Activation of alkanes : the biomimetic approach

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Abstract

Two kinds of biomimetic systems based on metalloporphyrin catalysts are able to perform the selective oxidation of alkanes. The first systems associate a Fe(III) or Mn(III) porphyrin catalyst and an oxygen atom donor (PhIO, H_2O_2 and O_2+ a reducing agent). Their mechanisms are of the monooxygenase type and involve the transfer of an oxygen atom from high-valent metal-oxo active species to the alkane. Iron porphyrins bearing electron-withdrawing substituents on the β-pyrrole positions are highly active for alkane hydroxylation. The second systems oxidize alkanes to the corresponding ketones (and alcohols) by O_2 itself, without consumption of any reducing agent, in the presence of a (porphyrin) Fe(III)-OH catalyst after photochemical or thermal activation of its Fe-OH bond. Oxidation of alkanes by these systems seem to involve a "dioxygenase-like" mechanism with radicals like 'OH as active species and the intermediate formation of alkylperoxy radicals.

1. INTRODUCTION

The finding of efficient catalysts for the selective oxidation of organic molecules, under mild conditions, remains a difficult challenge in organic chemistry. There is an always increasing demand of more selective and efficient oxidation catalysts not only in fine chemistry but also in bulk chemicals manufacture. In that respect one must keep in mind that the synthesis of many of the main chemicals of industrial chemistry (terephthalic acid, ethylene oxide, phenol, propylene oxide...) involve the use of an oxidation catalyst. The problem of the activation of the inert C-H bonds of alkanes with the formation of C-OH bonds (eq. 1) under mild conditions remains a particularly difficult problem in fine chemistry (regioselective hydroxylation of steroids for instance) and in industrial chemistry (selective transformation of methane into methanol for instance). A possible strategy to find new selective oxidation catalysts is to mimic the enzymatic systems which have been selected by living organisms during life evolution.

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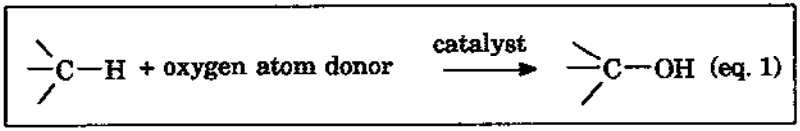
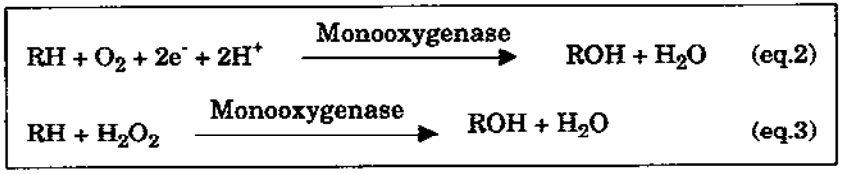
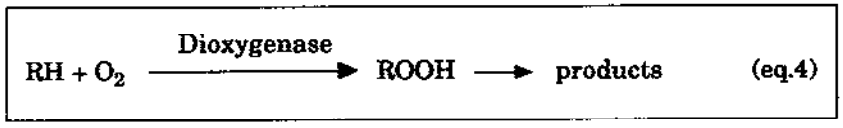


Ubiquitous enzymes called monooxygenases catalyze such a reaction. In fact, under physiological conditions, these enzymes most often use dioxygen as an oxygen atom donor and catalyze the activation of dioxygen with the consumption of two electrons and two protons and the insertion of one oxygen atom into the substrate and the formation of water (eq. 2). Moreover, at least in vitro, these monooxygenases also catalyze the transfer of an oxygen atom from other oxygen atom donors like H_2O_2 or ROOH to substrates (eq. 3).

Many of these monooxygenases contains an hemoprotein called cytochrome P450. Such cytochromes P450 are ubiquitous in living organisms. They catalyze some oxidative steps involved in the biosynthesis and biodegradation of endogenous compounds like steroids, and also play a key role in the oxidative metabolism of exogenous compounds of our environment such as drugs, allowing their functionalization and easier elimination out from the body [1]. Because of their ability to catalyze the insertion of an oxygen atom into almost any organic compounds including alkanes, these enzymes have attracted the interest of chemists involved in oxidation catalysis.

Another class of enzymes are able to activate C-H bonds of some particular substrates and to insert the two atoms of oxygen of dioxygen into these substrates. Because of this property, those enzymes are called dioxygenases. At least a priori, dioxygenase-type reactions (eq. 4) appear even more interesting than monooxygenase-type reactions, as, with dioxygenases, substrates are oxidized by O_2 and without stoichiometric consumption of any reducing agent. Unfortunately, dioxygenases known so far only catalyze the oxidation of a little number of substrates which are reactive by themselves like unsaturated fatty acids or phenols. Contrary to monoxygenases, dioxygenases so far reported cannot oxidize inert molecules like alkanes.





