



# The oxyfunctionalization of cycloalkanes with dioxygen catalyzed by soluble and supported metalloporphyrins

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Received 27 October 2003; accepted 26 March 2004

Available online 8 July 2004

## Abstract

Catalytic activity of a series of metalloporphyrin complexes in selective oxidation of cycloalkanes with molecular oxygen was investigated. The effects due to immobilization of these metallocomplexes on supports and their influences on the reaction course have been examined. Both, the type and the structure of the metallocomplexes as well as immobilization have been found to exert significant effect on the catalytic activity and selectivity. It has been demonstrated that the yields of oxidation products show an almost linear relationship with electronegativity of the axial ligands in the metalloporphyrin complexes. Extensive halogenation of the metal complex macrocycle enhances the catalytic activity of the metalloporphyrins. Parallel increase of the redox potential of metallocomplexes is observed showing a linear relationship with the number of the halogens on porphyrin macrocycle. Important conclusions concerning the reaction mechanism are advanced and the new reaction mechanism is discussed and proposed.

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*Keywords:* Metalloporphyrins; Supported metalloporphyrins; Hydrocarbon oxidation; Cycloalkanes

## 1. Introduction

Oxyfunctionalization of cycloalkanes in biomimetic systems with molecular oxygen in the presence of metalloporphyrins as catalysts is one of the most attractive transformations in organic synthesis [1–10]. It is evident that the use of molecular oxygen (as air) which is an inexpensive, abundant and readily available oxidant in place of oxygen donors is advantageous on economic and environmental grounds. Two major drawbacks have prevented progress with practical application of these metalloporphyrin catalysts for larger scale oxidation. First, the catalyst is deactivated by irreversible dimerization and secondly, the oxidative self-destruction of metalloporphyrins can take place in an intermolecular process. There are two strategies commonly employed which could permit to overcome both problems. The first one is extensive halogenation of the metalloporphyrins with electron-withdrawing substituents on porphyrin macrocycle. These complexes are known as efficient catalysts for the direct reaction of hydrocarbons with

molecular oxygen at high rates [11,12]. The second way is immobilization of metalloporphyrins by binding them to the solid supports [13–19]. Moreover, the immobilization of metalloporphyrins offers several practical advantages over soluble catalysts such as facilitation of catalyst separation from the reaction mixture, simplification of procedures for catalyst recycling and the possibility of adaptation of the immobilized catalyst for a continuous flow process.

A lot of information has been accumulated regarding both the mechanism and the reactivity of systems with oxygen donors but, in contrast, there are only a few papers concerning the direct oxidation of hydrocarbons with molecular oxygen in the presence of metalloporphyrins as catalyst without the use of sacrificial co-reductant [1–10]. The mechanism of this reaction is still a matter of discussion [4,9,11].

In this review we present the results of our studies on the application of soluble and supported metalloporphyrins in the oxidation of cycloalkanes with molecular dioxygen (as air) in Lyons system in the absence of a reducing agent. We have attempted to assess the effect of the structure of cycloalkanes, the choice of the metal centre, the type of axial ligand, halogenation and immobilization on solid support on catalyst yields and selectivities.

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## 2. Experimental

The catalytic oxidation of cycloalkanes has been carried out in a stainless steel batch reactor system at the optimum temperature of 120 °C and under the air pressure of 10 bar, with the molar ratio of cycloalkane/oxygen = 6.5. The Teflon-lined reactor of 1 L volume equipped with magnetic stirrer was used.

In the typical experiment, the catalyst in the amount of  $3.3 \times 10^{-4}$  M of a metalloporphyrin or its equivalent for the supported metallocomplexes was introduced into the reaction mixture when the required reaction conditions were attained. Reaction mixture had the composition cycloalkane:oxygen = 6.5:1. After 6 h of reaction time the oxidation was stopped by immersing the hot reactor in a cold water bath. The products were analyzed by means of Agilent Technologies 6890N gas chromatograph equipped with Innovax (30 m) column. The ligands TPP, TTP, T(p-Cl)PP, (see Fig. 2 for notation) were synthesized according to the procedure described previously [20]. The ligands TDCPP, TPFPP and TPCIPP were made by the procedure used by Lindsey et al. [21]. The ligands TPFPP $\beta$ Br<sub>8</sub>P and TDCPP $\beta$ Cl<sub>8</sub>P were obtained as described by Lyons et al. [4]. The manganese, iron and cobalt complexes were prepared by DMF metalation procedure [22]. The supported catalysts were synthesized according to the procedure previously described [23] by using metalloporphyrins and 3-aminopropyl-functionalized silica gel (Fluka), or aminomethyl-polystyrene (Fluka), or 3-amino propylmontmorillonite K10. Porphyrin ligands and metalloporphyrins were purified by successive chromatography on a silica gel or alumina columns, their purity being checked by UV–vis spectroscopy. The tetrakis(*N*-methyl-4-pyridyl)porphyrins (MnTMPyP, FeTMPyP and CoTMPyP) were purchased from MidCentury Company. The encapsulated complexes were prepared by the synthesis of zeolite X around these complexes [24].

