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Allylic oxidation of cyclohexene catalyzed by manganese porphyrins: DFT studies

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ABSTRACT

The present paper summarizes density functional theory studies on hydroxylation of cyclohexene catalyzed by manganese oxo porphyrin. The reaction is preceded by the physisorption of the substrate over the catalyst molecule at the distance of 2.18 Å. Next, a hydrogen atom form the C–H bond is abstracted by the catalyst oxo group and the cyclohexene radical is readily bound to the OH group formed at a catalyst active site. Formation of alcohol requires spin crossing on the reaction pathway. Present studies show that alcohol is formed on the catalyst active site via oxygen rebound mechanism without the cyclohexene radical dissociation. Results are compared with the data obtained earlier for epoxidation. The intermediate structures, found for both pathways, clearly indicate that each may lead to only one reaction product.

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1. Introduction

Among popular homogeneous catalysts for hydrocarbon oxidation, metalloporphyrins play a crucial role [1]. This is due to their biological function as cofactors in P450 class of enzymes responsible for bio-oxidation of both endogenous and exogenous compounds. In addition, their application as versatile homogeneous catalysts for oxidation of hydrocarbons is widely explored. On the one hand, metalloporphyrins are able to insert oxygen atom into C–H bonds, on the other, they may deliver oxygen atom to the double C=C bonds, yielding epoxide. This dual reactivity is clearly manifested in the case of alkenes, whose C=C bond and potentially reactive single C–H bonds in α (allylic) position with respect to the double bond, are both prone to oxygenation. In particular, experiments with cyclohexene oxidation by iodosylbenzene catalyzed by metalloporphyrins showed that, beside the cyclohexane oxide, unsaturated products of allylic oxidation (cyclohexen-3-ol and cyclohexen-3-on) are formed [2–9].

Significant efforts have been directed at elucidation of the mechanism of alkene oxidation by metalloporphyrins [2–22]. There is a consensus as to the assumption that a high-valent metal oxo complex acts as an intermediate for oxygen atom transfer to organic substrates, both in the case of epoxidation and hydroxylation. The final selectivity pattern is determined by a competition between the allylic C–H bond and the C=C double bond for the porphyrin oxospecies, and, consequently, the product distribution depends on the structure of the alkene and metalloporphyrin. Concerning the mechanistic steps involved in hydroxylation and epoxidation, the general conclusions have been summarized by Groves and Gross [19], who pointed out that two non-intersecting reaction pathways are involved in both processes. Allylic pathway leading to hydroxylation proceeds via a radical rebound mechanism where the first step involves abstraction of a hydrogen atom from the substrate by the high-valent metal-oxo species. As a result a M–OH complex and a hydrocarbon radical are formed. In the subsequent step the hydroxyl group from the metal centre recombines with the hydrocarbon radical to yield an allylic alcohol molecule. For the epoxidation pathway formation of a complex resulting from the interaction of olefinic double bond with the metalloporphyrin oxo group has been postulated. Groves and Gross [19] stressed that this complex is not involved in hydroxylation. According to Bruice and co-workers [18] the olefin/oxo metal complex transforms by a concerted charge and oxygen transfer into molecule of an epoxide.

Our interest in theoretical investigation of cyclohexene oxidation by metalloporphyrins has been prompted by experimental studies from our laboratory, which demonstrated that anchoring of metalloporphyrin inside the channels of ordered mesoporous silica may suppress the epoxidation function, leaving allylic oxidation as the major pathway [23–25]. The result was particularly striking for manganese porphyrins, known to have unusually high reactivity toward olefin epoxidation [1]. Our DFT study of the epoxidation of cyclohexene catalyzed by manganese porphyrins provided a rationale for the observed phenomenon [26]. Calculations showed that formation of epoxide required a specific mutual arrangement of cyclohexene molecule and metalloporphyrin ring, the condition difficult to fulfill in the limited space around the catalytic centre located within the mesopore.

In the present work we complete the theoretical investigation of manganese porphyrin reactivity towards cyclohexene by using

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Table 1

Calculated parameters of the key structures **A1** and **A2** found on the reaction pathway leading to the alcohol formation. As isolated molecules [MnPClO] [58] and cyclohexenol are taken. For the sake of comparison, the parameters of the intermediate structure leading to the epoxide are given [26]: C_1 and C_2 denote carbon atoms of the double bond.