Many chemical model systems based on metalloporphyrin catalysts and mimicking cytochrome P450-dependent monooxygenases have been described in the literature during these last ten years [2-8]. In that context, the strategy that we have followed to develop new model catalytic systems will be illustrated in the first chapter. In the second chapter, some very recent preliminary results showing that the activation of alkanes by a dioxygenase-type

mechanism could occur during the oxidation of some alkanes by O_2 in the presence of iron porphyrin catalysts activated either photochemically or thermally, will be reported.

2. DEVELOPMENT OF EFFICIENT CHEMICAL SYSTEMS FOR ALKANE HYDROXYLATION MIMICKING CYTOCHROME P450

The catalytic cycle of substrate hydroxylation by cytochrome P450 [1] involves the transfer of an oxygen atom, either directly from oxygen atom donors like PhIO or H_2O_2 or from O_2 after its reduction by $2e^-$ and $2H^+$, to the Fe(III)porphyrin of its catalytic site (Figure 1). This should lead to a high-valent iron-oxo species, formally a Fe(V)=O complex. This species is reactive enough to abstract hydrogen atoms from alkanes leading to the corresponding alcohols in two steps (Figure 1).

Two strategies have been used to build up new catalytic systems mimicking cytochrome P450. In the first strategy, a metalloporphyrin used as an homogeneous catalyst is associated with an oxygen atom donor like PhIO or H_2O_2 (or O_2 in the presence of a reducing agent).

In the second one, a metalloporphyrin is included in a polymer matrix, preferably an inorganic polymer, and associated with the same oxidizing agents. Such catalysts are very easily separated from the reaction mixture and recycled. Moreover, they could lead to some substrate shape selectivity and regioselectivity of the catalyzed oxidations because of specific interactions of the substrates with the inorganic matrix.

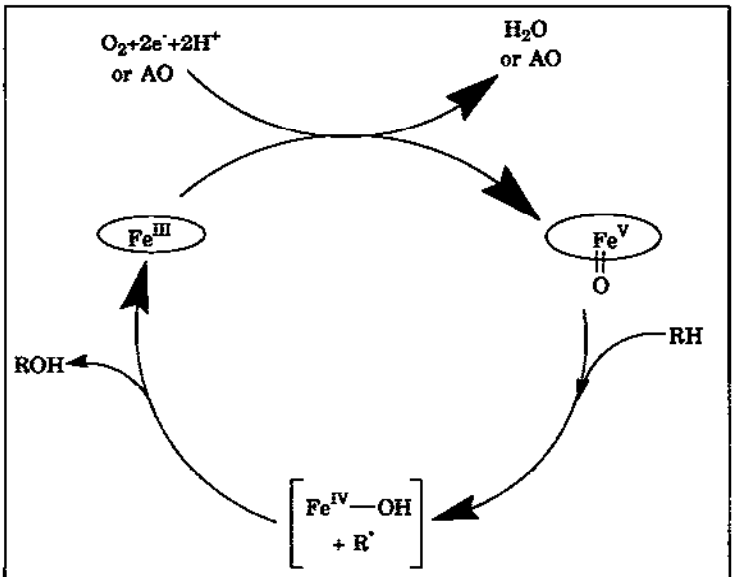


Figure 1. Simplified catalytic cycle for the hydroxylation of alkanes by O_2 (or by oxygen atom donors AO) and cytochrome P450

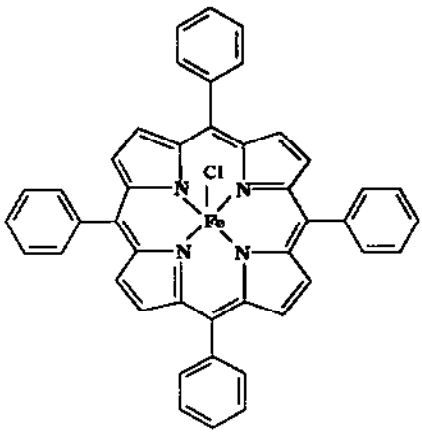
2.1. Towards very efficient metalloporphyrin catalysts for alkane hydroxylation by PhIO or H_2O_2

A huge effort of research has been made by many groups all over the world, during this last decade, in order to find efficient model systems mimicking either the short catalytic cycle of cytochrome P450, by the association of various Fe- and Mn-porphyrin catalysts with various oxygen atom donors (PhIO, ClO^-, ROOH, H_2O_2, $KHSO_5$, ClO_2^-, RCO_3H, R_3NO...), or the long catalytic cycle of P450 by using Fe- or Mn-porphyrins and O_2 in the presence of a reducing agent (BH_4^-, H_2+Pt, ascorbate, Zn...). The purpose of this paper is not to give a review of the corresponding results (in fact, this has been done in some recent review articles [2-8]) but more to illustrate recent tendencies in the field after a brief survey of its major developments during this last decade.

