

Sulfide and Sulfoxide Oxidations by Mono- and Diperoxo Complexes of Molybdenum. A Density Functional Study

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The molecular mechanism for the oxidation of sulfides to sulfoxides and subsequent oxidation to sulfones by diperoxo, MoO(O₂)₂(OPH₃) (**I**), and monoperoxo, MoO₂(O₂)(OPH₃) (**II**), complexes of molybdenum was studied using density functional calculations at the b3lyp level and the transition state theory. Complexes **I** and **II** were both found to be active species. Sulfide oxidation by **I** or **II** shows similar activation free energy values of 18.5 and 20.9 kcal/mol, respectively, whereas sulfoxides are oxidized by **I** ($\Delta G^\ddagger = 20.6$ kcal/mol) rather than by **II** ($\Delta G^\ddagger = 30.3$ kcal/mol). Calculated kinetic and thermodynamic parameters account for the spontaneous overoxidation of sulfides to sulfones as has been experimentally observed. The charge decomposition analysis (CDA) of the calculated transition structures of sulfide and sulfoxide oxidations revealed that **I** and **II** are stronger electrophilic oxidants toward sulfides than they are toward sulfoxides.

1. Introduction

Oxidations of organic sulfides to sulfoxides and sulfones hold great interest from both laboratory and biological perspectives.^{1–5} Cass et al.⁶ recently examined the use of Mimoun-type⁷ complexes MoO(O₂)₂(L)(H₂O) (L = pyridine *N*-oxide or pyrazole) to oxidize a wide variety of substituted sulfides. This procedure offers three major advantages: (i) control over the degree of oxidation of products, i.e., the method allows high purity sulfoxide or sulfone be obtained by a versatile variation of conditions; (ii) excellent chemoselectivity of these complexes toward the sulfur group of substituted sulfides and sulfoxides containing other functional group susceptible to oxidation (as an example, allyl methyl sulfoxide is formed without an epoxidation side product); (iii) the method conforms to several of the guiding principles of the green chemistry proposed by Anastas and Warner,^{8,9} inasmuch as the oxo-diperoxo metal complexes can be stoichiometrically recovered in the presence of hydrogen peroxide. A detailed understanding of the reaction mechanism, however, lags behind these achievements.

The use of Mimoun complexes in oxygen-transfer reactions is well established,^{10,11} and their utilization in the alkene epoxidation process has attracted theoretical interest.^{12–27} The corresponding oxygen-transfer process has been shown to follow the Sharpless mechanism,²⁸ in which a direct attack of an olefin at a peroxo oxygen center takes place along a transition structure (TS) with a spiro structure.^{12,18} However, no theoretical study on the mechanism of sulfide and sulfoxide oxidations by per-

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oxymolybdenum complexes has been reported so far. Here, for the first time, we used the density functional theory (DFT) calculations and transition-state theory to gain a deeper insight into the reaction mechanism of these types of oxidations. Our purpose is to contribute to a better understanding of the mechanistic features of these processes by locating and characterizing all the stationary points, minima, and transition structures (TSs) involved along this type of chemical reaction.

2. Models of the Complexes

Coordinatively saturated molybdenum diperoxo complexes, seven-coordinated, are reported to be easily dehydrated and the resulting forms are believed to be the ultimate reactive species.⁷ The main reasons for which six-coordinated oxo-peroxo complexes are more reactive than the seven-coordinated ones have already been addressed by Filatov et al.,¹⁹ Rosch et al.,^{18,27} Frenking et al.,^{15,16} and us.²⁵ After transferring an oxygen atom to an organic substrate, the diperoxo species are transformed into a monoperoxo complex, which displays some ability to oxidize another substrate molecule. Monoperoxo Mo complexes are proven to be less reactive than their diperoxo counterparts, as far as ethylene epoxidation is concerned.^{12,16,18,27} However, the energy difference of about 2.5 kcal/mol between the corresponding transition states is small, and therefore, monoperoxo species are expected to play a meaningful role in the oxidation process. In light of this, the parent models MoO(O₂)₂(OPH₃) (**I**) and MoO₂(O₂)(OPH₃) (**II**) were selected as representative of diperoxo and monoperoxo complexes of molybdenum in their dehydrated forms, respectively. Dimethyl sulfide (DMS) and dimethyl sulfoxide (DMSO) were selected to represent the sulfide and sulfoxide molecules, respectively. As far as the oxygen transfer from molybdenum peroxo complexes to sulfide and sulfoxide compounds is concerned, Di Furia et al. reported that no coordination between the metal and the substrate takes place.^{29,30} Furthermore, it has been shown that the rate of oxidation of sulfides by peroxo complexes of vanadium is only slightly sensitive to the different steric bulk of the sulfides, suggesting that the sulfides do not coordinate to the metal center.³¹ On the basis of these experimental findings, we assumed that the reaction involves a direct attack of the substrate on a peroxo oxygen atom trans to the -OPH₃ ligand, via Sharpless' mechanism, as has been proved to be the case for olefin epoxidation.^{12,18}