	A1	**A2**	Isolated species	Epoxide intermediate
Distances R [Å]/bond orders				
Mn–O	1.55/2.12	2.09/0.30	1.54/2.22	1.99/0.38
O–Cα	–	1.45/0.91	1.42/1.03	–
O–H	2.18/0.03	1.00/0.62	0.98/0.79	–
O–C_1/O–C_2	–	–	–	1.45/0.96
C_1–C_2	–	–	–	1.48/0.99
Mn–Cl	2.20/1.21	2.12/1.26	2.20/1.20	2.14/1.24
Charges/spin densities				
Mn	0.30/–	0.44/2.42	0.28/–	0.48/–
O	−0.22/–	−0.63/0.00	−0.17/–	−0.33/–
Cl	−0.15/–	−0.18/0.04	−0.16/–	−0.20/–
c-hex	0.00/–	0.79[a], 0.16[b]/–	0.00/–	0.55/–
P	0.07/–	−0.42/−0.46	0.05/–	−0.50/–
$\langle s^2 \rangle$	0.00	2.00	0.00	0.00

[a] c-Hexene molecule.

[b] c-Hexenol molecule.

density functional theory to study the hydroxylation pathway. To date theoretical studies of allylic oxidation addressed mainly reactions of oxoiron species, in view of their direct relation to the catalytic function of P-450 [27–47]. Manganese porphyrins have been studied by theoreticians only recently, in the context of catalytic hydroxylation of toluene [48–50], but the role of manganese porphyrin in allylic oxidation of cyclohexene is approached for the first time.

2. Theoretical model and methods

To perform the reported studies the density functional theory (DFT) within StoBe computer program [51] is applied. For geometric structure evaluation the LDA-VWN functional [52] is used. Electronic parameters of the systems are obtained at the GGA-RPBE level [53,54], and extended all-electron basis sets of contracted Gaussians are applied [55]. For singlet state systems calculations are performed in a spin-polarized manner. The charge transfers accompanying complex formations are accounted for by changes of Mulliken charges [56] for selected atoms or fragments of investigated systems. The covalent strength of the bonds is measured by Mayer bond indices [57]. Additionally, spin densities are computed.

As a case study the chloro- oxo- manganese porphyrin complex [MnPOCl] has been chosen, due to its high activity in catalytic hydroxylation reactions [1]. In order to investigate the first step of hydrocarbon oxidation, i.e. the hydrogen atom binding process on the manganese porphyrin complex, the [MnPClO] system is considered; for the mechanistic studies the model was extended by the whole cyclohexene molecule. During all calculations the geometry of the porphyrin ring is frozen, upon assumption that it is not affected by the investigated reactions. This assumption is justified by the results obtained for hydroxylation of toluene by manganese porphyrin [48], where full structure optimization was carried out and no changes in the porphyrin ring geometry were reported. Thus, the geometry optimization encompasses manganese, oxygen, chlorine and c-hexene. For all considered structures different possible multiplicities were taken into account, but only structures characterized with the lowest total energies are described in the text. The present calculations are performed in vacuum, the solvent effect on the geometries and energies of the obtained structures is not considered. The experiments with cyclohexene are performed in benzene or other apolar solvents and the process is expected to be charge neutral, therefore it is anticipated that the solvent would have only minor impact on the mechanism of the studied catalytic process.

3. Results and discussion

3.1. Mechanistic insights into allylic oxidation of cyclohexene

In agreement with the common view describing allylic oxidation of cyclohexene as a radical process, the first step considered in the present studies is the cyclohexene radical formation where the hydrogen atom from the substrate may be abstracted by the catalyst. At the oxo-porphyrin complex there is a number of possible sites to which the hydrogen radical may be bound. Essential for the hydroxylation process is hydrogen atom binding by the oxo ligand, and this option is considered in the calculations. Other possibilities, not relevant for hydroxylation, include attack at the porphyrin ring, with possible destruction of the conjugate system of double bonds, or attachment to the chlorine ligand.