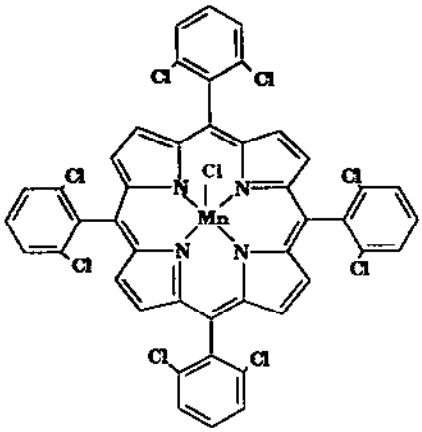
The first system described by J.T. Groves et al [9]., which is based on the very simple catalyst, Fe(TPP)Cl (Figure 2), and iodosylbenzene, PhIO, was found able to reproduce most cytochrome P450 reactions at least from a qualitative point of view. The main problem encountered with similar systems using PhIO or other oxygen atom donors and such simple catalysts, mainly Fe(TPP)Cl or Mn(TPP)Cl (that will be called **first generation catalysts** in the following of this paper), is a fast oxidative degradation of these catalysts under the strong oxidizing conditions used. Much better results were obtained with a **second generation** of Fe- and Mn-porphyrins bearing several electron-withdrawing substituents at each meso-aryl position [10]. This is the case of Mn(TDCPP=tetra-(2,6-dichlorophenyl)-porphyrin)Cl which contains eight chlorine substituents in ortho and ortho' positions of the meso-aryl groups. Besides the electron-withdrawing effect of these halogen substituents on the porphyrin ring, which is also found in the Fe and Mn complexes of another porphyrin of this generation TFPP (=tetra-pentafluorophenylporphyrin), the ortho-Cl substituents of TDCPP provides some steric protection to the Fe=O or Mn=O active species and prevents a too fast oxidative destruction of the porphyrin. For instance, Fe(TDCPP)Cl was found able to catalyze alkene epoxidation by C_6F_5IO with initial rates as high as 300 turnovers per second, and more than several hundreds of thousands moles of cyclooctene epoxide per mole of catalyst were obtained during oxidation of cyclooctene by PhIO in the presence of Mn(TDCPP)Cl.

Moreover, an efficient system [11] for hydrocarbon oxidation by diluted H_2O_2 was based on the use of two catalysts, Mn(TDCPP)Cl and imidazole, which was shown to act both as a ligand of Mn and as a base catalyst. This system involves a Mn(V)=O active species and performs a very efficient stereospecific epoxidation of alkenes. It also performs the hydroxylation of alkanes and the hydroxylation of aromatic compounds like anisole or naphthalene with good yields [12]. However, with poorly reactive substrates such as linear alkanes, the hydroxylation yields obtained with most Mn and Fe complexes of the second generation remain modest, and there is an important oxidative degradation of the catalyst.

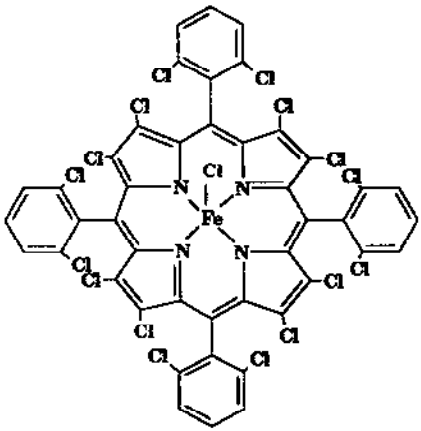
More recently, even more robust polyhalogenated metalloporphyrins involving withdrawing substituents (Br, Cl, F or SO_3H) on the β-pyrrole positions have been prepared and used as very efficient catalysts for



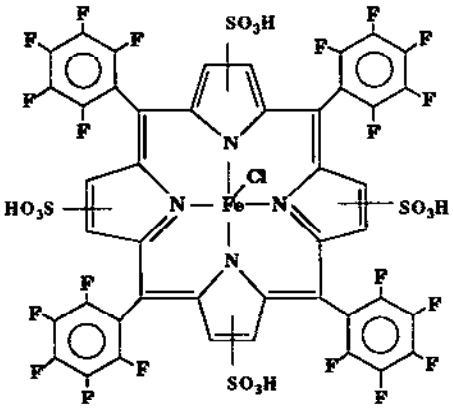
Fe(TPP)Cl



Mn(TDCPP)Cl



$Fe(TDCPCl_8P)Cl$



$Fe(TF_5PS_4P)Cl$

Figure 2. Formula of metalloporphyrins of the first, second and third generation used in model systems of cytochrome P450.

