Mechanistic Studies on the Roles of the Oxidant and Hydrogen Bonding in Determining the Selectivity in Alkene Oxidation in the Presence of **Molybdenum Catalysts**

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Abstract: When the molybdenum oxo-(peroxo) acetylide complex [CpMo(O-O)(O)C=CPh] is used as a catalyst for the oxidation of olefins, completely different product selectivity is obtained depending on the oxidant employed. When tert-butyl hydroperoxide (TBHP, 5.5 M) in dodecane is used as the oxidant for the oxidation of cyclohexene, cyclohexene oxide is formed with high selectivity. However, when H₂O₂ is used as the oxidant, the corresponding cis-1,2-diol is formed as the major product. Calculations performed by using density functional theory re-

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vealed the nature of the different competing mechanisms operating during the catalysis process and also provided an insight into the influence of the oxidant and hydrogen bonding on the catalysis process. The mechanistic investigations can therefore serve as a guide in the design of molybdenum-based catalysts for the oxidation of olefins.

Introduction

The conversion of olefins into epoxides is an extremely important reaction because it allows the conversion of available crude oil fractions into epoxides, which are important organic intermediates for the production of a wide variety of chemicals,^[1-4] for example, drugs, agrochemicals and food additives. They also play an important role in biological activity.^[2,5–7] Although epoxidation can take place in the absence of a catalyst, considerable attention has been focused in recent years^[8] on the metal-catalysed epoxidation process due, in part, to the increased possibility of achieving higher activity and selectivity by this route. Among the oxidants employed in the epoxidation process, the one most studied is $H_2O_2^{[9]}$ because of its low cost and ready availability. The transition-metal-based complexes that have been studied as epoxidation catalysts include complexes of iron,^[10,11] manganese,^[12,13] tungsten^[14] and molybdenum.^[15,16] Of these, the compounds most studied are the high-oxidation-state complexes of molybdenum.^[16]

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What is of interest in the epoxidation catalysis process is the mechanism of the reaction, which has been the subject of much debate. Assuming the presence of a peroxido ligand at the metal centre, Mimoun et al.^[17] suggested a [2+ 3] cycloaddition route for this process involving the reaction between the olefin and the metal-peroxo species (see Figure 1a). Sharpless et al.^[18] suggested the possibility of exogenous attack of the olefin at the electrophilic peroxo oxygen atom (see Figure 1b). Both these proposed mechanistic routes assume that the peroxido ligand attached to the molybdenum centre is the source of the oxygen atom in the epoxidation process. Several computational studies have been performed on the epoxidation reaction proceeding through the Sharpless and Mimoun pathways.^[15,19-29] Of the two mechanisms, the Mimoun pathway was found to have a higher barrier than the Sharpless mechanism.^[23] Experimental studies have confirmed this view.[30] However, recent work by Galindo and co-workers^[15] has shown that a molybdenum diperoxo species is a stable intermediate during the epoxidation of *cis*-cyclooctene with H₂O₂ as the oxidant, which indicates that the Sharpless mechanism cannot be entirely ruled out. However, it appears that a mechanism in which the epoxide oxygen is derived from H_2O_2 or *tert*-butyl hydroperoxide (TBHP) rather than from the oxido group on molybdenum would be at least competitive, if not operative, during the catalysis. Such a mechanism, shown in Figure 1c, was proposed by Thiel and co-workers.^[31,32] This pathway involves the coordination of the oxidant to the molybdenum centre followed by the transfer of the oxygen from the oxidant ligand to the olefin (see Figure 1c). Finally, a mechanism that involves the insertion of the olefin into the M-O bond was proposed by Calhorda and co-workers.^[33]

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a) The "Mimoun" mechanism



Figure 1. The different mechanisms proposed in the literature for the olefin epoxidation reaction.

We have recently reported the experimental results^[34] of a study of the oxidation of cyclohexene in the presence of the peroxo species [CpMo(O)(O-O)(C=CPh)] as catalyst and H_2O_2 as the oxidant. This was the first reported case of the formation of a cis-1,2-diol by using a molybdenum-based catalyst. Because cis-1,2-diols are important organic reagents in the pharmaceutical industry,^[35-38] the selectivity of the [CpMo(O)(O–O)(C=CPh)] catalyst in forming *cis*-1,2-diols was an important result. However, as will be discussed in the Results and Discussion section below, when, as an alternative to H₂O₂, organic TBHP in dodecane was used as the oxidant, the following interesting results were obtained: the oxidation of cyclohexene led to the formation of the cis-1,2diol rather than the epoxide when H_2O_2 was used as the oxidant, whereas the epoxide rather than the cis-1,2-diol was formed as the major product when organic TBHP in dodecane was used as the oxidant (Figure 2). It is clear that the selectivity shown by the catalyst is significantly dependent on the nature of the oxidant employed. Moreover, it is possible that the presence of water can also have an effect on the energy barriers, as has been shown by the results of the



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Figure 2. Experimentally observed change in the selectivity towards the epoxide and *cis*-1,2-diol in the oxidation of cyclohexene with TBHP or hydrogen peroxide as oxidant in the presence of a molybdenum catalyst.

calculations of Poli and co-workers^[39] in their investigations of the epoxidation of cyclooctene with H_2O_2 as oxidant.

