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THEORETICAL EVALUATION OF THE DEACTIVATION MECHANISM OF SUBSTITUTED DIBENZOTHIOPHENES

EVALUACIÓN TEÓRICA DEL MECANISMO DE DESACTIVACIÓN DE DIBENZOTIOFENOS SUSTITUIDOS

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Abstract

The petrol and diesel combustion in motors produces sulfur and nitrogen oxides, they are the precursors of acid rain. Unfortunately, the Mexican fuel shows high-sulfur content; this concentration should be reduced to 50 ppmw or lower in order to achieve the international regulations. The oxidative desulfurization (OD) is an alternative to obtain it. In this work, we propose a theoretical reaction mechanism for the OD; this pathway is carried out through a combination of the molibdate anion, the hydrogen peroxide and several dibenzothiophenes by Density Functional Theory (DFT) using the B3LYP functional and the DGDZVP double zeta basis. The results show that the energy of the determinant step of the reaction is lower than the experimental amount obtained without catalyst. Finally, the environment provided by water molecules is important for decreasing the reaction mechanism energy.

Keywords: oxidative desulfurization, DFT, B3LYP, reaction mechanism, dibenzothiophene.

Resumen

La combustión de gasolina y diesel en automotores produce, entre otros, óxidos de azufre y nitrógeno, los cuales forman parte de los precursores de la lluvia ácida. Desafortunadamente, los combustibles mexicanos presentan un alto contenido de azufre, el cual debe de ser reducido a menos de 50 ppm para cumplir con las normas internacionales. Una forma de llegar a esta concentración es por medio de la desulfuración oxidativa (DO). Este trabajo presenta una propuesta teórica del mecanismo de reacción para la DO utilizando como catalizador una combinación de molibdato y peróxido de hidrógeno y diferentes derivados de dibenzotiofeno, utilizando la Teoría de los Funcionales de la Densidad (TFD) con el funcional B3LYP y la base doble zeta DGDZVP. La etapa determinante de la reacción presenta menor energía que el valor experimental sin el uso de catalizador. Finalmente, la presencia de moléculas de agua es importante para disminuir la energía del mecanismo de reacción.

Palabras clave: desulfuración oxidativa, TDF, B3LYP, mecanismo de reacción, dibenzotiofeno.

1 Introduction

Recently, the fuel production free of contaminants is a very important topic. For example, diesel is a complex mixture of lineal, branched and cyclic alkanes and several organosulfur compounds are obtained from the oil separation; after combustion, sulfur oxides are emitted to the environment, poisoning also the catalytic converter in the automobile (Zhu *et al.*, 2008). In consequence, several countries have introduced sever regulations about the sulfur content limits in fuels (Campos-Martínez *et al.*, 2004). However, to reach these concentrations it is necessary to improve several processes. Traditionally, the hydrodesulphurization process allows to remove thiols, sulfurs and disulfur compounds from the fuel mixture, however, the organosulfur compounds with

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sterical hindrance like the 4,6-dimethyldibenzothiophene (4,6DMDBT) requires hard conditions in order to be removed (Babich and Moulija, 2003), including high hydrogen concentrations. On the other hand, those compounds shorten the catalyst half life.

An alternative to obtain low sulfur concentrations in diesel is the oxidative desulfurization (OD), where the organosulfur compounds are oxidized to sulfone, then they are removed by extraction, adsorption, distillation or decomposition (Huela *et al*., 2001; Anisimov *et al*., 2003; Palomeque *et al*., 2002; Yazu *et al*., 2001; Djangkung *et al*., 2003; Shiraishi *et al*., 2003). This process is carried out in liquid phase under mild conditions.

Several oxidant agents were used in the OD process (Campos-Martín *et al*., 2004); however, the hydrogen peroxide (H_2O_2) is the most used due to its low cost, no-contaminant characteristics and oxidant properties. Unfortunately, without a catalyst, the oxidation velocity is very slow, but several catalysts have proven to increase its reaction velocity (Shiraishi *et al*., 2003; Ramírez-Verduzco *et al*., 2004). Other catalysts have been tested as Cu-supported in TiO_2 where the activity of this catalyst was attributed to its capacity to decompose the oxidant and the interaction Cu-support (Cedeño-Caero *et al*., 2005); Ag-supported in TiO_2 and Au-supported in TiO_2, for silver catalyst, the particles crystallized better and this catalyst is more active when the temperature of thermal treatment is increased whereas the gold catalyst improves the sulfone production at low temperature (Zanella *et al*., 2007); in the catalyst V_2O_5-supported in Al_2O_3 the temperature is a very important factor in the thermal decomposition of H_2O_2 (Navarro-Amador *et al*., 2006; Gómez-Bernal and Cedeño-Caero, 2006; Becerra-Hernandez *et al*., 2006). On the other hand, polyoxymetalic catalyst as tungstenate (Torres-Garcia *et al*., 2011) and molybdate (Garcia-Gutierrez *et al*., 2006, 2008) have shown excellent results in the oxidation of organosulfur compounds.