Formation of alcohol requires that the Cα–H bond of cyclohexene points towards the catalyst oxo-group. For such an orientation the reaction pathway is considered. The distance between the catalyst oxo group and H atom of the Cα–H bond is chosen as a reaction coordinate R, that changes from 5.0 Å to 1.2 Å, with step equal to 0.2 Å.

On the examined path, the physisorption structure **A1** is found (see Fig. 1 and Table 1). The substrate is distant by 2.18 Å from the catalyst active site. None of the structures, neither that of the catalyst nor that of the substrate is changed in the resulting physisorbed complex. At this stage no electron transfer between the substrate and the catalyst is observed. The only change induced by the approaching cyclohexene molecule is that the oxo ligand

Table 2

Calculated parameters of the [MnPOHCl] structure resulting from H binding by [MnPOCl]. For comparison, data for [MnPOCl] are listed from [58].

	[MnPOHCl]	[MnPOCl]
Distances R [Å]/bond orders		
Mn–O	1.75/1.20	1.54/2.22
O–H	0.99/0.75	–
Mn–Cl	2.16/1.25	1.30/1.20
Charges/spin densities		
Mn	0.30/1.37	0.28/–
O	−0.24/−0.06	−0.17/–
Cl	−0.16/0.04	−0.16/–
H	0.12/0.01	–/–
OH	−0.12/−0.05	–/–
P	−0.02/−0.36	0.05/–
$\langle s^2 \rangle$	1.00	0.00

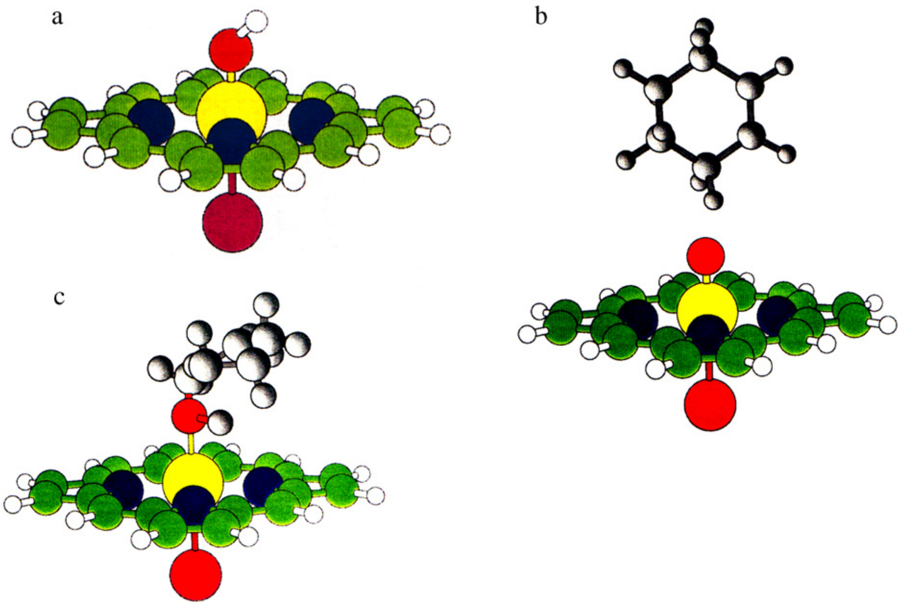

Fig. 1. Geometry structures of the investigated complexes: (a) [MnPOHCl] (binding energy of an isolated H atom to [MnPOCl]: dE = −71.7 kcal/mol), (b) physisorbed **A1** structure (relative energy in respect to isolated [MnPOCl] and cyclohexene: dE = 0.6 kcal/mol) and (c) intermediate structure **A2** (relative energy in respect to isolated [MnPOCl] and cyclohexene: dE = −9.4 kcal/mol).

becomes slightly more nucleophilic ($\Delta q = -0.05$) as a result of the charge shift from the rest of the complex. The similar intermediate 'prereaction' complex was observed also in case of toluene oxidation, as reported by Balcells et al. [48].