3. Computational Methods

Density functional calculations were carried out at the b3lyp level,^{32,33} as implemented in the Gaussian98 program.³⁴ The standard 6-311+G(2fd,2p) basis set was employed to represent the H, C, O, P, and S atoms. To represent the Mo center, a valence basis set (8s6p7d2f) tailored with application of the

TABLE 1. Selected Thermodynamic and Kinetic Parameters (in kcal/mol) of Different Reaction Pathways

	ΔG°	ΔH^\ddagger	$-T\Delta S^\ddagger$	ΔG^\ddagger
(i) I + DMS	-33.6	7.6	10.9	18.5
(ii) II + DMSO	-50.3	17.6	12.7	30.3
(iii) II + DMS	-30.8	10.3	10.6	20.9
(iv) I + DMSO	-53.1	9.1	11.4	20.6
(v) I + C ₂ H ₄	-34.0	17.8	10.4	28.2

generator coordinate method (GCM)²⁶ was used in conjunction with the RECP (quasi-relativistic effective core potential) of Hay and Wadt.³⁵ All geometry optimizations of transition states were performed without any symmetry constraints, and all stationary points were characterized by calculating vibrational frequencies. Wavefunctions related to all stationary points were checked for stability under default perturbations controlled by the stable directive of the Gaussian program. Starting with the TS geometries, calculations of the intrinsic reaction coordinated (IRC) were made in order to find out the respective reactants and products.³⁶ The reported energies refer to 298.15 K and were corrected with respect to unscaled zero-point energies (ZPE). CS ChemDraw Std. 4.5 and Ortep3³⁷ programs were used to represent the calculated structures. The NBO method³⁸ was employed to calculate atomic partial charges. The charge decomposition analysis (CDA)³⁹ was applied to TSs in order to assess the electronic character of the corresponding oxygen-transfer reaction.¹³

4. Results and Discussion

An understanding of the oxygen-transfer mechanism relating to the sulfide and sulfoxide oxidations by molybdenum peroxo complexes requires the consideration of four reactive pathways, whose corresponding calculated energetic and kinetic parameters are shown in Table 1. Complex **I** reacts with DMS, via TS1, to produce the corresponding oxo-monoperoxo complex **II** and dimethyl sulfoxide (DMSO) (see entry i). Once **II** is obtained in the first stage, it might oxidize either the DMSO initially formed to yield the trioxo complex of molybdenum MoO₃(OPH₃) (**III**) and dimethyl sulfone (DMSO₂), through TS2 (channel (ii)), or it may oxidize a second DMS molecule affording DMSO and **III** (TS3, channel iii). Complex **I** can also oxidize DMSO, via TS4, to yield **II** and DMSO₂, channel iv.⁴⁰ For the sake of comparison,

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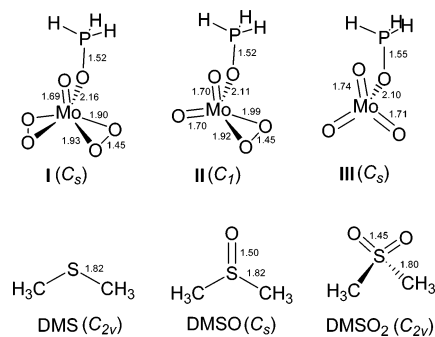


FIGURE 1. Calculated structures of reactants and products. Distances are given in angstroms.

activation parameters relating to the ethylene epoxidation by **I** were also calculated and are included in Table 1 (entry v). Calculated structures of reactants and products are shown in Figure 1, whereas optimized transition structures, as well as the corresponding NBO charges, are presented in Figure 2.

