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Epoxidation of cyclohexene catalyzed by manganese porphyrins: Ab initio DFT studies

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Abstract

The reaction of catalytic epoxidation of cyclohexene molecule over the manganese porphyrin has been studied by the DFT methods. Parallel and perpendicular mutual orientations of reacting species have been considered leading to eight different reaction paths, with the cyclohexene species approaching the catalyst oxo-group from above and from the side of the porphyrin plane (at three different heights). Three possible positions in which the cyclohexene molecule may physisorb on the catalyst have been found. Results of calculations indicate that the formation of the epoxide may occur when the cyclohexene molecule approaches the catalyst oxo-group from above in a parallel orientation.

Keywords: Oxo-group; Cyclohexene; Manganese porphyrin; DFT calculations

1. Introduction

Synthetic metalloporphyrins are known to be efficient catalysts for oxidation of hydrocarbons in the liquid phase. A variety of metal ions have been tested as central atom, among them manganese which, when coordinated by the porphyrin ligand, shows a remarkable catalytic activity. It has been found that manganese porphyrin and its derivatives are efficient homogenous catalysts for epoxidation of olefins [1]. There is a number of hypotheses concerning the reaction mechanism, all of which are based on the experimental data [2]. In the present work theoretical investigations have been employed to clarify this problem by modeling the reaction paths, which, in the oxidation of cyclohexene over manganese porphyrin, lead to the formation of the cyclic epoxide. The present theoretical study is intended to define the main steps of the investigated reaction in order to verify the mechanism of the formation of cyclic alkane oxide.

2. Model and method

The chemical system may be described in terms of mesoscopic parameters such as temperature, pressure, the presence of solvent, the concentration of reactants, etc., and microscopic ones, such as electronic states of reactants, the symmetry and energy of reacting orbitals, etc. Each of them influences the chemical reaction by changing its energetics. In our work we focused only on determining the influence of mutual orientation of the reacting molecules on the energetics of the cyclohexene epoxidation over manganese porphyrin.

It is known that the first step of the catalytic reaction is the formation of the oxomanganese porphyrin species. The resulting complex acts as an oxidizing agent and reacts with the substrate to form the epoxide [2]. Thus, the system to be considered in the theoretical modeling consisted of the oxomanganese porphyrin and the cyclohexene molecule. Solvent effect was neglected.

Quantum chemical DFT method within the Vosko–Wilk–Nusair LDA functional was chosen to study the reaction [3]. In order to obtain more meaningful energetics, the energies of the most important stages were recalculated within general gradient approximation by using revised Perdew–Burke–Ernzerhof functional [4,5]. The method used in this study is widely applied for catalytic processes, both heterogenous and homogenous. The non-local RPBE functional is especially designed to reproduce the energetics of chemisorption and physisorption in systems having transition metal elements. One should stress that, in this approach, of primary importance are the energy differences between different structures rather than the absolute energy

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values. Kohn–Sham orbitals were described by extended all-electron basis sets of contracted Gaussians [6,7]. The electronic structure of the system was discussed by means of electronic parameters such as bond orders obtained according to Mayer analysis [8,9]. The calculations were performed using StoBe computer code [10].

Initially, the cyclohexene molecule approached the oxo-group of the catalyst along the direction perpendicular to the porphyrin plane. The distance between the oxo-group and the double bond of the olefin was taken as a reaction coordinate (R). Two different orientations of the reacting species were investigated. In the first, the cyclohexene ring was parallel to the porphyrin ring (Path 1), in the other the orientation of cyclohexene was perpendicular to the porphyrin plane (Path 2). For both paths the sets of single point LDA calculations were done for R changing form 5.0 to 1.2 Å with step equal to 0.2 Å. If thought necessary, geometry optimizations were performed. Relevant groups of atoms that are cyclohexene molecule, manganese, oxo and chlorine ions were allowed to move. Furthermore, for the values of R corresponding to the minima of the reaction curves ($R = R_{\mathrm{min}}$), the additional reaction paths were studied as described below. The cyclohexene was approaching the catalyst along the line parallel to the porphyrin plane. For that reason the new parameter (S) was introduced as the distance between the R_{min} and the olefin double bond. Single point calculations were performed for S varying from 0.2 to 8.0 Å with step equal to 0.2 Å for every path. Finally, the case in which the cyclohexene approached the catalyst having its double bond at the height of the oxo-group was examined. Here, the reaction coordinate S, defined in a similar way as the parameters previously described, changed from 1.0 to 8.0 Å with step equal to 0.2 Å. In each case, two mutual orientations of the reactants, parallel and perpendicular, were considered. All studied paths are schematically presented in Fig. 1.