Catalysts of tungsten (Torres-García *et al*., 2011; Rodríguez-Gattorno *et al*., 2009; and Galano *et al*., 2008) and molybdenum (Vergara-Méndez *et al*., 2011) mixed with H_2O_2 have been studied by computational techniques. Torres-García *et al*. (2011) concluded that the reaction mechanism with tungstenate supported in zirconia is carried out by the addition reaction followed by the elimination reaction, where the last one is more energetic than the first one; whereas Vergara-Méndez *et al*. (2011) concluded that the water molecules take part in the complex formation of the catalyst and also play an important role in the energy minimization. On the other hand, the reaction mechanism in heterogeneous phase was studied by Density Functional Theory (DFT), for the following examples: the propene oxidation to acroline (Pudar *et al*., 2007) and the aminoxidation of propene (Jang *et al*., 2002).

This work proposes a theoretical reaction mechanism for the oxidation of the 4,6-dimethyldibenzothiophene compound present in the diesel fuel using a peroxomolybdate catalyst presented by Vergara-Mendez *et al*. (2011). In this mechanism, the monomer of molybdate was used as a catalyst model because this specie was found in alkaline aqueous solution as Srinivasan (2004) informed.

2 Methodology

All calculations were carried out by Gaussian 03W package (Frish *et al*., 2004). Geometry optimization and vibrational mode calculations of all molecules were performed by B3LYP functional (Becke, 1988, Lee *et al*., 1998) and DGDZVP double zeta base set.

The vibrational modes were calculated to confirm the behavior of stationary points (all positive frequencies for minimums of energy and only one imaginary frequency for transition state with internal coordinate in direction of the reaction trajectory). The vibrational frequencies were scaled by 0.9614, the standard factor proposed by Scott and Radom (1996) to consider the zero-point energy in B3LYP functional.

The solvent effect was simulated as explicit manner placing two water molecules surrounding the catalyst as Vergara-Méndez *et al*. (2011) proposed.

Additionally, the NBO analysis was carried out as Carpenter and Weinhold (1988), Foster and Weinhold (1980), Reed and Weinhold (1983), Reed *et al*. (1985) and Reed *et al*. (1988) recommend it for determining which hybrid orbitals and their energies take part in the electronic interactions of the oxidation reaction path. The NBO analysis represents correctly the bonding orbitals and their occupation, the core orbitals, the lone pair, the antibonding orbitals and the Rygberg vacancies.

3 Results and discussion

3.1 Oxidation mechanism

Torres-García *et al*. (2011) proposed that the sulfur oxidation into the DBT and its derivatives is

reached in two steps: an addition followed by an elimination. Considering that the peroxotungstenate was used as a catalyst, the determinant step is the catalyst elimination. Whereas, Vergara-Méndez *et al*. (2011) studied the oxomolybdate catalyst formation, suggesting that the oxomoybdate intermediate could play a determinant role in the oxidation of the sulfur atom in aqueous solution considering water molecules in the environment.

Figure 1 shows the energetic profile of the oxidation mechanism for 4,6DMDBT and the oxomolybdate catalyst. This reaction mechanism shows three steps: the first one is the peroxomolybdate formation, whereas the second and third ones are the consecutive sulfur oxidation of 4,6DMDBT.

In the first step to form the oxomolybdate specie (Table 1 and Fig. 2) the transition state (TS01) is observed at 4.07 kcal/mol over the reagents, this energy is lower than the energy reported by Vergara-Mendez *et al*. (2011); for the oxomolybdate and dioxomolydate catalyst formation, that energy was 29.01 kcal/mol without explicit water molecules and around 22.00 kcal/mol with two water molecules. These data drive us to conclude that the peroxomolybdate specie is formed *in situ*, and this one is the active specie in the oxidation of the sulfur atom.