The adsorption of the hydrogen atom on the O═Mn group, which follows the formation of physisorbed **A1** structure, leads to the formation of the OH ligand (see Fig. 1 and Table 2 for the computed parameters of the investigated system), whose binding energy amounts to −48.6 kcal/mol. The ligand is characterized by a small negative charge (−0.12). The Mn–O bond changes its character from double to single, what is reflected by the change of its length from 1.54 Å to 1.75 Å and its bond order from 2.20 to 1.20. The atomic charges of both chlorine and manganese ions are not changed upon the hydrogen binding process. The Mn–Cl bond is shortened by 0.04 Å, and its bond order slightly increases (by 0.05). Similar hydroxo intermediate has been also observed by Balcells et al. [48,50] for toluene hydroxylation.

Next, a situation in which Cα–H bond is cleaved and cyclohexene radical diffuses away from the catalyst active site is examined to check on the efficiency of radical trapping. The energy profile (see Fig. 2) indicates that radical dissociation would be disadvantageous from thermodynamic point of view ($\Delta E = 12.9$ kcal/mol). This conclusion may be further supported by the results of the DFT calculations on hydroxylation of toluene [48] in which no dissociation of intermediate toluene radical is observed. Therefore, a possibility to form an alcohol molecule on the catalyst active site as a result of rearrangement involving hydrocarbon radical and OH group, without prior diffusion of the radical, is considered.

The optimized alcohol bound structure (in Table 1 referred to as structure **A2**, see also Fig. 1) has lower total energy by −22.3 kcal/mol than the sum of the energies of the [MnPClOH] complex and the cyclohexene radical. This confirms that the proposed pathway is a conceivable way for alcohol formation. Such a rearrangement is known as oxygen rebound mechanism.

In order to study the hydrogen migration process accompanying the insertion of the oxygen atom into Cα–H bond, the following reaction path is examined. The Cα–O–H valence angle is chosen as a reaction coordinate R and is changed from 0° to 60°. The calculation scheme applied here consists of point by point geometry

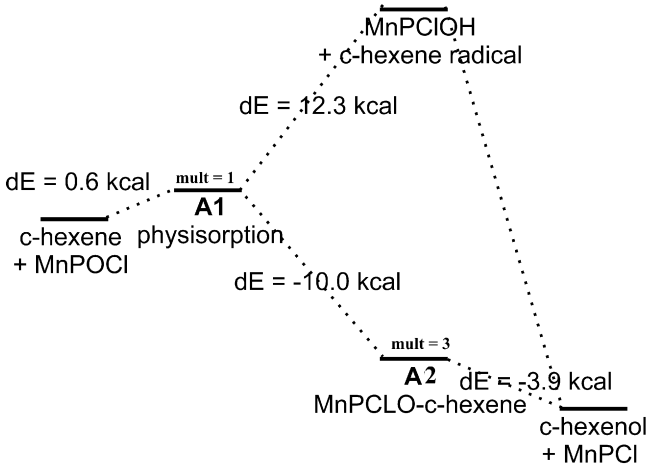

Fig. 2. Energy diagram for different possible mechanisms leading to the alcohol formation.

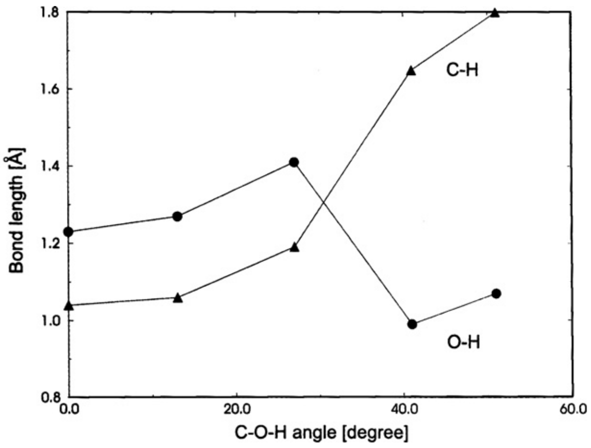

Fig. 3. Chart showing the O insertion into the Cα–H bond.