An analysis of the results of Table 1 shows that all channels are exergonic processes. DMSO oxidation by either **I** (iv) or **II** (ii) presents the largest values of ΔG° , -53.1 and -50.3 kcal/mol, respectively. A comparison of ΔG° values between the channels (i) and (iii), and between the channels (ii) and (iv) reveals that **I** is a slightly more oxidant agent than **II** from a thermodynamic standpoint. Using kinetic parameters, it can be

noted that the DMS oxidation by **I** displays the lowest activation energy (TS1, 18.5 kcal/mol), whereas DMSO oxidation by **II** shows the highest value of activation (TS2, 30.3 kcal/mol).

A comparison of the activation parameters between the channels (i) and (iii) reveals that **I** presents a slightly larger oxidizing ability toward DMS than **II**. Indeed, the corresponding activation barriers are similar (18.5 and 20.9 kcal/mol, respectively), indicating that both species **I** and **II** are active in the oxidation of sulfides to the respective sulfoxides. In contrast, monoperoxo complex **II** exhibits a much a higher barrier for sulfoxide oxidation (30.3 kcal/mol) than the diperoxo complex **I** ($\Delta G^\ddagger = 20.6$ kcal/mol). Thus, channel (iv) is by far the more important pathway affording sulfones. In other words, DMS oxidation is almost insensitive to the oxo-peroxo nature as far as the number of peroxo groups is concerned, whereas DMSO is remarkably dependent.

The values of entropic contribution, $-T\Delta S^\ddagger$, are in a narrow range 10.6–12.7 kcal/mol. A similar behavior is found in the enthalpic term except for channel (ii), in which a value of 17.6 kcal/mol accounts for a high value relating to the activation energy of TS2. The absolute values of ΔH^\ddagger and $-T\Delta S^\ddagger$ terms show that the entropic contribution is greater than the enthalpic one in channels (i), (iii), and (iv) by 3.3, 0.3, and 2.3 kcal/mol, respectively, while the opposite effect is found in channel (ii), at which ΔH^\ddagger is greater than $-T\Delta S$ by 4.9 kcal/mol.