hydrocarbon oxidation [13]. The two following examples illustrate the better catalytic activity of these **third generation metalloporphyrin** catalysts.
As mentioned previously, Fe(TDCPP)Cl leads only to modest yields for the hydroxylation of the poorly reactive substrate, heptane, by PhIO. The corresponding third generation catalyst, $Fe(TDCPCl_8P)Cl$(Figure 2), which derives from Fe(TDCPP)Cl by substitution of its eight β-pyrrole hydrogens by chlorine substituents, is much more potent and leads to a very high yield of heptane hydroxylation (about 80%) within a few minutes at room temperature [14].

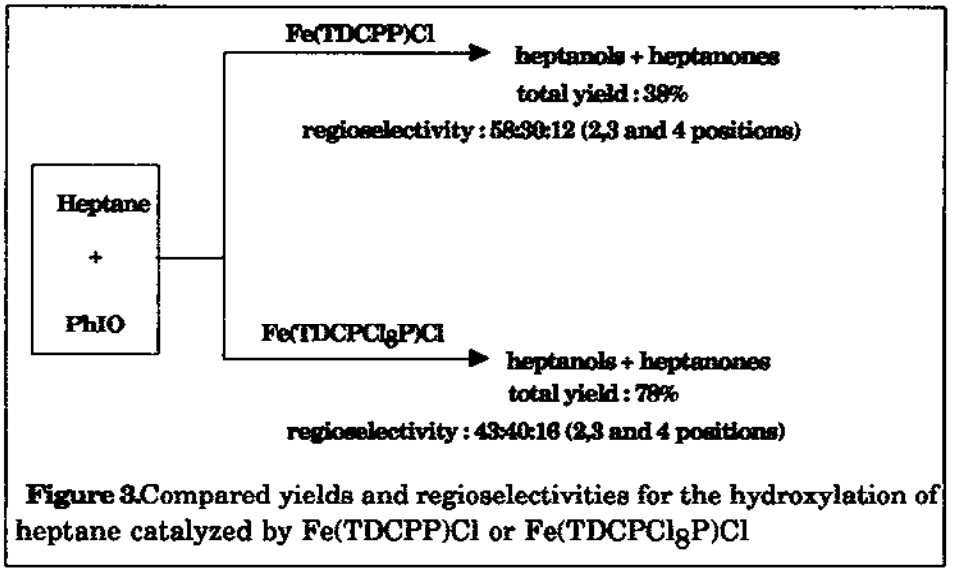


Figure 3. Compared yields and regioselectivities for the hydroxylation of heptane catalyzed by Fe(TDCPP)Cl or $Fe(TDCPCl_8P)Cl$

The main differences observed between the catalytic properties of the iron porphyrins of the second generation (like Fe(TDCPP)Cl) and of the third generation (like $Fe(TDCPCl_8P)$ Cl or $Fe(TDCPBr_8P)Cl$) should be due at least in part to an increase of the electrophilic character of the Fe(V) = O active species. In fact, the presence of eight β-Br or β-Cl subtituents were also found to greatly modify the structure of the porphyrin ring. In fact, a recent X-ray structure determination of $Ni(TF_5PBr_8P)$ [15] and recent studies of $TDCPCl_8PH_2$ and $TDCPBr_8PH_2$ by molecular mechanics calculations and semi-empirical quantum calculations [16] have clearly shown that all these third generation porphyrins adopt a saddle-shape structure for their tetrapyrrole ring, each pyrrole ring being tilted by more than 30°. Thus, whereas $TDCPPH_2$ exhibits a planar porphyrin ring and four meso-aryl groups almost perpendicular to this ring, $TDCPBr_8PH_2$ shows a saddle-shape structure with each meso-aryl group very much tilted in order to minimize the strong steric interactions between the meso-aryl and β-halogen groups. These structure differences between Fe(TDCPP)Cl and $Fe(TDCPCl_8P)Cl$ should lead to a different accessibility of the corresponding iron-oxo intermediates formed in the presence of PhIO. This should be at the origin of the very different regioselectivities observed for the

hydroxylation of heptane and pentane by PhIO catalyzed by these two iron porphyrins [14] (Figure 3).

2.2. Biomimetic oxidation catalysts supported on inorganic matrices

There are several possible strategies to obtain supported catalysts involving immobilized metalloporphyrins. We have selected mineral supports because of their inertness in strongly oxidizing media.Immobilization of metalloporphyrins was obtained by polymerisation of the porphyrin [17], simple adsorption of tetracationic or tetraanionic metalloporphyrins on silica or alumina [18] and covalent binding of metalloporphyrins to various supports [19]. A suspension of these supported Fe(III) or Mn(III) porphyrins very efficiently catalyzes the epoxidation of alkenes and the hydroxylation of alkanes by PhIO [20].