3. Results

Table 1 summarizes the most important structural and electronic parameters describing selected intermediate structures for the studied paths, whereas Fig. 2 shows the energy diagrams for the paths in which the cyclohexene molecule is approaching the catalyst from above (Paths 1 and 2). As shown in Fig. 2 at large distances ($R > 2.8$ Å) Path 2 is energetically slightly more favorable than Path 1. This result may suggest that the cyclohexene species prefers perpendicular orientation when distant from the catalytic center. Both energy curves have shallow minima at $R = 2.8$ Å. The systems corresponding to both structures are referred to as Structure 1 and Structure 2 for Path 1 and Path 2, respectively. The geometry optimizations for both structures have not led to significant changes in geometry of the systems or in their energies. As can be seen from Table 1, the length and order of the C1–C2 bond of the olefin (1.34 and 1.89/1.85, respectively) is intact in both structures, as compared to these values in the isolated cyclohexene molecule (1.34 and 1.89, respectively). At the same time, the distance between the catalyst oxo-group and the olefine double bond is equal

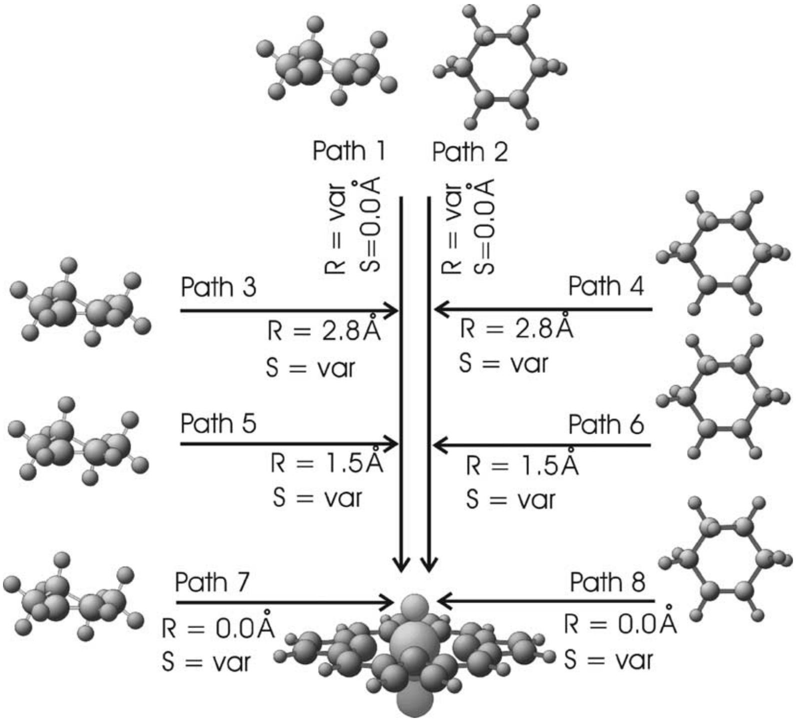

Fig. 1. The schematic presentation of the investigated paths.

Table 1
The main structural and electronic parameters describing the most important structures found

	Structure 1	Structure 2	Structure 3	Structure 4	Structure 5	Structure 6	Isolated species
Distances (Å)							
Mn–O	1.54	1.54	1.54	1.87	1.55	1.54	1.54
Mn–Cl	2.20	2.20	2.20	2.13	2.21	2.20	2.20
O–C1/O–C2	2.88/2.88	2.88/2.88	1.64/1.64	1.43/1.43	2.89/2.89	1.37/1.37	1.43/1.43
C1–C2	1.34	1.34	1.34	1.50	1.34	1.34	1.34/1.47
Bond orders (a.u.)							
Mn–O	2.13	2.03	0.71	0.40	2.15	0.65	2.22
Mn–Cl	1.22	1.21	1.20	1.36	1.20	1.20	1.20
O–C1/O–C2	0.01/0.01	0.03/0.03	0.66/0.66	0.84/0.84	0.02/0.02	0.70/0.67	0.97/0.97
C1–C2	1.89	1.85	0.97	0.99	1.76	0.94	1.89/1.15

MnPOCl, cyclohexene molecule and epoxide molecule were taken as isolated molecules. C1 and C2 denotes C atoms of the double bond. In case of C1–C2 distance the first value corresponds to the cyclohexene molecule, the other to the epoxide one. Distances are in Angstroms, bond orders in atomic units.

to 2.8 Å. This value corresponds to the O–C1/O–C2 bonds length equal to 2.88 Å. The order of such a long bond is negligible and is equal to 0.01 and 0.03 for Structure 1 and Structure 2, respectively. Therefore, it may be deduced that both structures describe the situation in which the cyclohexene molecule is physisorbed at the catalytic center. Energetic cost of physisorption, calculated as a difference between the energy of the system and the sum of energies of the isolated MnPOCl and cyclohexene molecules, is equal to 3.7 and 3.1 kcal/mol for Structures 1 and 2, respectively. The cyclohexene molecule seems to be physisorbed either as Structure 2 or as Structure 1; the difference between the energies of both systems is too small to allow one to draw a definite conclusion.

