene (*17*). The site geometry was drawn from interatomic distances in the MoS_2 crystal (*13*) and H_2S.

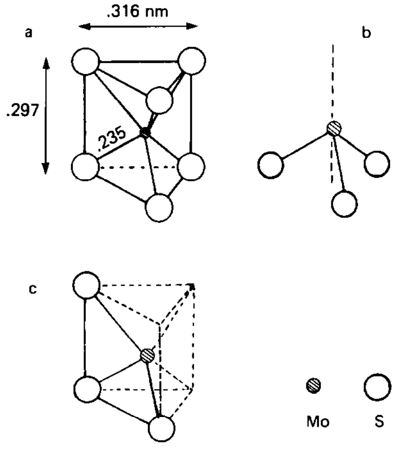

FIG. 1. (a) Unit cell of MoS_2 layer structure. (b) Model site 1 with its C_{3v} axis shown as a dashed line. (c) Model site 2.

RESULTS

The energy values *E*, expressed as the interaction energy between the thiophene molecule and the site, are defined as the difference between the computed energy for the complex (site + thiophene) and the sum of the energies of isolated thiophene and the site.

A. Adsorption Process

Defining the horizontal plane of the catalyst as the plane of the three sulfurs, several orientations of the entering thiophene molecule can be observed.

If the thiophene molecule is approached along a vertical axis going through the Mo atom (Fig. 2, curves 1*v* and 2*v*), for both sites, the interaction energies are high and similar in shape. It should be noted that the absolute value of the minimum on the energy curves is not relevant to our analysis because the corresponding distance between Mo and S* (S* represents the S atom of thiophene) is probably too short with respect to the experimental one. This artifact is expected when using EHT because not all repulsions are accounted for.

For a flat adsorption (thiophene in a horizontal plane), two different behaviors are observed depending on the symmetry of the site. For site 1, adsorptions are much stronger and the energy curves are steeper than for the asymmetric site 2. This is true whether one considers binding through the S* atom or through the C_α carbons (Fig. 2). In the latter case the destabilization due to the asymmetry of the site is greater (a shift from curve 1*hc* to curve 2*hc*).

The interaction energies between one double bond of thiophene and Mo (Fig. 3) are weaker than the previously computed

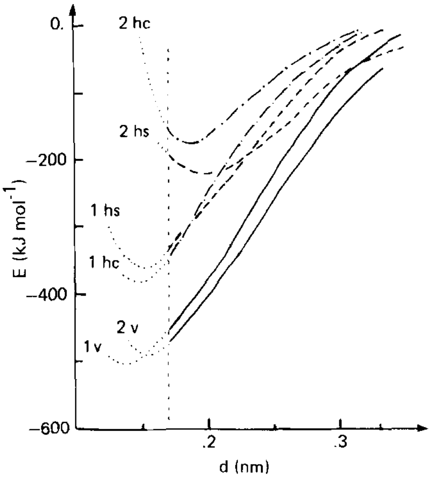

FIG. 2. Vertical and horizontal adsorption of thiophene on $MoS_3H_3^+$ sites: interaction energy for different geometries of the interacting molecules. Distances are taken along the vertical *z* axis, with Mo at the origin. Curves 1*v* and 2*v*: vertical adsorptions on respectively site 1 and site 2; S* vertically above Mo, with the Mo–S* distance as abscissa. Curves 1*hS* and 2*hS*: horizontal adsorptions; S* vertically above Mo, with the Mo–S* distance as abscissa. Curves 1*hc* and 2*hc*: horizontal adsorptions, Mo vertically above the middle point (m) of the C_α–C_α fragment, with the Mo–m distance as abscissa.

values, except for the vertical (side-on) adsorption on site 1 (curve 1*vp*). Even in this case the interaction energy is much smaller than vertical adsorption through S*.

A number of different spatial configurations for the model site and its interaction with thiophene were computed, namely S–H bonds directed toward the substrate, rotations of thiophene around the O_z axis or slight modifications in Mo–S bond length S–Mo–S angle (109.5° instead of 84.3°) and tilting thiophene in a vertical plane. All these modifications induced only minor changes in the interaction energies.

Comparison of the curves in Figs. 2 and 3 leads to the conclusion that vertical adsorption is the favored process. This conclusion is reinforced when considering the asymmetric site.

In order to know which type of binding is involved in the adsorption, the overlap population between Mo and S* can be considered. One sees in Table 1 that σ and π binding (with respect to the Mo–S* bond) occur together and that both bonds are stronger in vertical adsorption than in the horizontal case. The loss of symmetry does not affect the σ binding but slightly lowers the π binding.