Another possible approach is to intercalate metalloporphyrins into layered minerals such as clays. The tetracationic Mn(TMPyP) catalyst was intercalated into the interlayer space of layered minerals [21], like montmorillonite, by simple ion-exchange with already present cations.An X-ray study of the obtained material indicated that most of the Mn-porphyrin has been intercalated, the interlayer distance being 4.2 Å(Figure 4). An intriguing property of this supported Mn-porphyrin is its particular ability to efficiently catalyze the hydroxylation of heptane or pentane. In fact, it gave a better yield for heptane hydroxylation (60%) than the same Mn-porphyrin simply adsorbed on silica (40%) and the Mn-porphyrin alone used as an homogeneous catalyst (3%) [21]. The origin of this particular efficacy of Mn(III)porphyrins supported on montmorillonite (either by intercalation as Mn(TMPyP) or by covalent binding as Mn(TF_5PP)) as catalysts for the hydroxylation of linear alkanes remains to be determined.

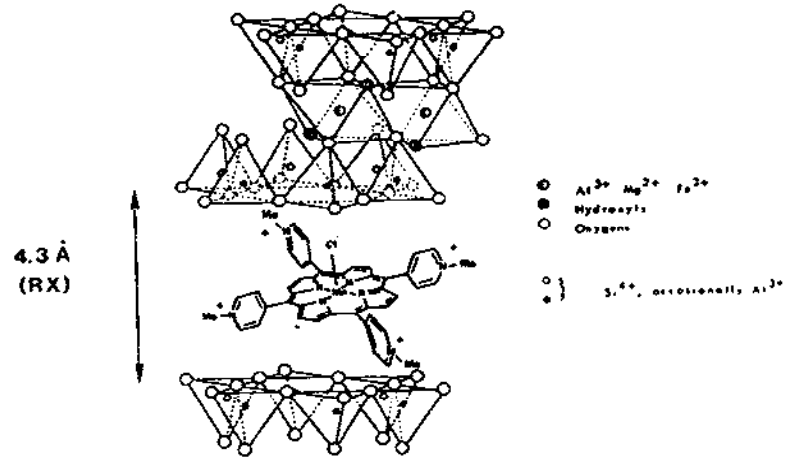


Figure 6. Schematic view of the supported catalyst involving the tetracationic Mn(III)porphyrin, Mn(TMPyP), intercalated into the interlayer space of montmorillonite.

Another interesting property of Mn(TMPyP) intercalated in montmorillonite is its ability to select substrates of different shapes. This was shown by experiments on the oxidation of two substrates in competition, adamantane, which is very reactive because of its tertiary CH bonds but relatively bulky, and pentane, which is one of the least reactive substrate for the electrophilic Fe(V)=O or Mn(V)=O species but is much less bulky than adamantane [21]. Oxidation of a pentane : adamantane (2:1) mixture by PhIO in the presence of Mn(TMPyP) itself or of Mn(TMPyP) adsorbed on silica led to the almost exclusive oxidation of adamantane (adamantanols+adamantanone : pentanols+pentanones=97:3). On the contary the oxidation of this mixture by PhIO in the presence of Mn(TMPyP) intercalated into montmorillonite led to a clearly different adamantanols : pentanols ratio of 77:23, which is much in favor of pentane. This is presumably due to the easier access of pentane, which is much less bulky than adamantane, to the Mn(V)=O active species burried in the interlayer space.

3. OXIDATION OF ALKANES BY O_2 ITSELF (IN THE ABSENCE OF A REDUCING AGENT) CATALYZED BY IRON PORPHYRINS : A DIOXYGENASE-LIKE REACTION ?

Iron porphyrins of the first or second generation, like Fe(TPP)Cl or Fe(TDCPP)Cl, are not able to catalyze the oxidation of cyclohexane by O_2 at room temperature in the absence of a reducing agent. However, we recently found that irradiation by a UV-visible light, of a solution of Fe(TDCPP)OH in O_2-saturated cyclohexane led to a progressive formation of cyclohexanone [22]. This formation was linear as a function of time and cyclohexanol was only detected as a very minor product. Cyclooctane was similarly oxidized with the formation of cyclooctanone as a major product. Other iron(III)porphyrins involving different axial ligands, like Fe(TDCPP)Cl and Fe(TPP)Cl, were much less efficient and less selective. Irradiation of Fe(TDCPP)OH in the presence of O_2 and cis-stilbene failed to give any formation of stilbene epoxide, and cyclohexene was mainly oxidized on its allylic positions under such conditions with the formation of cyclohex-2-enol and cyclohex-2-enone. Finally, the intermediate formation of $^{\cdot}OH$ radicals was detected by spin trapping experiments during cyclohexane oxidation by O_2 with photochemically-activated Fe(TDCPP)OH (Figure 5).