The observed differences in selectivity when using different oxidants suggest that there are competing mechanisms operating during the catalysis process that lead to the formation of either the *cis*-1,2-diol or the epoxide as the major product. It is necessary to understand the nature of these competing mechanisms because such an understanding can help in the design of systems for specifically obtaining the epoxide or the cis-1,2-diol as the major product, which was the objective of this work. Detailed quantum mechanical computational studies were performed on the following catalytic systems by using DFT: [CpMoO(O)₂C=CPh] with cyclohexene as the substrate and H₂O₂ or organic TBHP in dodecane as the oxidant. Three of the four mechanistic possibilities shown in Figure 1 were considered: the Mimoun mechanism was not considered because it has been computationally shown to be a high-barrier process.^[23] Furthermore, a new mechanism was proposed to account for the formation of the cis-1,2-diol product. It has been shown that the presence of water has a significant influence on the selectivity of the catalyst. It has also been shown that changing the oxidant from H_2O_2 to TBHP leads to a change in the preference for one mechanism over another and thus in the eventual product (epoxide in the case of organic TBHP and *cis*-1,2-diol in the case of H_2O_2 as the oxidant). The results therefore shed light on the mechanistic possibilities of the important epoxide and cis-1,2-diol forming processes, and also provide an insight into how one could tune molybdenum-based catalytic systems through the choice of oxidant to obtain, as desired, the epoxide or the cis-1,2-diol as the major product.



In the first sub-section of the Results and Discussion section, we discuss the experimental evidence for the formation of the peroxo species upon addition of H₂O₂ or TBHP under the given reaction conditions, as well as the aforementioned observed selectivity for the epoxide when using TBHP as the oxidant and the *cis*-1,2-diol when H_2O_2 was employed as the oxidant. In the following sub-sections we discuss the computational studies of the different mechanisms that are possible for the different systems and the results that corroborate the experimental findings.

Results and Discussion

Experimental evidence for the formation of the peroxo species of the acetylide-ligated molybdenum complexes: Experimental evidence was found for the formation of the peroxo molybdenum species [CpMo(O)2OC=CPh] during the catalytic oxidation of cyclohexene. [CpMo(O)₂OC=CPh] was obtained from [CpMo(CO)₃C=CPh], which was prepared by the previously reported procedure.^[40-42] The FTIR spectrum of the catalyst after the addition of H₂O₂ confirmed the formation of the (oxo)peroxo molybdenum species (Figure 3).



Figure 3. IR spectrum showing evidence for the formation of the oxo-(peroxo) species after treatment of cyclohexene with H₂O₂ in the presence of [CpMo(CO)₃C=CPh] as catalyst.

The peak at 953 cm⁻¹ shows the presence of a Mo=O terminal bond. The peak in the range of 930-950 cm⁻¹ corresponds to the O-O stretching vibration of the peroxo species. The weak bands at 668 and 573 $\rm cm^{-1}$ can be assigned to Mo-O₂ (peroxo) asymmetric and symmetric stretching vibrations, respectively. The IR peaks for the Mo-oxo and -peroxo bonds are in good agreement with the values reported in the literature^[34,41,42] for various molybdenum (oxo)peroxo complexes. The bands due to C-H stretching vibrations of the phenyl ring are observed in the range $2854-2955 \text{ cm}^{-1}$ and the C=C stretching vibrations of the ring are observed at 1464 and 1377 cm⁻¹, even after the addition of hydrogen peroxide (see Figure 1 in the Supporting

Information). The bands due to carbonyl stretching (1940 and 2031 cm⁻¹) disappeared after the addition of H₂O₂. This clearly indicates the loss of all the CO ligands after the addition of hydrogen peroxide with the formation of the higher oxidation state molybdenum(VI) complex with retention of the acetylide C=CPh group attached to the molybdenum centre.

The addition of TBHP (0.02 mol) to the catalyst results in the formation of the oxo(peroxo) species, which is clearly indicated by the peaks in the range of 930–950 cm⁻¹ due to the Mo=O bond and the broad peaks in the range of 840-860 cm^{-1} due to the O–O bond (Figure 4).



Figure 4. IR spectrum showing evidence for the formation of the oxo-(peroxo)-molybdenum species after treatment of cyclohexene with TBHP in dodecane in the presence of [CpMo(CO)₃C≡CPh] as catalyst.