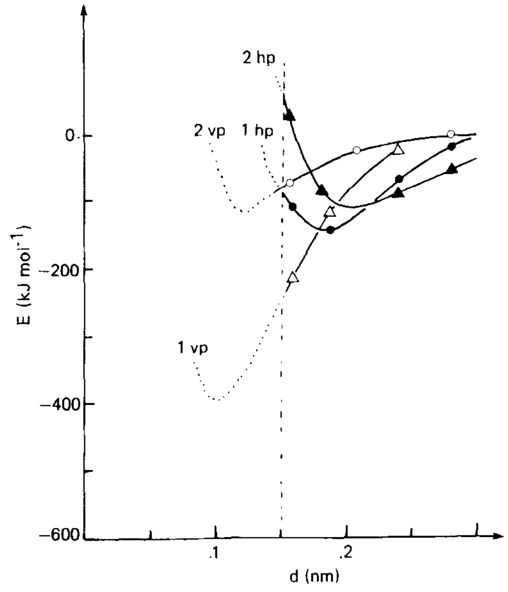

FIG. 3. Two-points π adsorption on $MoS_3H_3^+$, with the middle point (mp) of a C_α–C_β bond vertically above Mo, and with the Mo–mp distance as abscissa. Curves 1*hp* and 2*hp*: horizontal adsorptions on site 1 and site 2. Curves 1*vp* and 2*vp*: vertical adsorptions on site 1 and site 2.

B. Desulfurization

To study the desulfurization process, a

Table 1

Overlap Population of the Mo–S* Bonds

Mo–S* distance:	0.17 nm		0.19 nm		0.22 nm	
Adsorption type[a]	a	b	a	b	a	b
σ bonding (site 1)	0.722	0.505	0.719	0.528	0.656	0.484
σ bonding (site 2)	0.711	0.505	0.710	0.520	0.650	0.489
π bonding (site 1)	0.539	0.426	0.389	0.291	0.209	0.147
π bonding (site 2)	0.495	0.392	0.346	0.255	0.179	0.103
Total (site 1)	1.261	0.931	1.108	0.818	0.855	0.641
Total (site 2)	1.206	0.898	1.056	0.744	0.828	0.592
E (site 1)[b]	−450	−333	−406	−285	−317	−218
E (site 2)	−436	−194	−411	−216	−343	−207

[a] a = Vertical adsorption. b = Horizontal adsorption on S*.

[b] *E* = Interaction energy in kJ mol^{-1}.

suitable configuration attained in one of the preceding adsorption steps is considered. The C_4H_4 fragment of thiophene is then separated from its S* atom, keeping the Mo–S* distance constant. In this hypothetical process the two C–S* bond scissions are synchronous and the fate of the C_4H_4 fragment, which could evolve into a biradical if any further interactions with the catalyst were avoided, will not be examined.

The energy profile obtained when the C–S* distance is increased can be divided into two steps (Fig. 4). First there is a slight but meaningful rise of $|E|$ (the energy of the complex becomes more negative) compared to the initial value. This means that adsorption weakens the C–S* bonds and that this step corresponds to an optimization of the C–S* distance in the adsorption complex. Then as the C–S* distance is increased further, the absolute value of the interaction energy falls until a minimum is reached. This minimum can be interpreted as an activation energy since after this state the separation of the Mo and S* atoms lowers the overall energy.

The activation energy greatly depends on the initial configuration. As there are no experimental data on the actual Mo–S* distance, we scanned, in the 0.19-nm region, the minimum Mo–S distance measured in Mo complexes (*18*).

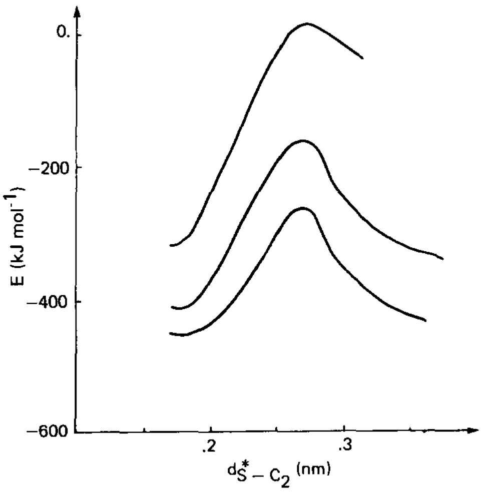

FIG. 4. Vertical desulfurization of thiophene starting from a vertically adsorbed configuration and for different Mo–S* distances. Curve 1: Mo–S* = 0.17 nm. Curve 2: Mo–S* = 0.19 nm. Curve 3: Mo–S* = 0.22 nm.