All these data are in favor of the "dioxygenase-like" mechanism shown on Figure 6. The first step is a photodissociation of the Fe(III)-OH bond of the catalyst leading to (TDCPP)Fe(II) and $^{\cdot}OH$. Abstraction of an hydrogen atom of cyclohexane by $^{\cdot}OH$ and reaction of O_2 with the cyclohexyl radical derived from this reaction shoud lead to a situation where a cyclohexylperoxy radical is formed in closed proximity of (TDCPP)Fe(II). A simple combination of this radical with (TDCPP)Fe(II) should lead to an alkylperoxo-Fe(III) complex which is known to undergo a fast dehydration reaction with the eventual formation of cyclohexanone and regeneration of the starting (TDCPP)Fe(III)-OH catalyst [22]. This oxidation of cyclohexane by this system is completely different from that catalyzed by cytochrome P450 and its model systems, as (i) the final product is cyclohexanone instead of cyclohexanol as with

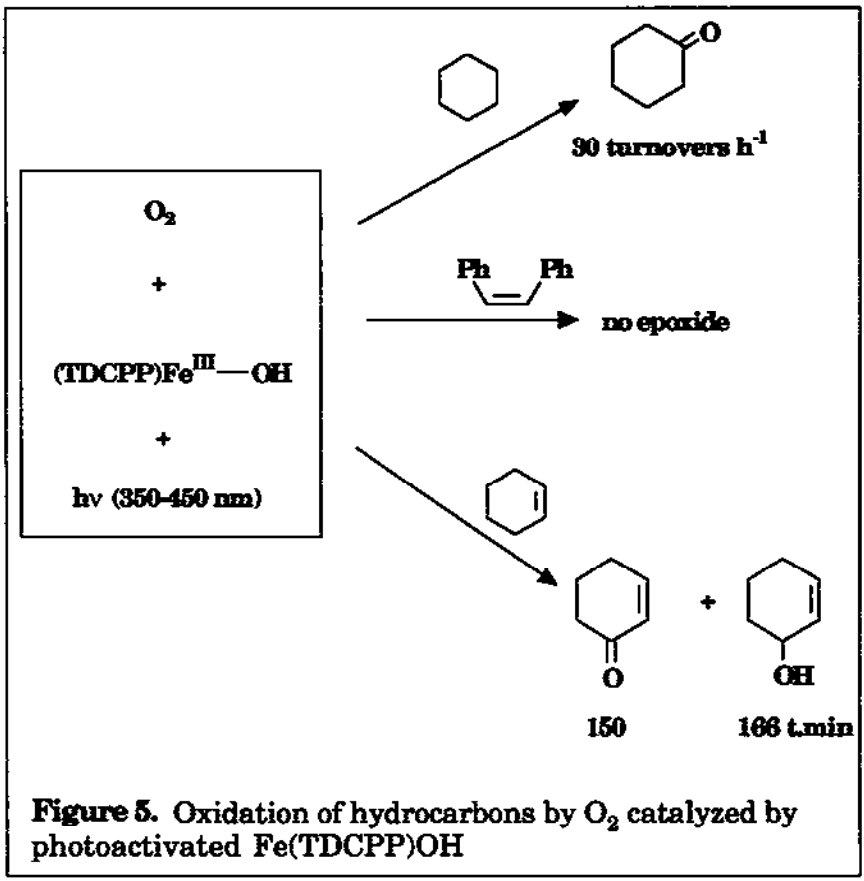


Figure 5. Oxidation of hydrocarbons by O_2 catalyzed by photoactivated Fe(TDCPP)OH

monooxygenases, and (ii) the active species is ·OH instead of Fe(V)=O. This explains why the Fe(TDCPP)OH-O_2-hv system contrary to monooxygenases does not epoxidize alkenes. The mechanism shown on Figure 6 is similar to that of dioxygenases as it involves the incorporation of the two oxygen atoms of O_2 into the substrate and a control of the intermediate peroxy radical by the Fe(II) catalyst which should explain the selective formation of cyclohexanone.