Cyclohexene oxidation experiments conducted with [CpMo(CO)₃C=CPh] and TBHP as oxidant and 1,2-dichloroethane as solvent led to the formation of the epoxide with a selectivity as high as 79.2% within 12 h (Table 1). 1,2-

Table 1. Oxidation of cyclohexene with [CpMo(CO)₃(C=CPh)] as catalvst.[a]

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Oxidant	Solvent	<i>t</i> [h]	Conv. [%]	Selectivity [%]		
				Epoxide	Diol	Others
ТВНР	$C_2H_4Cl_2$	12	53	79.2	14.4 ^[b]	6.4
$H_2O_2(50\%)$	<i>tert</i> -butyl	9	95	-	$-91^{[c]}$	9
	alcohol					

Reagents and conditions: cyclohexene (0.02 mol), catalyst [a] (0.01 mmol), oxidants H₂O₂ (0.04 mol) and TBHP (0.02 mol), 80 °C. [b] trans-Diol. [c] cis-Diol.

Dichloroethane was selected as the solvent to eliminate hydrogen-bonding effects observed with protic solvents such as tert-butanol. It has previously been shown^[34] that the C= CPh-substituted molybdenum-peroxo catalyst gives cis-1,2diol with 91% conversion and 95% selectivity towards cisdihydroxylation when tert-butanol is employed as the sol-

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Importance of hydrogen bonding on the oxidation reactions:

Sharpless mechanism: As stated in the Introduction, the fact that the use of $[CpMo(CO)_3C=CPh]$ as the catalyst produces the epoxide as the major product with TBHP as the oxidant, whereas it produces the *cis*-1,2-diol as the major product^[34] when 50% H₂O₂ was used, indicates that there are competing mechanisms at work in the homogeneous catalysis systems. The possible mechanisms for the oxidation are illustrated in Figures 5–7. In the "Sharpless" mechanism, also discussed in the Introduction (see Figure 1b), the catalyst is approached directly by the cyclohexene (Figure 5). It is well established^[18] that $[CpMo(CO)_3C=CPh]$ acts as the precursor for [CpMo(O-O)(O)(C=CPh)] (b-1). As indicated in Figure 5 b-1 can be converted into the corresponding dioxo



Figure 5. Potential energy surfaces for the first step of the "Sharpless mechanism" for the oxidation of cyclohexene in the presence of the molybdenum catalyst [CpMo(O)(OO)(CCPh)]. The influence of hydrogen bonding by water and TBHP is considered. Energy values outside of parentheses are values of ΔG in *tert*-butanol and those in parentheses are values of ΔG in 1,2-dichloroethane. All values are given in kcal mol⁻¹.



Figure 6. Potential energy surfaces for the first step of the Thiels mechanism: approach of the oxidants TBHP and H_2O_2 towards the molybdenum catalyst. Energy values (ΔG) are given in kcalmol⁻¹.

intermediate b-2 and in the process yield the epoxide, denoted as a-2. The activation barriers (ΔG) were determined to be 26.2 and 28.5 kcal mol⁻¹ for the reaction in *tert*-butanol and 1,2-dichloroethane, respectively. For the case of aqueous H_2O_2 as the oxidant (with *tert*-butanol as the solvent), there is the possibility that water molecules present in solution during the reaction, as well as the H₂O₂ oxidant itself, can form a hydrogen bond with the [CpMo(O-O)(O)(C=CPh)] catalyst molecule, and thereby affect the energy barrier for this epoxidation reaction. These possibilities were considered in the epoxidation reaction with one and two water molecules coordinated through hydrogen bonds to the [CpMo(O-O)(O)(C=CPh)] catalyst. The presence of one water molecule was found to lower the energy barrier to 22.3 kcalmol⁻¹ (see Figure 7 (ts-1/1) in the Supporting Information), whereas the presence of two water molecules, as shown in Figure 5 (t-2), was found to lead to a barrier of 24.3 kcalmol⁻¹ for this epoxidation reaction. These results therefore indicate that the presence of water molecules does have an effect on the kinetics of the epoxidation process. Similar calculations to show the involvement of hydrogenbonded H₂O₂ in the "Sharpless mechanism" revealed a lower energy barrier of 24.7 kcalmol⁻¹ (see Figure 9 (t-4/1) in the Supporting Information). Hence, the results indicate that the interaction, through hydrogen bonding, of one H_2O_2 or two H₂O molecules shows the same lowering of the



Figure 7. Potential energy surfaces for the alternative reaction pathway for the reaction of the molybdenum catalyst [CpMo(O)(OO)(CCPh)] with the two oxidants TBHP and H_2O_2 . Energy values (ΔG) are given in kcal mol⁻¹.