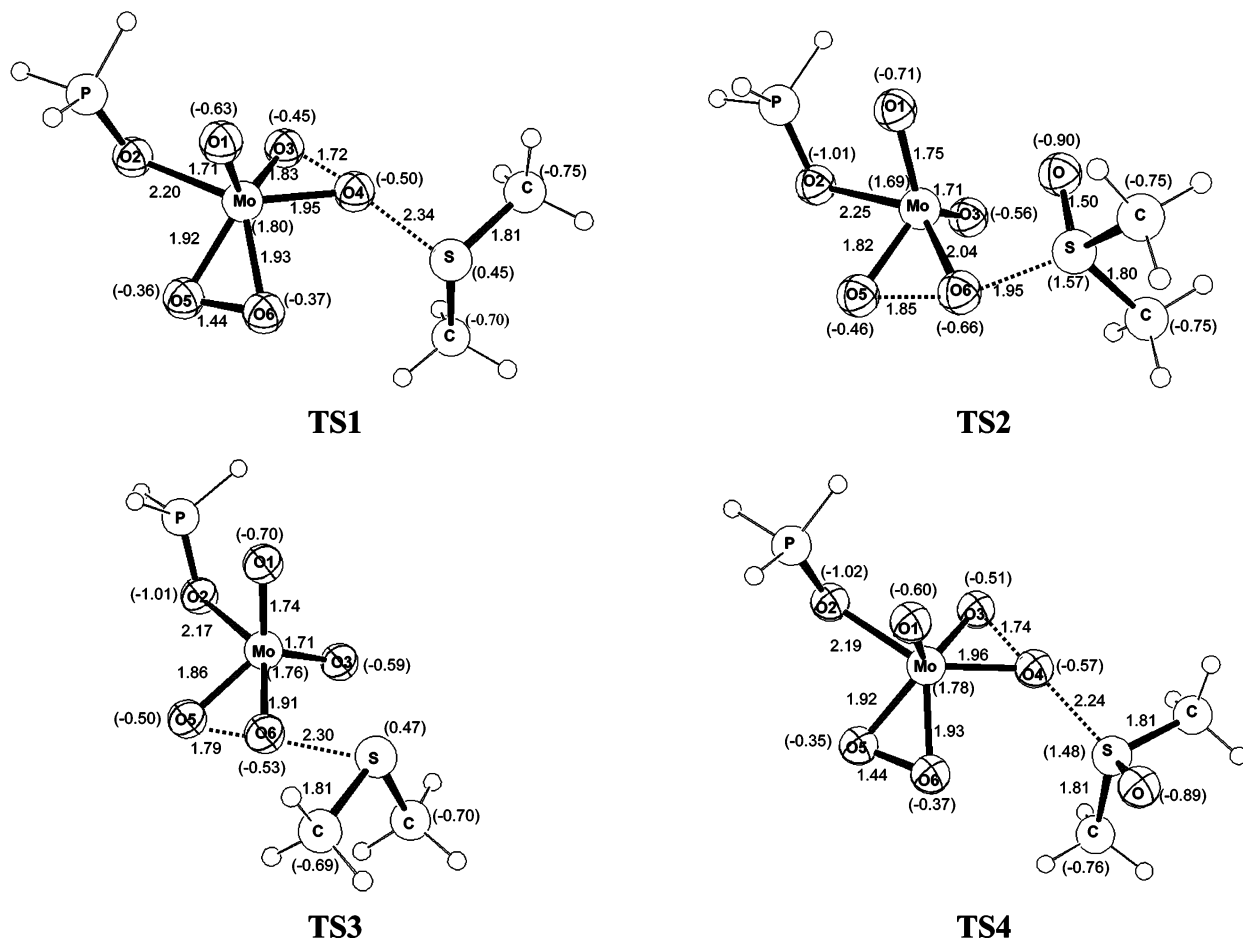


FIGURE 2. Optimized structures and NBO charges of TS1, TS2, TS3, and TS4.

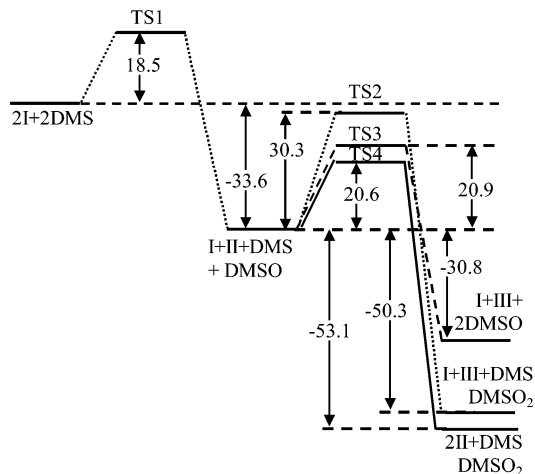


FIGURE 3. Free energy profile (in kcal/mol) of reactive channels involving two consecutive concerted oxygen-transfer steps, via TS1 and TS2 (dotted line) or through TS1 and TS3 (dashed line). The channel along TS1 and TS4 (solid line) corresponds to the reaction pathway in which **I** oxidizes DMS to DMSO, which in turn is oxidized to DMSO₂ by a second molecule of **I**. The free energy of two molecules of **I** and two molecules of DMS is taken as reference.

It is worth noting that the ethylene epoxidation with **I** (Table 1, entry (v)) requires considerably higher activation energy than the sulfide and sulfoxide oxidations. The difference in energy of about 10 kcal/mol between the respective TSs offers a clue of the reasons why peroxymolybdenum complexes chemoselectively oxidize olefinic sulfides (e.g., allyl methyl sulfide) to the corresponding sulfoxide and the latter to sulfone without concomitant epoxidation of the double bond, as has been experimentally observed.⁶ Thus, the attack of the oxidant on the sulfur center is supposed to be kinetically favored over the attack on the double-bond moiety of unsaturated sulfides. A comprehensive study of the chemoselective oxidation of functional sulfide by metal peroxo complexes is now ongoing.