The sulfur oxidation is carried out in two consecutive steps, each one for an oxygen addition from the catalyst to the organosulfur compound (Fig. 3). The transition states (TS02 and TS03) show energies of 27.34 and 23.83 kcal/mol respectively, *i.e.*; the second oxidation is easier than the first one. These energy amounts are comparable with the elimination energy calculated by Torres-Garcia *et al*. (2011), they calculated the transition state using ZrO_2 as support and the transition energies obtained are 23.64 and 13.37 kcal/mol for the first and second elimination reaction respectively. Clearly, it is seen that the first elimination is again more complicated than the second one.

Geometrically, the interaction between the catalyst and the 4,6DMDBT in both oxidations is completely different. Table 2 shows some notable geometric data as distances, bond angles and dihedral angles of this interaction. Particularly, the direction of the peroxo group and the metallic center of the catalyst regarding to the rings forming the 4,6DMDBT; for the first oxidation, this direction is close to be parallel, whereas for the second oxidation, the direction is near to be perpendicular. This change is related to the sterical interaction observed in the sulfoxide group formation.

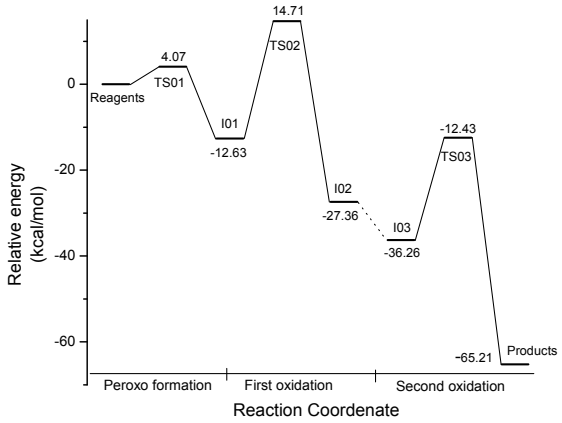

Fig. 1. Reaction path of the oxidative desulfurization.

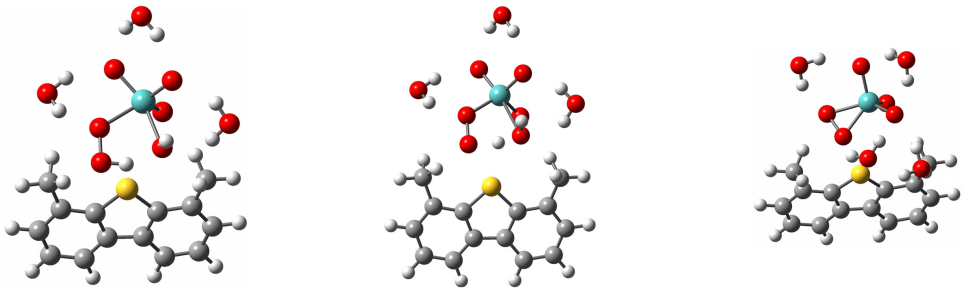

Fig. 2. Geometries of the peroxo species calculated by B3LYP/DGDZVP.

Table 1. Molecular energies and Zero Point Energy calculated by B3LYP/DGDZVP. Imaginary vibrational mode are shown for the transitions states.

Species	Energy (hartrees)	ZPE (hartrees)	ΔE (Kcal/mol)	Vibrational mode
Reagents	-5598.2384068	0.331175	0.00	—-
TS01	-5598.2289623	0.328111	4.07	119.0570i
I01	-5598.2582651	0.330889	-12.63	—-
TS02	-5598.2140185	0.330206	14.71	523.8324i
I02	-5598.2835349	0.332751	-27.36	—-
I03	-5673.4341170	0.334238	-36.26	—-
TS03	-5673.3956335	0.333707	-12.43	533.8906i
Products	-5673.4830243	0.337120	-65.21	—-

Table 2. Geometrical values of the first and second oxidation of interaction between the catalyst and the 4,6DBT ion.

Geometrical parameter	First oxidation	Second oxidation
	Distance (Å)	
S-Mo	4.086 (3.757)	4.047 (4.467)
Mo-O_{per1}	2.030 (2.414)	2.013 (2.741)
Mo-O_{per2}	2.060 (1.902)	2.108 (1.896)
O_{per1}-O_{per2}	1.487 (1.900)	1.486 (1.746)
S-O_{per1}	3.740 (1.913)	3.222 (1.943)
S-O_{per2}	3.253 (3.769)	2.824 (3.624)
	Bond angle (°)	
S-Mo-O_{per1}	51.90 (26.14)	51.91 (14.65)
S-Mo-O_{per2}	65.61 (75.69)	41.16 (51.92)
	Dihedral angle (°)	
Mo-O_{per1}- O_{per1}-S	-96.6 (-63.5)	-110.8 (-122.5)
C_α-S-Mo-O_{per1}	54.9 (62.3)	-33.4 (21.6)
C_α-S-Mo-O_{per1}	7.10 (47.9)	24.2 (-4.5)
C_β-C_α-S-Mo	156.6 (159.1)	95.2 (136.8)