energy barrier for the "Sharpless mechanism". Henceforth, when considering aqueous H₂O₂ as the oxidant, the model that will be employed that takes into account the effect of hydrogen bonding will be that involving the presence of two water molecules hydrogen-bonded to the molybdenum catalyst. Note also that the solvent employed when aqueous H₂O₂ was used as the oxidant, tert-butanol, can also form hydrogen bonds with the molybdenum catalyst and thus could also influence the energetics of the oxidation process. However, it is likely that water would displace tert-butanol from the molybdenum catalyst because of its superior ability to form hydrogen bonds with the catalyst. The calculations indicate that given a choice of forming a hydrogen bond with tert-butanol or water, the peroxo group of the catalyst shows a preference, by 3.6 kcalmol⁻¹, for bonding to the water molecule (see Figure 6a in the Supporting Information).

For the case of organic TBHP as the oxidant, then there are no water molecules present that can contribute to hydrogen bonding with the catalyst. Moreover, the solvent that is used in the oxidation reaction with TBHP, 1,2-dichloroethane, also cannot form hydrogen bonds or participate in other weak interactions with the catalyst. We attempted to perform calculations in which the chlorine atoms of 1,2-dichloroethane are non-covalently bound to the oxygen atoms of the catalyst, however, the results show that the two moieties drift apart in the optimised structures. However, TBHP itself, in addition to acting as an oxidant, can interaction also reduces the energy barrier for the epoxidation process, from 28.5 kcal mol⁻¹ (see Figure 5) to 25.8 kcal mol⁻¹ with one TBHP molecule hydrogen-bonded to the catalyst (see Figure 9e (**t-3/1T**) in the Supporting Information), and to 23.7 kcal mol⁻¹ with two TBHP molecules hydrogenbonded to the catalyst (see Figure 5 (**t-3/2T**)). These results therefore underline the importance of the hydrogen bonding of the oxidant and/or water molecules in the oxidation processes occurring in the presence of molybdenum systems.

Thiel mechanism: The first step of the Thiel mechanism involves the conversion of the [CpMo(O)(OO)C=CPh] catalyst complex into $[CpMoC \equiv CPh(O)(OOH)(OOR)]$ (R = H (H₂O₂) and tert-butyl (TBHP)). In the absence of any hydrogen-bonding interactions, the energy barriers are 28.6 kcal mol^{-1} for H_2O_2 as oxidant and 30.5 $kcal\,mol^{-1}$ for TBHP as oxidant (see Figures 3 (ts-2) and 5 (t-4-H), respectively, in the Supporting Information). These barriers are reduced when two hydrogen-bonding water molecules are considered in the mechanism for the H2O2 oxidant and when two TBHP molecules are considered in the mechanism for the TBHP oxidant. For the case of H₂O₂, the barriers are reduced from $28.6 \text{ kcal mol}^{-1}$ (see Figure 3 (ts-2) in the Supporting Information) to 24.7 kcalmol⁻¹ when one water molecule is hydrogen-bonded to the peroxo group of the catalyst (see Figure 7 (ts-2/1) in the Supporting Information) and to 22.7 kcal mol⁻¹ when two water molecules are considered (see Figure 6 (t-6)). For the case of TBHP, the corresponding barriers are 30.5 kcalmol⁻¹ when no extra TBHP molecules are employed (see Figure 5 (t-4-H) in the Supporting Information), 29.4 kcalmol⁻¹ with the addition of one extra TBHP molecule (see Figure 9e (t-4/1T) in the Supporting Information) and 26.5 kcal mol⁻¹ when two extra TBHP molecules are considered (see Figure 6 (t-4/2T)). The reason for the sharp decrease in the barrier, from 28.6 to 22.7 kcalmol⁻¹ for the case of H_2O_2 is due to the fact that one of the two water molecules that have been considered performs the task of a "hydrogen atom relay" in the transition state (t-6): the water molecule accepts a hydrogen atom from the coordinating H₂O₂ oxidant species and donates one of its own hydrogen atoms to the peroxo group of the molybdenum catalyst (see Figure 6 (t-6)). This leads to the conversion of the four-membered transition state for the hydrogen transfer in the absence of the water molecule to a sterically more favoured six-membered transition state when the water molecule is considered.

A similar hydrogen atom relay mechanism also occurs in the case of TBHP. However, the effect with TBHP is less pronounced, with the energy barrier decreasing by 6.1 kcal mol^{-1} , as compared with a decrease of 4.0 kcal mol^{-1} in the case of water.