As shown in the energetic profile characterizing Path 2 (Fig. 2), for shorter distances the energy curve steadily increases indicating a repulsive interaction between the reacting molecules. In contrast to Path 2, the curve describing Path 1 possesses a minimum at $R = 1.5$ Å connected with Structure 3. The main parameters describing Structure 3 are summarized in Table 1. This structure is characterized by O–C bond, which is longer (1.64 Å) that the corresponding bond in the epoxide molecule (1.43 Å). The bond order of this bond is 0.66, which is less by 0.31 than in the isolated molecule of the epoxide. Structure 3 was fully optimized keeping porphyrin ring frozen. Table 1 summarizes the parameters describing the resulting optimized structure, referred to as Structure 4. As one can see, the bond distance

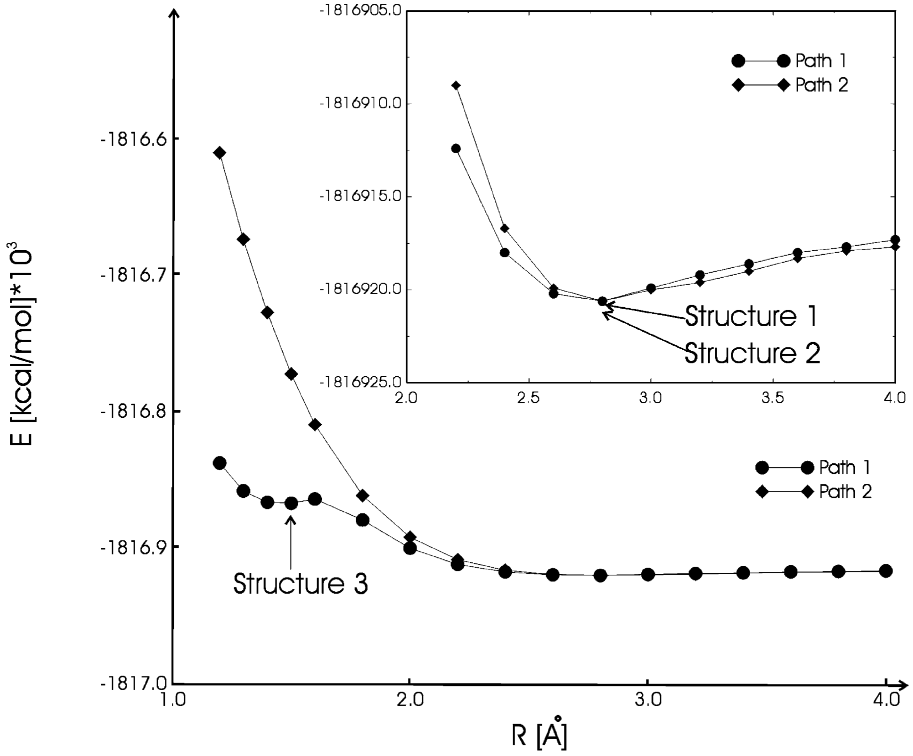

Fig. 2. The energy curves describing Paths 1 and 2. Energies are in kcal/mol, distances are in Å.

and bond order characterizing C1–C2, O–C1, and O–C2 bonds indicate that the epoxide molecule has been formed. The C1–C2 bond has lengthened by 0.16 Å from its initial length, and now is longer only by 0.03 than in the isolated epoxide species. The O–C1 and O–C2 distances are equal to their values in the isolated product. The analysis of bond orders indicates that all these bonds are weaker than in the epoxide itself. The order of both O–C bonds is equal to 0.84, whereas in the epoxide this value is equal to 0.97. Similarly, the C1–C2 bond order is smaller by 0.16 in the resulting structure than in the isolated epoxide. The formed epoxide is still adsorbed on the manganese porphyrin. Noteworthy, in the resulting structure the Mn–O distance increased from 1.54 to 1.87 Å and, what follows, its bond order diminished from 2.22 to 0.40. This might have been the cause of the previously described differences between structural parameters describing the resulting product and the isolated epoxide molecule. The change in Mn–O distance leads to the decrease in the Mn–Cl bond length from 2.20 to 2.13 Å. As a result, this bond becomes stronger. It is reflected by increase of its bond order by 0.16 in comparison to the isolated catalyst molecule. The formation of Structure 4 from the isolated molecules of cyclohexene and catalyst requires almost no energy input (costs only 1.4 kcal/mol).

Next, the paths in which the cyclohexene species approaches the catalyst along the direction parallel to the porphyrin ring plane at the level of 2.8 Å above the catalyst oxo-group (Paths 3 and 4, see Fig. 1) are considered. The changes in energy in both cases are negligible and no minima are observed on either of the curves.