As far as the geometrical parameters of TSs are concerned, the most noticeable structural effect involved in the formation of all characterized TSs is the elongation, with respect to the separated reactants, of the distance between the peroxo oxygen atoms belonging to the peroxo moiety attacked by either DMS or DMSO. The corresponding elongations are 0.269, 0.395, 0.337, and 0.294 Å for TS1, TS2, TS3, and TS4, respectively. On the other hand, the distance between Mo and the cis oxygen atom of the same peroxo moiety contracts by about 0.07 Å in TS1 and TS4 and by about 0.15 Å in TS2 and TS3. The distance between the Mo center and the attacked front-side peroxo oxygen remains unaltered in TS1, TS3, and TS4, while it is elongated by approximately 0.1 Å in TS2, which is the least early TS. The distances between the substrate sulfur atom and the attacked trans oxygen atom are about 2.2–2.3 Å in TS1, TS3, and TS4 and approximately 1.9 Å in TS2.

We have envisaged three multistep processes, which could play a pivotal role in this kind of oxidation. The corresponding free energy profiles are given in Figure 3. Two of them refer to a concerted pathway, in which a single diperoxo species would be able to transfer two oxygen atoms consecutively. The first one is the combina-

TABLE 2. Values of CDA Parameters and NBO Charges of TSs

TJLS	q^a	d^b	b	d/b	r	Δ^c
TS1	0.33	0.161	0.076	2.12	-0.210	-0.002
TS2	0.56	0.430	0.292	1.47	0.476	-0.025
TS3	0.37	0.173	0.073	2.37	-0.225	-0.005
TS4	0.42	0.200	0.128	1.56	-0.206	-0.013

^a q is the sum of NBO charge at the DMS or DMSO moiety. ^b In CDA, the interaction among the occupied orbitals of the oxidizable substrate and the vacant orbitals of the oxidant is defined as donation d ; back-donation b is the interaction of the occupied orbitals of the oxidant and the vacant orbitals of the oxidizable substrate; r is the interaction among occupied orbitals of both oxidant and substrate. Small values of rest terms, Δ , indicate that the electronic structure of TSs can be properly described in terms of donor–acceptor interactions. ^c The larger values of Δ appearing in TS2 and TS4 correspond to less early TSs.

tion of channels (i) and (ii) and depicts the oxidation of DMS by **I** via TS1 to give **II** and DMSO, which, in turn, react with each other through TS2 affording **III** and DMSO₂ (dotted line). The second pathway combines the channels (i) and (iii) and assumes that **II** initially formed via TS1 can react with a second DMS molecule to give **III** and two DMSO molecules (channel (iii) is represented by the dashed line). The first multistep reactive pathway is intended to mimic the overoxidation of sulfides with the Mo peroxo complex, whereas mild oxidation is taken into account in the second pathway. In both cases, the second step associated with TS2 and TS3, respectively, is the rate-limiting step of the consecutive oxygen transfer process. Inasmuch as TS2 (30.3 kcal/mol) exhibits much higher activation energy than TS3 (20.9 kcal/mol), mild oxidation is thought to be kinetically favored over the overoxidation. This finding, however, conflicts with the experiment, since sulfones are the main oxidation product when mild reactional conditions are not employed.^{6,41} The third multistep pathway encompasses channel (i) via TS1 and channel (iv) via TS4 (solid line) and renders that **I** oxidizes DMS, which, in turn, is oxidized to DMSO₂ by a second molecule of **I**. The similar activation parameters relating to TS1 (18.5 kcal/mol) and TS4 (20.6 kcal/mol) account for the spontaneous overoxidation of sulfites to sulfones by peroxymolybdenum complexes. It is worth noting that, when the oxidation is carried out using equimolecular amounts of diperoxo complex and sulfide (1:1), equivalent quantities of the corresponding sulfones are yielded.⁶ This fact implies that the monoperoxo species is also active in the oxygen transfer reaction. As a matter of fact, DMS oxidation by **II** via TS3 requires a relatively low activation energy (20.9 kcal/mol), which is similar to that of TS1 and TS4. Therefore, complex **II**, formed in channels (i) and (iv), is believed to play a pivotal role in the sulfide oxidation process by oxidizing DMS to DMSO, which would be further oxidized to sulfone by **I** via TS4.