In the transition state, the distance between the sulfur and molybdenum atoms in the first oxidation is longer than in the second oxidation, allowing the oxygen addition (O_{per1}) from the peroxo group. On the other hand, the catalyst elimination occurs nearby the 4,6DMDBT rings plane. The first oxidation represents the elimination of the catalyst at the angle of 159.1°, whereas for the second oxidation this angle is 136.8°. Pettersson *et al.* (2003) proposed that the formation of peroxo- and diperoxo moieties in hepta and octamolybdate compounds can be observed on the terminal molybdenum atoms. Our results show that the monomer molybdate catalyst containing the peroxide groups reflects a positive effect on the success of the oxidation reaction.

García-Gutiérrez *et al.* (2008) suggested that the oxidation mechanism is driven by the nucleophilic attack of the sulfur atom of 4,6DMDBT to the oxygen of the peroxo group of the catalyst; such attack is activated by the high coordination number and the high oxidation state of the molybdenum atom. The molybdenum atom charge changed from 1.62 to 1.15 charge units when the catalyst acts as oxo form (reagent) or as peroxo form (Intermediate 1, I01). It is important to note that the oxidation state and electrical charge of the molybdenum atom are practically constant along the reaction trajectory and that the oxygen of oxo and peroxo groups shows similar behavior (Table 3).

Table 3. Atomic charge of some atoms in the catalyst and the dibenzothiophene molecules.

Atom	Reagents	TS01	I01	TS02	I02	I03	TS03	Products
Mo	1.62	1.15	1.18	1.19	1.14	1.20	1.19	1.10
O_{per1}	-0.52	-0.49	-0.49	-0.665	-0.82	-0.47	-0.59	-0.74
O_{per2}	-0.49	-0.54	-0.49	-0.61	-0.70	-0.52	-0.54	-0.53
O	-0.98	-0.93	-0.90	-0.89	-0.92	-0.90	-0.90	-0.91
H	0.41	0.47	0.43	0.46	0.46	0.45	0.45	0.42
S	0.41	0.41	0.41	0.56	0.88	0.78	0.94	1.13