The upshot of the calculations for the important first step of the competing Sharpless and Thiel mechanisms is this:

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for the case of aqueous H2O2, the first step of the Thiel mechanism is more favoured than the first step of the Sharpless mechanism, whereas for the case of TBHP, it is the other way around (see Figures 5 and 6). This indicates that when TBHP is employed as the oxidant, the Sharpless mechanism would be favoured, leading to the formation of the epoxide as the major product. This corroborates the experimental findings reported in the previous section. For the case of H₂O₂, the epoxide would not be formed in the first step, instead, the species [CpMo(O)(OOH)(OOH)C=CPh] (b-11) would be preferred. As we will show in a later section, this will lead to the formation of the cis-1,2-diol as the preferred major product.

Activation of the Mo=O bond: In addition to the two mechanisms already considered, the Sharpless and Thiel mechanisms, a third possibility, proposed earlier by Poli and coworkers,^[23,39] has also been considered. In this mechanism, as in the Thiel mechanism, the oxidant, H₂O₂ or TBHP, approaches the molybdenum catalyst, but unlike in the Thiel mechanism, the oxidant transfers a hydrogen atom to the oxygen atom coordinated through a double bond to the molybdenum centre. As shown in Figures 3 (ts-3) and 5 (t-7-H) in the Supporting Information, such a reaction has an energy barrier of 29.6 kcalmol⁻¹ for the H₂O₂ oxidant and 35.5 kcalmol⁻¹ for the TBHP oxidant. The presence of two H_2O molecules (for the case of aqueous H_2O_2 as oxidant) and two extra TBHP molecules (for the case of TBHP as oxidant) reduces the barrier to 23.6 and 27.6 kcal mol⁻¹, respectively. For the case of H_2O_2 , the barrier (23.6 kcal mol⁻¹) is higher than for the first step of the Thiel Mechanism, whereas for the case of TBHP, the barrier $(27.6 \text{ kcal mol}^{-1};$ see Figure 7 (t-5/2T)) is higher than the first step of both the Sharpless and the Thiel mechanisms. This indicates that the activation of the Mo=O bond would not be a favoured pathway during the oxidation reaction for either of the H_2O_2 and TBHP oxidants.

Completion of the epoxidation cycle: In the previous sections we have established that the first step of the Sharpless mechanism is preferred when organic TBHP is considered as the oxidant, and that the first step of the Thiel mechanism is preferred when aqueous H_2O_2 is employed as the oxidant. In this section we discuss the completion of the catalytic cycle for the Sharpless mechanism. Only the TBHP oxidant case is considered here because the catalyst will prefer the Thiel pathway when aqueous H_2O_2 is used. The freeenergy pathway for the conversion of the molybdenum dioxo species, formed at the end of the first step of the Sharpless mechanism, into the [CpMo(C≡CPh)(O)(OH)-(OOtBu)] species is shown in Figure 8. The aid of an additional tert-butyl species as a hydrogen relay agent has also been considered for this conversion. The next step of the cycle, the step that would convert the [CpMo(C=(O)(OH)(OOtBu) species into the original catalyst, [CpMo(O)(O–O)(C=CPh)], and also form *tert*-butanol (one of the observed products of the reaction) is shown in

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Figure 8. Potential energy surface for the conversion of the molybdenum dioxo species [CpMo(O)(O)(CCPh)] into [CpMo(O)(OH)(OOtBu)-(CCPh)]. Energy values (ΔG) are given in kcalmol⁻¹.

Figure 9. This intermolecular rearrangement reaction (see Figure 9) is made more facile by the aid of a hydrogenbonded TBHP species. The barriers to the two steps shown in Figures 8 and 9 are 24.5 and 23.0 kcalmol⁻¹, respectively.

Note that the species [CpMo(C=CPh)(O)(OH)(OOtBu)](b-16), formed as shown in Figure 8, can also undergo attack by a cyclohexene species leading to further epoxidation, as has been speculated in the past.^[33,43] As shown in Figure 13 (ts-4) in the Supporting Information, such an attack will be less favoured (energy barrier of 33.8 kcalmol⁻¹) than the intramolecular pathway shown in Figure 9. Hence, the most likely outcome of the oxidation process when using TBHP as the oxidant will be the Sharpless mechanism, which yields the epoxide as the major product.



Figure 9. Potential energy surface for the regeneration of the catalyst from the intermediate [CpMo(O)(OH)(OOtBu)(CCPh)]. Energy values (ΔG) are given in kcal mol⁻¹.