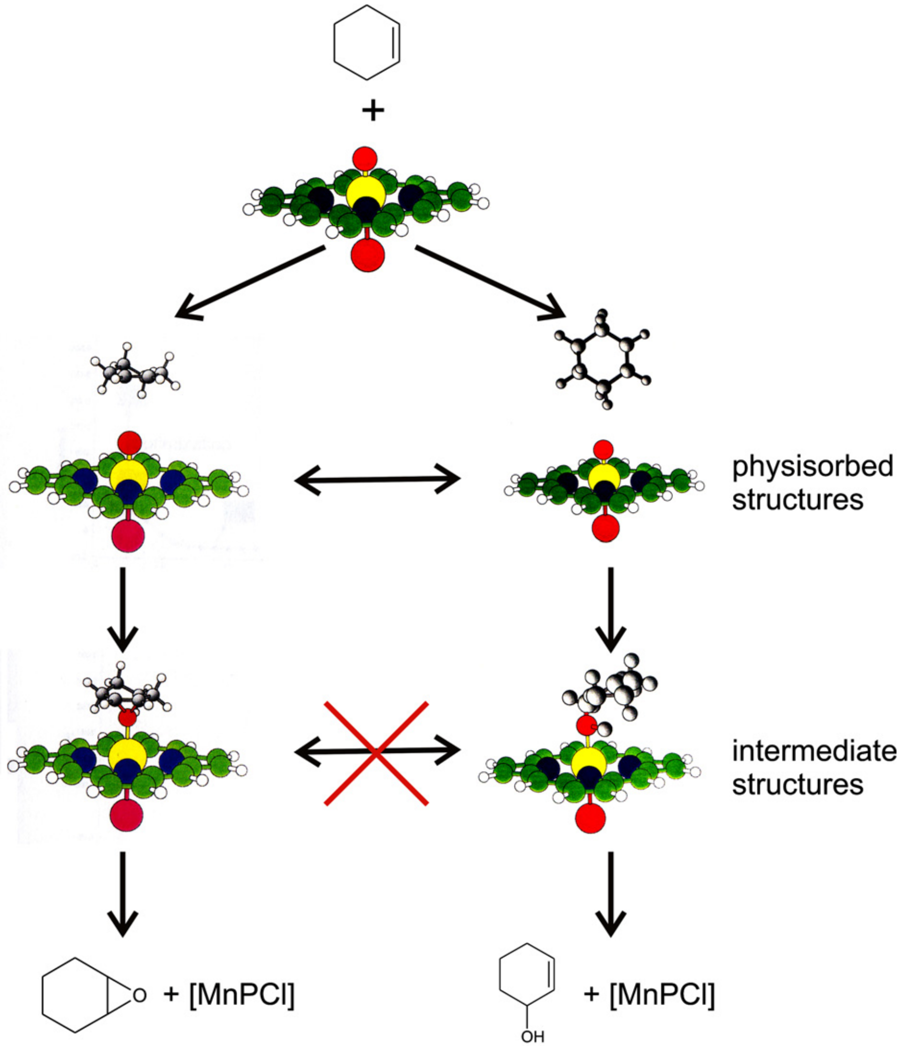

Fig. 4. Reactivity of cyclohexene.

optimizations in which the Cα–H and O–H bond lengths are optimized. The rest of the cyclohexene molecule is also freed. Fig. 3 shows the calculated dependence of the Cα–H bond length on the Cα–O–H valence angle. The analysis of the diagram demonstrates that the new bond is formed when the Cα–O–H angle equals to 41°.

The analysis of the parameters describing structure **A2** shows that after the reaction the obtained alcohol is bound to the catalyst active center (Mn–O bond distance being equal to 2.09 Å with bond characterized by bond order equal to 0.30). The bond distances (1.45 Å and 1.00 Å) and bond orders (0.91 and 0.62) characterizing Cα–O and O–H bonds indicate that the alcohol molecule is formed (for the isolated cyclohexenol the respective values amount to 1.42 Å and 0.98 Å and 1.03 and 0.79). The Mn–Cl bond is shortened by 0.08 Å in comparison to its initial value (2.20 Å), and, as a consequence, its bond order increased by 0.06 and in **A2** intermediate amounts to 1.26. While bound to the catalyst, the alcohol moiety is positively charged ($q = 0.16$). Its formation is accompanied by the reduction of the porphyrin ligand ($\Delta q = -0.47$) and the oxidation of the manganese ion ($\Delta q = 0.16$). The chlorine ion is practically inactive in the above mentioned electron transfer processes.