For illustration, three vertical adsorption distances were selected, viz., 0.17, 0.19, and 0.22 nm. As expected, the activation energy decreases as the initial adsorption distance increases.

In the vertical adsorption–desulfurization process, the energy profiles are almost identical but the energy levels are less stabilized.

DISCUSSION

The aim of our model studies is to obtain an understanding of the initial step which occurs during HDS in a low pressure of hydrogen. In fact most laboratory experimental studies have been carried out under these conditions until recent times. Under these conditions, it is usually accepted that thiophene leads to the formation of butadiene. To show where and how our model stands, we can refer to the paper of Lipsch and Schuit (*21*). In the first step of this model, a thiophene molecule adsorbs end-on (one point mechanism) on a Mo^{4+} ion which is part of the active site. The results of our calculations agree with this view.

The difference between the descriptive mechanism of Lipsch and Schuit (*21*) and our model is related to the choice of the following step. They consider that adsorbed hydrogen addition on C_α carbons is necessary for one C–S bond rupture. In this study we chose to examine whether a straight desulfurization, without any participation of hydrogen, is possible. There is recent experimental evidence for such a process on an industrial catalyst (*19*) and on the clean and partially sulfided Mo(100) crystal face (*20*).

The last step, namely, reduction by hydrogen of the sulfurized catalytic site and formation of the active site, is supposed to be the same in both mechanisms. The study of the hydrogenation steps is part of our project.

The adsorption step is the subject of an unresolved controversy related to the actual orientation of the organic adsorbate with respect to the site. Zdražil and Seláček (*10*) considered three different geometries for proton and thiophene interactions, using CNDO/2 and HMO calculations. They concluded that one-point adsorption occurred at the S atom. Vertical adsorption did occur, but flat adsorption is preferred with respect to energy. For Duben (*22*), who also used an HMO approach but chose a Mo^{3+} site, the vertical geometry appeared to be favored. This shows that the nature of the model site is an effective factor. Otherwise the handling of large clusters (*11, 12*) was very difficult and did not lead to precise conclusions.

To summarize our studies on adsorption we can say that our $MoS_3H_3^+$ model site leads to the conclusion that the vertical adsorption on sulfur is preferred. Introducing an asymmetry in the site reinforces this statement.

Let us now examine how this model stands vis-à-vis experimental work. There is no direct clue for the one-point, two-point, or four-point chemisorption of thiophene and derivatives. Kwart *et al.* (*23*) interpreted the small steric hindrance effect in the HDS behavior of 4,6-dimethyldibenzothiophene as evidence against the vertical adsorption, but this speculates as to the accessibility of the HDS site. The experimental work which is the closest to our "experimental" calculation conditions (unsupported and unpromoted MoS_2 catalyst, low hydrogen pressure) is that of Blake *et al.* (*7*). They found by ^1H NMR spectroscopy that thiophene is chemisorbed in a vertical position as H exchange occurs only at the 1- and 4-positions.

For the desulfurization step, we considered only a process in which both C–S bonds are broken simultaneously and we obtained almost identical behavior for the energy profiles, irrespective of the initial adsorption geometry. This is valid for the two prominent features of the profile, the energy dip at the onset and the activation energy. Thus for this step, our model cannot favor one of the processes.

The energetic barriers estimated from our calculations (120–400 KJ mol^{-1}) are higher than the experimental apparent activations energies (51 KJ mol^{-1}) (*7*). However, the computed values are still not high enough to forbid this simple desulfurization step at high temperature.

If one wishes to push the analysis further and propose a scheme for the reaction of the C_4H_4 fragment, it appears that the flat adsorption geometry should lead readily to adsorbed C_4H_4 species. Such species, which have previously been considered (*7*), could then react with hydrogen or lose hydrogen giving butadiene or diacetylene, respectively (*24*). For the vertical adsorption case, one could expect a cyclization process leading to a cyclobutadiene derivative as is possibly formed in HDS of tetraphenylthiophene (*25*). These last considerations are mainly hypothetical; however, the development of our model in this direction as well as studies of its application to a number of sulfurized, nitrogenated, and oxygenated molecules is in progress.

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