By contrast, the analysis of further paths (Paths 5 and 6, see Figs. 1 and 3), when the substrate diffuses towards the catalytic center along the direction parallel to the porphyrin plane at the height of 1.5 Å above the catalyst oxo-group, reveals that there is an additional possibility for the cyclohexene to physisorb. Namely, in the case of perpendicular orientation of the reacting molecules (Path 6), there is a shallow minimum on the energy curve for $S = 2.0$ Å. This defines the structure in which the distance between the catalyst oxo-group and the olefine double bond is equal to 2.5 Å. The geometry optimization of that structure (keeping porphyrin ring frozen) results in species described as Structure 5 (see Table 1) in which the O–C bond lengths are equal to 2.89 Å and their orders are equal to 0.02. Similarly to species denoted as Structures 1 and 2, in this structure the C1–C2 bond preserves its character. Its length is the same (1.34 Å) and its bond order is slightly smaller (1.76 in comparison to 1.89) as in the isolated cyclohexene molecule. As stated before, this point at the reaction path describes the structure in which the substrate is physisorbed at the catalyst (the energy needed for this physisorption is equal to 5.8 kcal/mol, which is more than to physisorb cyclohexene in a way defined by Structures 1 and 2).

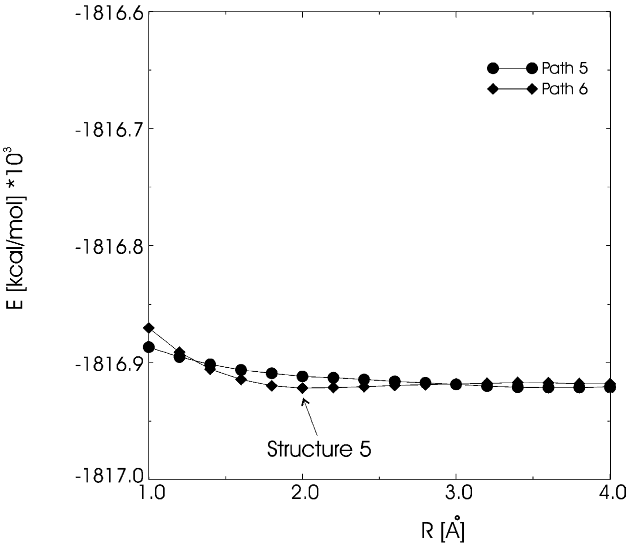

Fig. 3. The energy curves describing Paths 5 and 6. Energies are in kcal/mol, distances are in Å.

Finally, when the cyclohexene approaches the catalyst oxo-group parallel to the porphyrin ring plane at the height of the catalyst oxo-group (Paths 7 and 8, see Fig. 1), the energy curves of both systems drastically increase once the cyclohexene arrives above the porphyrin ring plane. This is due to the strong repulsive interaction between the two reacting molecules resulting from a very short distance between them. In general, the trend is continued for Path 7. For Path 8, by contrast, after the large energy barrier of 816.5 kcal/mol a minimum appears at $S = 1.2$ Å. This corresponds to Structure 6 (see Table 1), in which O–C bond lengths are equal to 1.37 Å, and their bond orders are equal to 0.67 and 0.70. The C1–C2 bond has length of 1.34 Å, while, as a result of interaction with the catalyst oxo-group, its bond order diminished to 0.94. This structure might represent the precursor for the reaction of the epoxide formation, however its total energy is by 220.0 kcal/mol higher than the one of Structure 3. Moreover, as stated before, much energy is needed to make the substrate approach the catalyst along Path 8. Therefore, one may assume that the epoxide molecule would rather be formed in a way described by Path 1.

4. Conclusions

The cyclohexene molecule may become physisorbed at the distance of 2.8 Å from the catalyst active site, although the physisorption requires additional energy introduced to the system. Three possible structures describing physisorption have been found: Structures 1, 2 and 5 (see Figs. 2 and 3). Taking into account the energetics of the process, Structure 2 is the most probable to occur in real system although the energy differences among Structures 1, 2 and 5 do not allow for the definite indication of the physisorbed structure. Moreover, in the way defined by Path 1 the epoxide precursor is formed. This may be explained in terms of Frontier Orbital Theory. The advantageous overlap of reacting orbitals is possible only in case of parallel orientation of the reacting atoms. Such a mutual orientation of reacting molecules allows cyclohexene π orbitals and oxygen σ lone pairs to overlap in an effective way to form carbon–oxygen bond. Our calculations indicate that the formation of the epoxide on a catalytic center is an endoenergetic process with the total energy needed equal to 1.4 kcal/mol. However, it should be born in mind that in the real systems there are a number of factors, e.g. thermal vibrations, effect of solvent and concentration, that may change the order of energies of the investigated structures and, what follows, the proposed reaction pathway.

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