Further reactions of the $[CpMo(C \equiv CPh)(OOH)(OOH)]$ intermediate: The previous sections have shown that the molybdenum-based catalyst, in conjunction with the H₂O₂ oxidant, will preferentially produce the [CpMo(C=CPh)-

 $(OOH)(OOH)(2H_2O)$] (b-11) species. Subsequent calculations (shown in Figure 10) indicate that this species can be converted, with a low energy barrier of 3.6 kcal mol⁻¹, into



Figure 10. Facile interconversion between the possible different conformers of the intermediates formed from the reaction of hydrogen peroxide with the acetylide-coordinated molybdenum catalyst. Energy values (ΔG) are given in kcalmol⁻¹.

the conformer [CpMo(C=CPh)(OH)(OOH)(OO)(2H₂O)] (b-20), which, in turn, can convert with a barrier of 6.6 kcal mol^{-1} into the conformer [CpMo(C=CPh)(OH)- $(OOH)(OO)(2H_2O)$] (b-14). Hence, there are three conformers of the intermediate that can exist in solution during the catalysis process, as illustrated in Figure 11. Of the three, the most stable intermediate is **b-20**, with a slightly lower energy than the other two conformers. This species, with two hydrogen-bonding water molecules, can undergo further conversion into the structure referred to as b-20(i) in Figure 12: in **b-20(i)**, the hydrogen-bonding water molecules are at the same end of the complex (the OOH end), instead of the water molecules separately binding to the OOH and the OH ends, as in **b-20**. Such a rearrangement of the hydrogen-bonding water molecules is quite a facile process, as evidenced by the small difference in the energies of the structures **b-20** and **b-20(i)**, calculated to be $1.1 \text{ kcal mol}^{-1}$, with b-20(i) being slightly higher in energy (see Figure 6b in the Supporting Information). Such a rearrangement of the water molecules has been considered in order to study the reaction shown in Figure 12: a cyclohexene approaches the peroxo group of the species **b-20(i)** and is oxidised to the corresponding cis-1,2-diol through a two-step process. This is a



Figure 11. Interconversions between different isomers of the molybdenum catalyst after its coordination.



Figure 12. Potential energy surface for the formation of the *cis*-1,2-diol from the reaction of cyclohexene with **b-20(i)**, the most stable of the three conformers of the intermediate of the reaction of hydrogen peroxide with the acetylide-coordinated molybdenum catalyst. Energy values (ΔG) are given in kcal mol⁻¹.

facile process, with the barriers for the two reactions being 15.9 and 10.5 kcalmol⁻¹, respectively. Hence, for the case of the molybdenum catalyst with aqueous H_2O_2 as the oxidant, the first step, the approach and attack of the H_2O_2 moiety, is the slowest step of the reaction, having a barrier of 22.7 kcal mol⁻¹. Note also that the *cis*-1,2-diol can also be formed by the approach and attack of the cyclohexene species on the intermediate conformers **b-14** and **b-11**. As the potential energy surfaces shown in Figures 13 and 14 indicate, the re-

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Figure 13. Potential energy surface for the formation of the *cis*-1,2-diol from the reaction of cyclohexene with **b-14(i)**, one of the three conformers of the intermediate of the reaction of hydrogen peroxide with the acetylide-coordinated molybdenum catalyst. Energy values (ΔG) are given in kcalmol⁻¹.



Figure 14. Potential energy surface for the formation of the *cis*-1,2-diol from the reaction of cyclohexene with **b-11(i)**, one of the three conformers of the intermediate of the reaction of hydrogen peroxide with the acetylide-coordinated molybdenum catalyst. Energy values (ΔG) are given in kcalmol⁻¹.

actions in each of these cases, leading to the eventual formation of the *cis*-1,2-diol, were also found to have low barriers, lower than the first step of the catalytic cycle, the approach and attack of the hydrogen peroxide species.

It may also be possible for the intermediates **b-11**, **b-14** and **b-20** to form the epoxide by the approach and attack of the cyclohexene. This has also been computationally investigated and the results for the reactions of **b-11**, **b-14** and **b-20** with cyclohexene to yield the epoxide are shown in Figure 21 in the Supporting Information. For each of the cases **b-11**, **b-14** and **b-20**, the barriers are 19.7, 18.1 and 24.0 kcalmol⁻¹, respectively. All the energy barriers discussed for the formation of the epoxide are found to be

higher than the corresponding energy barriers for the formation of the *cis*-1,2-diol by approach and attack of the cyclohexene on **b-11(i)**, **b-14(i)** and **b-20(i)** (see the energy barriers in the Figures 14, 13 and 12, respectively).

Thus, overall, for the molybdenum catalyst complex with aqueous H_2O_2 as the oxidant, the calculations predict that the preferred product would be the *cis*-1,2-diol, thus corroborating the experimental findings discussed earlier.