The key step for the oxidation of alkanes by O_2 shown in Figure 6 is the photoactivation of the Fe(III)-OH bond of the catalyst leading to the ·OH active species. Such an homolytic cleavage of the (TDCPP)Fe(III)-OH bond does not occur by simple heating of a solution of Fe(TDCPP)OH in O_2-saturated cyclohexane at 80°C as shown by the lack of any formation of cyclohexanone and cyclohexanol after 20h under these conditions. Presumably, the strength of the (TDCPP)Fe(III)-OH bond is too high to be homolytically cleaved by simple heating at moderate temperature. However it appeared to us that such an homolytic cleavage of a (porphyrin)Fe(III)-OH bond could be easier in the case of the porphyrins of the third generation mainly because of their greater ability to stabilize the Fe(II) state due to the presence of their electron-withdrawing β-

substituents. In agreement with this assumption, we found that heating an O_2-saturated solution of Fe(TDCPCl$_8$P)OH in cyclooctane or cyclohexane around 80°C led to an important oxidation of these alkanes into the corresponding ketones and alcohols (Figure 7). Reactions performed under identical conditions but in the absence of iron porphyrin did not lead to these oxidation products.

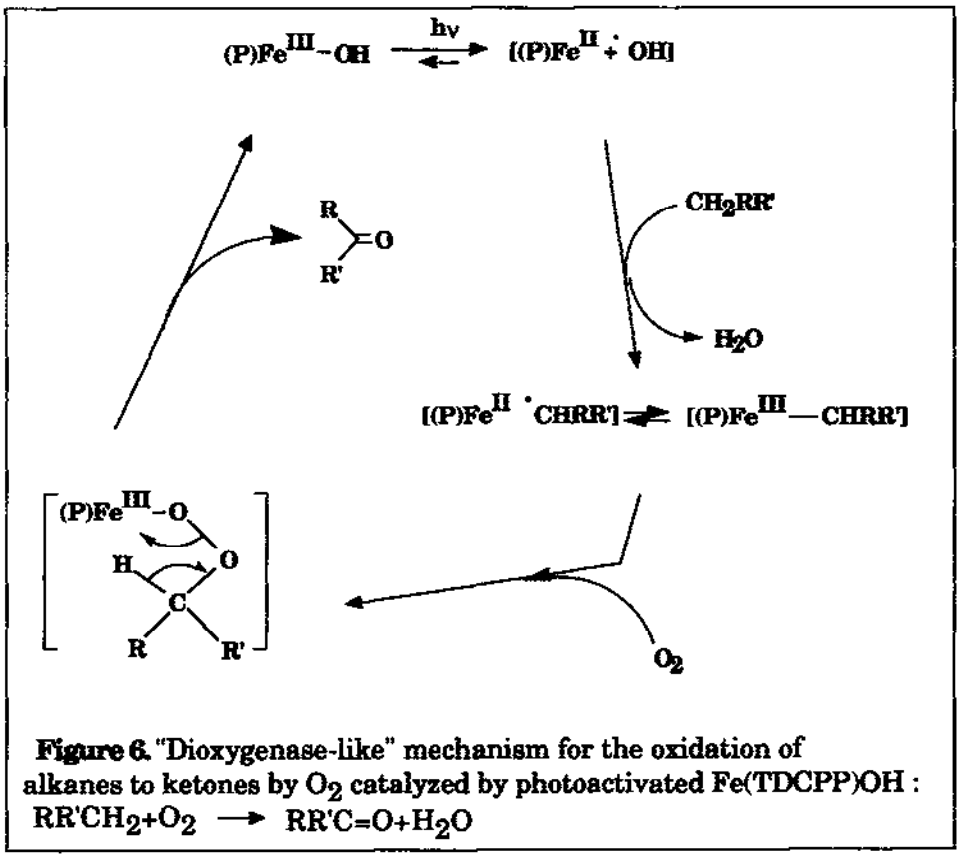


Figure 6. "Dioxygenase-like" mechanism for the oxidation of alkanes to ketones by O_2 catalyzed by photoactivated Fe(TDCPP)OH : $RR'CH_2+O_2 \longrightarrow RR'C=O+H_2O$

Many characteristics of this system were similar to those previously found for the Fe(TDCPP)OH-O_2-hv system. Alkanes are oxidized to ketones and alcohols with the major formation of ketones. Alkenes like cis-stilbene are not epoxidized and alkenes containing allylic C-H bonds like cyclohexene, are mainly oxidized at their allylic positions. This led us to propose an identical active species, ·OH, for the Fe(TDCPP)Cl-O_2-hv and Fe(TDCPCl$_8$P)OH-O_2-Δ systems and very similar catalytic cycles for the oxidation of alkanes by these two systems (Figure 6). The main difference between their catalytic cycles concerns the first step, the homolytic cleavage of the Fe(III)-OH bond, which is done either photochemically or thermally. Such a "dioxygenase-like"

mechanism of the oxidation of alkanes by O_2 in the presence of catalytic amounts of Fe(TDCPCl8P)OH could explain, at least in part, the results recently published by Lyons et al. on the oxidations of alkanes like propane and isobutane by O_2 in the presence of iron porphyrins of the second and third generation [23].