In order to obtain alcohol structure, a spin crossing on the reaction pathway is required and, as a result, **A2** structure is characterized by multiplicity of 3. The unpaired electrons are located mostly on manganese ion (spin density of 2.42) and are antiferromagnetically coupled with those on porphyrin ligand (spin density of −0.46). The presence of spin crossing in reactions with transition metal complexes, especially porphyrins, is a well known fact in porphyrin chemistry, reported also for systems containing manganese ion [1,48–50]. In fact, spin crossing is indispensable for the reaction to occur, as proven by previous and present studies.

Results of our calculations agree fully with the mechanistic considerations originally proposed for allylic oxidations [2–22]. The first step of the reaction comprises hydrogen atom abstraction from the substrate molecule and formation of the hydroxo group bound to the porphyrin. Next, the resulting hydroxo species is transferred back to the substrate radical and the alcohol molecule is formed. Thus, the reactivity pattern of manganese porphyrins in cyclohexene hydroxylation is similar to allylic oxidation mechanism reported by DFT studies for iron and ruthenium porphyrins [27–47,59].

3.2. *Allylic oxidation vs. epoxidation of cyclohexene*

It is of interest to compare the present results with our earlier studies of the epoxidation pathway. Fig. 4 gathers key intermediates found for both reaction pathways. Initially, in both cases, the prereaction complexes, described as physisorbed structures, are formed. These species are loosely bound to the catalyst molecule. Almost no changes in their geometries are observed, neither charge transfers between the two reactants are found. In case of hydroxylation process, cyclohexene molecule points with its allylic C–H bond towards the oxo ligand of the manganese porphyrin, whereas parallel orientation of cyclohexene ring and porphyrin moiety with double bond above the oxo ligand is required for epoxidation. It should be stressed that although mutual orientation of the reagents would determine further pathway of cyclohexene transformation, at this stage, when reaction conditions permit, the substrate molecule may easily undergo rotation or translation and change the mode of physisorption. Indeed, no energy barriers were found in [26] for translation of physisorbed species.

However, once a particular intermediate is formed, its structure clearly indicates that reaction may proceed further along one reaction pathway only. In this sense, our studies fall in line with the postulate of Groves and Gross [19] that the epoxidation and the hydroxylation pathways do not intersect. Their conclusion, based on the experimental evidence, was drawn for iron porphyrins, but our theoretical studies allow for the extension of this observation also on manganese systems. In view of strong bonding between cyclohexene and oxo-porphyrin moiety in structure **A2** leading to alcohol (Table 1), a rearrangement of atoms to form intermediate required for epoxide, is unlikely.

Last but not least, the structure representing the key intermediate on the reaction pathway leading to epoxide, lies lower by 4.2 kcal/mol on the potential energy surface than **A2** structure, leading to alcohol. This result may help to explain why the epoxide is the main product observed in case of cyclohexene oxidation by manganese porphyrin in solution.

Noteworthy, the intermediate epoxide structure is characterized by a significant charge accumulated on the cyclohexene moiety (charge transfer of 0.55) and elongation of Mn–O bond from 1.54 Å to 1.99 Å (see Table 1). This result is in line with the concerted oxygen and electron transfer within epoxide intermediate proposed by Ostovic et al. [18].

4. Conclusions

DFT calculations show that a physisorbed prereaction complex is formed in the first stage of interaction between cyclohexene and manganese porphyrin. Subsequent cyclohexen-2-ol formation proceeds via oxygen rebound mechanism. The hydrogen atom is abstracted by the catalyst oxo group. The analysis of the energy profile for the reaction indicates that the alcohol is formed after the hydrogen migration step without prior dissociation of the hydrocarbon radical from the catalyst active site. The reaction involves spin crossing since the catalyst is initially in its singlet state, while during catalytic process it is promoted to its triplet state. The key intermediate on the reaction pathway leading to epoxide lies lower on the potential energy surface than the intermediate leading to alcohol, which explains high reactivity of manganese porphyrins toward olefin epoxidation. Although allylic hydroxylation and epoxidation are initiated by different physisorbed prereaction complexes, they may transform into each other. Once beyond the stage of physisorption, the substrate is not able to switch easily between the reactivity funnels. The intermediate structures, found for both pathways, clearly indicate that each may lead to only one reaction product.

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