It has been suggested that the charge decomposition analysis (CDA)³⁹ applied to the TS could be used to probe the electronic character, i.e., whether the oxidant attacks the substrate in an electrophilic or nucleophilic manner, of oxygen transfer reactions.¹³ Thus, we have used CDA in order to determine whether the corresponding oxidations are a nucleophilic or an electrophilic attack of the molybdenum peroxo complex toward the sulfide and sulfoxide molecules. The results are shown in Table 2.

For the sake of comparison, the sum of NBO charges at the DMS or DMSO fragment in the respective TSs is also presented. From a CDA standpoint,⁴² all processes investigated here take place along an electrophilic attack of the molybdenum peroxo complex on the organic substrate ($d/b > 1$) as has been determined experimentally.^{29,43} However, the oxygen transfer from peroxomolybdenum complexes to the sulfur group of DMS is a more electrophilic process (TS1, $d/b = 2.12$ and TS3, $d/b = 2.37$) than the oxygen transfer to the sulfinyl group of DMSO (TS2, $d/b = 1.47$ and TS4, $d/b = 1.56$). This result corroborates the experimental evidence that the sulfide sulfur is usually more nucleophilic than the sulfoxide sulfur. In fact, this feature has been explored to investigate experimentally the electronic character of oxygen-transfer reactions, for instance, in competitive kinetic experiments, in which a suitable pair of a sulfide and a sulfoxide is in competition for the oxidant, or in the use of thianthrene 5-oxide, which is a molecule that contains two oxidizable competing centers (sulfide and sulfoxide sulfur) so that electrophilic oxidants preferentially oxidize the sulfide sulfur, whereas nucleophilic oxidants oxidize the sulfoxide sulfur.^{44,45}

CDA reveals that the predominant orbital interaction of donation d and back-donation b in the corresponding TSs refers to the electron transfer from the lone pair of the donor species (DMS or DMSO) to the $\sigma^*(\text{O}-\text{O})$ level of the oxidant (**I** or **II**). In this context, it is plausible to probe the dependence of ΔG^\ddagger upon the difference in energy between the $\sigma^*(\text{O}-\text{O})$ level of the oxidant and the HOMO of the oxidizable molecule (DMS or DMSO).⁴⁶ A linear correlation is observed for most of the channels (see Figure 4) except for channel (ii), which displays the least early TS; therefore, its chemical behavior could not be predicted on the basis of donor–acceptor interactions only. The prediction of the reactivity, based on the reac-

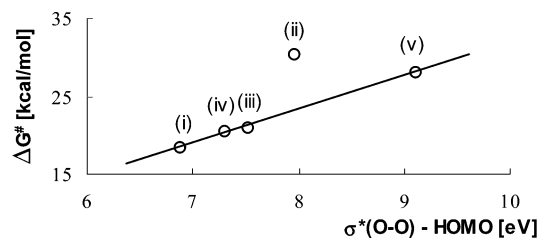


FIGURE 4. Correlation of ΔG^\ddagger to the difference in energy between the $\sigma^*(\text{O}-\text{O})$ of **I** and **II** complexes and the HOMO of the oxidizable molecule for channels (i), (ii), (iii), and (iv). Channel (v) refers to ethylene epoxidation by **I**, and it is also included for the sake of comparison. Channel (ii) is not taken into account in the linear regression line.

tants's properties, is a useful tool, but appears to fail as long as the corresponding TS is not found to be early-like.

5. Conclusions

We have, for the first time, reported DFT calculations on the mechanism of oxygen-transfer reaction from mono and diperoxo complexes of molybdenum to DMS and DMSO molecules. Similar activation energies of TS1, TS3, and TS4, as well as the significant exergonic character of sulfone formation, account for the quantitative and spontaneous overoxidation of sulfides to sulfones. The results presented here can be explored in order to adjust experimental conditions that ensure control over the process.

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Supporting Information Available: Cartesian coordinates and calculated total energies of reactants, products, and corresponding transition states. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(46) In a recent study on ethylene epoxidation by oxo-diperoxo complexes of transition metals, Rosch et al.¹⁸ found a linear correlation between the energy of the $\sigma^*(\text{O}-\text{O})$ level of the complex and the height of the activation barrier: for a fixed electron donor, the higher the energy of the $\sigma^*(\text{O}-\text{O})$ level, the higher the activation energy.