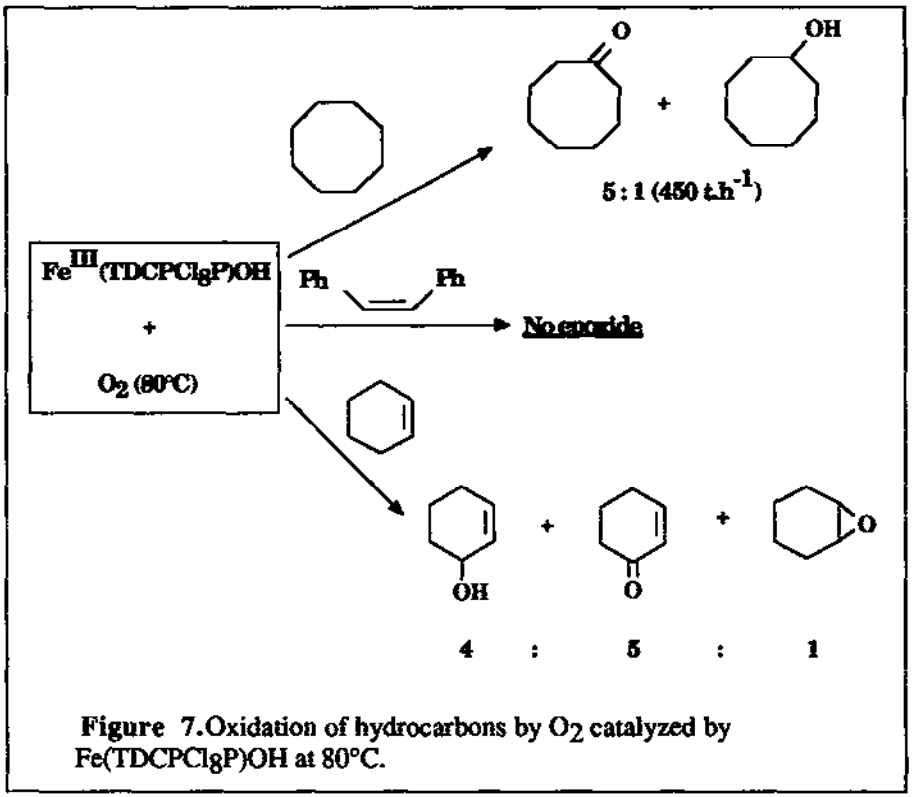


Figure 7. Oxidation of hydrocarbons by O_2 catalyzed by Fe(TDCPCl8P)OH at 80°C.

4. CONCLUSION

Two kinds of systems which are based on metalloporphyrin catalysts and are very efficient for the selective oxidation of alkanes under mild conditions have been obtained by following the biomimetic approach.

The first ones associate a Fe(III) or Mn(III) porphyrin catalyst with an oxygen atom donor (PhIO, H_2O_2 or O_2 + reductant) and reproduce quite well the reactions catalyzed by monooxygenases. They involve a high-valent metal-oxo active species, formally Fe(V)=O or Mn(V)=O, which epoxidizes alkenes, hydroxylates alkanes and aromatic rings and oxidizes thiothers to the corresponding sulfoxides. Iron porphyrins of the third generation which bear several electron-withdrawing β-substituents, like Fe(TDCPCl8P)Cl, are particularly good catalysts for alkane hydroxylation at room temperature, as

they oxidize the poorly reactive heptane with a 80% yield. Intercalation of tetracationic metalloporphyrins into layered minerals like clays has led to supported catalysts very efficient for the hydroxylation of linear alkanes by PhIO, their more pronounced reactivity towards these linear alkanes being presumably due to a more easy access of such substrates into the interlayer space. These homogenous and supported metalloporphyrin models for monooxygenases should be very good tools for oxidation in fine chemistry and for the study and prediction of the oxidative metabolism of drugs.

The second class of systems associate some iron (III) porphyrin catalysts with O_2 itself in the absence of any reducing agent. After a photochemical or thermal activation of their iron-axial ligand bond, these metalloporphyrins catalyze the oxidation of alkanes by O_2 to the corresponding ketones by a dioxygenase-like mechanism. The active species appears to be a free radical derived from the axial ligand of the catalyst like ·OH, explaining why the system is able to oxidize alkanes but not to epoxidize alkenes. Alkane oxidation by these systems involves several steps classical in simple free radical chain autoxidations except that the intermediate alkylperoxy radicals seem to be well controlled by the Fe(II)-porphyrin. Although more work is needed to completely understand their detailed mechanisms, these systems are very interesting for two main reasons : (i) they perform the oxidation of alkanes by O_2 itself without any consumption of any reducing agents, as in monooxygenase reactions, and (ii) they seem to act on alkanes by a dioxygenase-like mechanism although there is so far no dioxygenase reported to oxidize alkanes in living organisms.

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