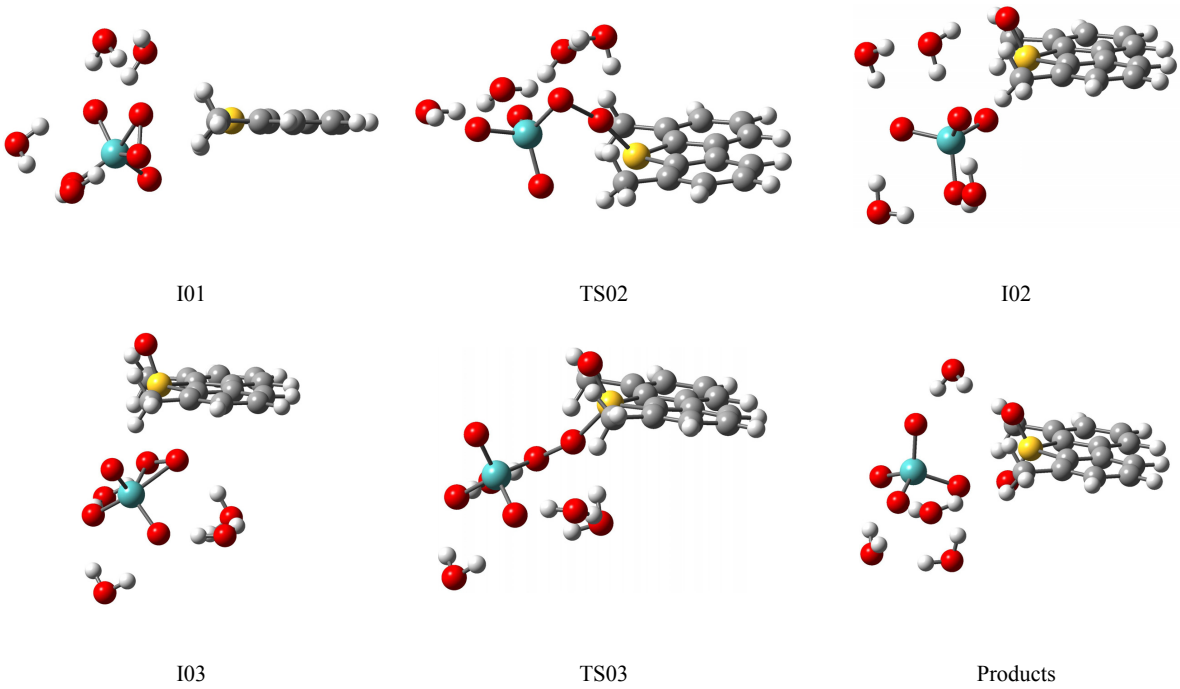

Fig. 3. Geometries of the species formed in the two stage of the oxidative desulfurization.

The electrical charge of the peroxo group oxygens (around of -0.50 charge units) is smaller than that observed in the water oxygen (around -0.90 charge units). These results confirm the electrophilic characteristic of the peroxo group oxygens. On the other hand, the positive charge of the sulfur atom was increasing according to its oxidation state going from 0.41 to 0.78-0.88 units up to 1.13. These results indicate that the sulfur atom is not the nucleophilic center, and the reaction cannot be reached.

The NBO analysis was performed on the intermediates (I01 and I03) and on the transition states (TS02 and TS03). This analysis shows that the lone pairs of the sulfur atoms (LP1S or LP2S) are the nucleophilic sites, whereas the sigma bond and sigma antibond orbitals of the peroxo oxygens in the catalyst are the electrophylic sites.

Figure 4 shows the energy localization of the main orbital that interacts in the first oxidation, the lone pairs of the sulfur atom represented at -0.44 and -0.05 hartrees; it is clear that there are different interactions and energies between the LP1S and LP2S. The LP2S is the first nucleophilic center, whereas the sigma antibond orbital of the peroxo group ($\sigma_{Oper1-Oper2}$) is localized at 0.32 hartrees.

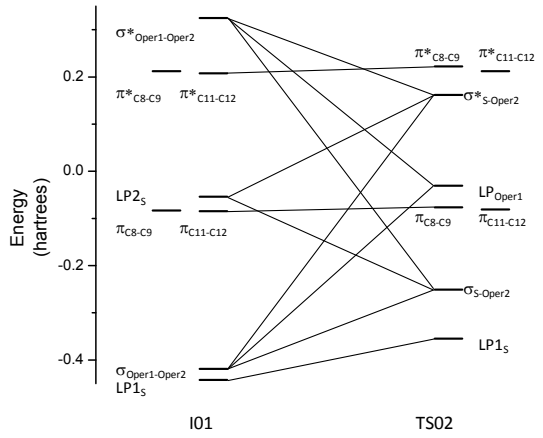

Fig. 4. Hybrid orbitals transformation from Intermediate 1 to Transition State 2 (first oxidation).

Table 4. NBO occupation of some hybrid orbitals and charge of molecular species in the reaction path.

Orbital	I01	TS02	I03	TS03
		Electronic occupation		
$LP1_S$	1.9646	1.9054	1.9506	1.6241
$\sigma_{Oper1Oper2}$	1.9788	1.8606[a]	1.9783	1.9071
π_{C8C9}	1.6256	1.6223	1.6305	1.6263
π_{C11C12}	1.6020	1.6026	1.6191	1.6351
$LP2_S$	1.6607	1.3617[a]	—-	—-
$\pi*_{C8C9}$	0.4642	0.4592	0.3466	0.4053
$\pi*_{C11C12}$	0.4232	0.3988	0.3872	0.4029
$\sigma_{Oper1Oper2}$	0.0102	0.4556[a]	0.0095	0.3878
Species		Electronic charge		
4,6DBT[b]	-0.0313	-0.4485	-0.0646	0.1829
MoO_5^c	-1.8521	-1.4532	-1.8263	-2.0931
H_2O^d	-0.0291	-0.0246	-0.0273	-0.0224

[a]Orbitals that shown transformations, see Fig. 4. [b]46DBT is transformed to oxidative species. [c]MoO_5 is transformed to some different species. [d]Average charge of 4 water molecules.