We also note here that the other mechanism possible after the formation of the [CpMo(CCPh)(OOH)(OOH)-(2H₂O)] species, the "Calhorda" mechanism (see Figure 15), which would lead to the formation of the epoxide, was also studied and was found to have high barriers of 36.2, 43.5, and 45.1 kcalmol⁻¹ for **b-14**, **b-11**, and **b-20**, respectively. Hence the calculations indicate that the two competing mechanisms during the cyclohexene oxidation processes would be the Sharpless mechanism and our proposed mechanism, which can be considered a modified Thiel-type mech-



Figure 15. Potential energy surfaces for the Calhorda mechanism for epoxide formation from **b-14**, **b-11** and **b-20**. Energy values (ΔG) are given in kcal mol⁻¹.

anism, with the Sharpless mechanism being favoured when TBHP is used as the oxidant and the mechanism with features common to the Thiel mechanism being preferred when H_2O_2 is employed as the oxidant.

Summary of the mechanistic studies: The calculations discussed in the preceding sections show the complete reaction cycle for the formation of the epoxide in the presence of the molybdenum catalyst [CpMo(O)(OO)C=CPh] when organic TBHP is employed as the oxidant as well as the formation of the *cis*-1,2-diol when aqueous H_2O_2 is used as the oxidant. Figure 16 encapsulates the essential features of the two dif-



Figure 16. Trend in reactivity for the competitive reactions between the catalyst and the other species present in solution. When TBHP is the oxidant, cyclohexene is seen to approach first followed by the TBHP molecule, but when H₂O₂ is used as the oxidant, the order of approach is reversed.

ferent catalytic cycles. The principal difference between the two cycles lies in the sequence in which the two species, cyclohexene and the oxidant (TBHP or H₂O₂), approach the molybdenum catalyst centre. For the case in which the oxidant is TBHP, the preferred order is cyclohexene followed by TBHP, whereas for the case in which the oxidant is H_2O_2 , the preferred order is H_2O_2 followed by cyclohexene. This difference in the order in which the substrates attack the catalyst centre determines the difference in the selectivity of the two cases.

Conclusion

It has been experimentally observed that the oxidation of cyclohexene in the presence of molybdenum peroxo acetylide as catalyst and TBHP in dodecane or 50 % H₂O₂ as oxidant can lead to different oxidation products. For the oxidation of cyclohexene, when TBHP in dodecane is used as the oxidant, the epoxide is formed as the major product, and when 50% H_2O_2 is used as the oxidant, the *cis*-1,2-diol is formed as the major product. This indicates that there are competing mechanisms at work during the catalytic oxidation process in these systems. Calculations with DFT were performed to elucidate the nature of these competing mechanisms, with a new mechanism being proposed to explain the formation of the *cis*-1,2-diol when aqueous H_2O_2 is used as the oxidant. The DFT studies showed that the order in which the two substrates, the olefin and oxidant, attack the molybdenum centre is crucial for determining the nature of the oxidation product that is formed. For the case of TBHP in dodecane, it was found that the preferred order of attack is that of cyclohexene followed by TBHP, which leads to the preferential formation of the epoxide product. In contrast, with 50% H_2O_2 , the preferred order of attack is that of H_2O_2 followed by cyclohexene, which leads to the preferential formation of the cis-1,2-diol product. What is of crucial importance in determining the selectivity of the catalyst with the different oxidants is the hydrogen bonding that occurs between the water or oxidant molecules and the oxygen atoms of the catalyst.

The calculations have thus provided an insight into the nature of the olefin oxidation processes at the catalytic centre, and may serve as a guide in choosing the appropriate oxidant to obtain the desired product in the oxidation of olefins.

Experimental Section

Preparation of [CpMo(CO)₃C=CPh]: All reagents of commercial grade (Aldrich, SD Fine) were used as received unless stated otherwise. The hydrogen peroxide used was 50 % w/w in water. THF was dried according to the standard method and freshly distilled prior to use. Cyclopentadiene was prepared from dicyclopentadiene (Aldrich) by distillation prior to use and was prepared according to the literature procedure.^[40] Yield of $[CpMo(CO)_3(C=CPh)]$: 1.5 g, 68 %. ¹H NMR: $\delta = 5.5$ (C-H_{Cp}), 7.15–7.38 ppm (C-H_{Ar}); ¹³C NMR: δ = 87.85 (C_{cp}), 126.01, 127.0, 129.39, 130.8, 130.87 (C_{Ph}), 222.2–238.8 ppm (C=O); IR (KBr): $\tilde{\nu} = 1940$, 1980, 2038 (CO), 2109 (C=C), 2958 cm⁻¹ (C_{Cp}); elemental analysis calcd (%) for [CpMo(CO)₃(C=CPh)]: C 55.49, H 2.89; found: C 55.53, H 3.05.