The main interaction for the initial oxidation is between PL2S and the $\sigma_{Oper1-Oper2}$. This interaction is confirmed in the transition state TS02 because these orbitals are transformed to $\sigma_{S-Oper2}$, $\sigma_{S-Oper2}$ and LP_{Oper1}. Clearly, it is seen that the peroxo group in the catalyst is not completely broken in the TS02; its distance is 1.9 Å (Table 2). On the other hand, the geometry of this transition state could be named an anti-Hammond belated transition state as Thorton (1967) proposed.

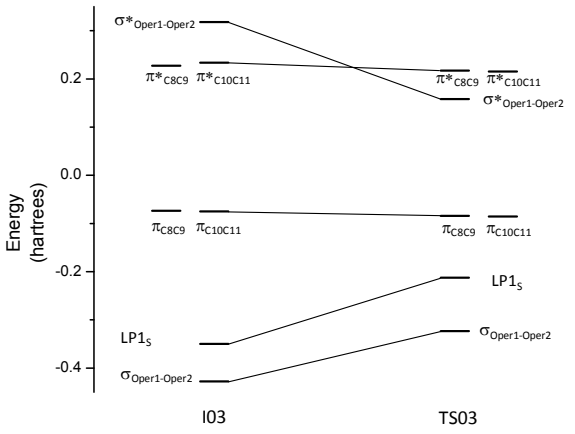

Fig. 5. Hybrid orbitals transformation from Intermediate 3 to Transition State 3 (second oxidation).

Table 4 shows the electronic occupations of the orbitals directly involved in the oxidation reaction. In the TS02, $\sigma_{S-Oper2}$ occupation is 1.8606 electrons, occupation minor than a single bond, whereas the $\sigma_{S-Oper2}$ occupation is 0.4556 electrons, these results permit to establish the electronic transference to be carried out in this transition state. On the other hand, the peroxo bond broken originates a new lone pair on the oxygen 1 with an electronic occupation of 1.3617 electrons. In TS02, the global electronic charge transference is around 0.4 electrons from the catalyst to the 4,6DMDBT, this result is observed in the charge changes from I01 to TS02.

Figure 5 shows the energy localization of the main orbital that interacts in the second oxidation reaction; in this case, there is one LP1S from the sulfoxide molecule of 4,6DMDBT to be considered. This orbital is localized at -0.35 hartrees and it behaves as a nucleophilic center, on the other hand, the $\sigma_{Oper1-Oper2}$ is again the electrophilic center. The interaction between these orbitals in the transition state decreased the energy gap by 0.4813 hartrees. It is important to note that the symmetry of the hybrid orbitals did not change from I03 to TS03, this transition state is classified as an early Hammond transition state as Hammond (1955) proposed.

In this case, the LP1S transfers electronic density to the $\sigma*_{Oper1-Oper2}$ in the TS03 and the orbital occupation is 1.6241 and 0.3878 respectively. The global charge changes from the sulfoxide to the catalyst molecules respectively, *i.e.*, the sulfoxide group is a positive molecule and the catalyst is a negative molecule (Table 4).

Conclusions

The catalyst transformation from oxo form to peroxo form was calculated by B3LYP functional theory; and the DGVZVP double zeta basis requiring low transition energy was only 4 kcal/mol. This result suggests that the peroxomolybdate molecule is the active specie in the oxidation reaction, and it is expected to appear *in situ*.

The oxidation reaction is carried out for two consecutive additions of oxygens from the catalyst to the sulfur atom of 4,6DMDBT; the first one is the determinant step of reaction, because this transition energy is higher than the transition energy of the second oxidation. Geometrically, the reaction mechanism of the first oxidation is carried out following a parallel direction between the catalyst and the organosulfur compound, whereas in the second oxidation, the direction is perpendicular.

Finally, the geometry of the transition states was classified as belated and early, respectively, for the two oxidation reactions on the sulfur atom. The lone pairs of the sulfur atom in the 4,6DMDBT are the nucleophillic centers, whereas the $\sigma*_{Oper1-Oper2}$ orbital of the catalyst is the electrophilic center in these reactions.

Nomenclature

B3LYP	Becke, Lee, Yang and Parr functional
H_2O_2	hydrogen peroxide
DBT	dibenzothiophene
DFT	density Functional Theory
4,6DMDBT	4,6-dimethyldibenzothiophene
NBO	natural Bond Orbital
I0n	n-th intermediate
LPnS	n-th lone Pair of sulfur atom in 4,6-dimethyldibenzothiophene
OD	oxidative desulfurization
O_{pern}	n-th oxygen of peroxo in the catalyst
TS0n	n-th transition State
Greek symbols	
σ	sigma Bond orbital
$\sigma*$	sigma Antibond Orbital

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