Catalytic reaction: The liquid phase catalytic oxidation reactions were carried out in a two-necked round-bottomed flask equipped with a magnetic stirrer and immersed in a thermostatted oil bath. The reactions were carried out at 80°C in tert-butanol (10 g) for the reaction in which 50% H₂O₂ was used as the oxidant and in 1,2-dichloroethane for the reaction in which TBHP in dodecane was used as the oxidant. The flask was charged with cyclohexene (0.02 mol) and either 50 % H₂O₂

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(0.04 mol) or TBHP (0.02 mol) and the reactions were performed for 12 h. Samples were withdrawn periodically and analysed on an Agilent 6890 gas chromatograph equipped with a HP-5 dimethylpolysiloxane column (60 m length, 0.25 mm diameter and 0.25 μm film thickness) with a flame ionisation detector. The products were characterised by GCMS on an 6890N instrument and by GC-IR with a Perkin–Elmer Spectrum 2001 spectrometer.

Computational details: The computational procedure adopted is as follows: all the structures reported in the manuscript were optimised by DFT with Turbomole Version 6.0^[44] by using the BP-86 functional.^[45] The electronic configurations of the atoms were described by using a triplezeta basis set augmented by a polarisation function (TURBOMOLE basis set TZVP). $\ensuremath{^{[46]}}$ Because it is possible that the geometry optimisation procedure performed by DFT may be sensitive to the nature of the functional, to ensure the reliability of the obtained geometry-optimised structures, all the structures were also optimised with the Perdew, Burke, and Erzenhof density functional (PBE)[47] as well as with the B3LYP functional^[48,49] and the TZVP basis set. The resolution of identity (RI)^[50] and the multipole-accelerated resolution of identity (marij)^[51] approximations were employed for an accurate and efficient treatment of the electronic Coulomb term for both sets of the density functional calculations. A comparison was then made between the corresponding structures obtained with the BP-86 and the PBE and B3LYP functionals. The comparison showed very little difference in bond lengths, bond angles or dihedral angles between the corresponding structures for all cases. Further corroboration of the smallness of the difference between the structures obtained with the two functionals came from a comparison of the potential energy surfaces for the different reactions discussed in the manuscript. The values of ΔE for the insertion and termination barriers for the oligomerisation mechanism, obtained from the three separate sets of calculations, were compared and the results, shown in the Supporting Information, indicate that there is only a small difference between the corresponding values for almost all the cases for the energies obtained with the BP-86 and the PBE functionals. The energies obtained with the B3LYP functionals were found to be different by 8-10 kcalmol⁻¹ from the corresponding BP-86 and PBE values, but the trends discussed in the manuscript with regard to the preference for the Sharpless and the Thiel mechanism were found to remain unchanged for the set of calculations performed with the B3LYP functional. This suggests that changing the functional may result in a change in the absolute values of the barriers in the different mechanisms, but also that the essential conclusions reached in the manuscript will remain unchanged. With regard to the transition states obtained in the three sets of calculations, care was taken to ensure that the transition-state structures obtained possessed only one imaginary frequency corresponding to the correct normal mode.

The contributions of internal energy and entropy were further obtained from frequency calculations performed on the DFT structures at 298.15 K. Thus, the energies reported in the figures of the paper are the ΔG values. To account for the fact that all the species are in solution, the translational entropy term in all the calculated structures was corrected through a free volume correction introduced by Mammen et al.^[52] and was used for all the atoms. Solvent effects were incorporated by using the COSMO model,^[53] with *tert*-butanol ($\varepsilon = 12.4$) as the solvent for the cases in which H_2O_2 was used as the oxidant and 1.2-dichloroethane ($\varepsilon =$ 10.4) as the solvent for the cases in which TBHP was used as the oxidant. Note that different conformational possibilities were considered for the structures reported for the different reactants, intermediates and products described in the paper. The structures that have been reported and employed for evaluating the free energies and enthalpies for the different reactions were the ones that were the most stable conformers. It is possible that a very exhaustive conformational search, by using search algorithms to look at hundreds or thousands of conformations, could have been employed to locate unequivocally the lowest energy conformer, the "global minima" in each case, but such an approach is currently beyond the scope of full quantum chemical methods. Note also that the difference in energy between the competing pathways is sometimes quite small, about 2.0 kcal mol⁻¹ in some cases, but, given that 1) the same relative differences are obtained at the same level of theory in these cases

and 2) the calculations were performed with three different functionals and have yielded the same conclusions in each case, it is believed that the results obtained, even for cases in which the competing mechanisms have small differences in energy barriers, are reliable.

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Homogeneous Catalysis -

P. Chandra, S. L. Pandhare, S. B. Umbarkar,* M. K. Dongare,* K. Vanka*.....

Mechanistic Studies on the Roles of the Oxidant and Hydrogen Bonding in Determining the Selectivity in Alkene Oxidation in the Presence of Molybdenum Catalysts



Molybdenum-catalysed oxidation: Calculations performed by using density functional theory indicate that different mechanisms compete during the homogeneous catalysis of olefin oxidation carried out in the presence of molybdenum-based catalysts (see scheme).