The amounts of metalloporphyrins on the supports were determined by elemental analysis and by subtracting the amount left in the solution after impregnation, as determined by UV–vis spectroscopy, from its initial amount in the solution.

Electronic spectra of the supported metalloporphyrins were obtained in nujol mull between quartz plates.

## 3. Results and discussion

### 3.1. The effect of the metal centre and of the structure of cycloalkane

At first, the oxidation reaction of three cycloalkanes with ring sizes 5, 6 and 8 carbons, catalyzed by cobalt porphyrin Co(TTP)Cl, was investigated. The main products of cycloalkanes oxidation with molecular oxygen were cycloketone and cycloalcohol. No oxidation occurred in the absence

Table 1

Oxidation of cyclooctane catalyzed by metalloporphyrins M(TTP)Cl with different metals<sup>a</sup>

Catalyst	Cyclooctanone		Cyclooctanol		Ratio c-one/c-ol
	Yield (%)	TON <sup>b</sup>	Yield (%)	TON <sup>b</sup>	
Mn(TTP)Cl	10.7	23584	1.3	2860	8.2
Fe(TTP)Cl	8.9	19580	1.4	3168	6.4
Co(TTP)Cl	7.3	16016	1.2	2728	6.1

<sup>a</sup> See conditions in text.

<sup>b</sup> Mol product  $\times$  mol catalyst<sup>-1</sup>  $\times$  h<sup>-1</sup>.

of the catalyst. The yield of products depended on the structure of the cycloalkane and increased in the following order: cyclopentane < cyclohexane < cyclooctane.

The most reactive among studied cycloalkanes was cyclooctane and therefore this hydrocarbon was chosen for further investigations. We have examined the influence of the character of the metal centre on the activity of catalysts. Oxidation reactions were carried out with metalloporphyrins of the first generation having the same ligand TTP but different metals: Mn(TTP)Cl, Fe(TTP)Cl and Co(TTP)Cl. The results are reported in Table 1. As indicated by the data of Table 1, these complexes turned out to be active catalysts for oxidation of cyclooctane in Lyons system. The oxidation of cyclooctane produced cyclooctanone as the main product and cyclooctanol in small yield. It is interesting to notice that with metalloporphyrins as catalysts and in the presence of molecular oxygen oxidation of cyclooctane leads to the formation of ketone with high selectivity, while oxidation of acyclic alkanes produces mainly an alcohol or mixture of alcohol and ketone [3–5]. The most active among studied catalysts was a manganese complex showing the highest yields and the highest ketone/alcohol ratio.

### 3.2. The role of axial ligand

The axial ligands attached to metalloporphyrins played an important role in determining their catalytic activity. This is illustrated by the results of experiments, in which manganese meso-tetraphenyl porphyrins XMnIII(TTP) with different axial ligands like F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, OH<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup> were used as catalysts in the oxydation of cyclooctane. These manganese complexes are soluble enough to allow the reactions to proceed in the pure alkane solution. The main products of the cyclooctane oxidation using molecular oxygen (as air) as the oxidant were cyclooctanone and cyclooctanol, but ketone was the predominant product of the reaction. The data summarized in Table 2 indicate that the reaction yield varies with the change of the axial ligand, but the ratios of ketone to alcohol remain nearly the same. It has been found that FMnIII(TTP) complex with fluoride as axial ligand is the best catalyst in the oxydation of cyclooctane. When the axial ligand was acetate, chloride or hydroxyl ions, cyclooctane was oxidized with two times lower yields and for iodide ion as an axial ligand even a three times lower conversion

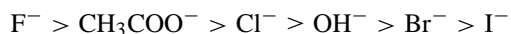
Table 2  
Oxidation of cyclooctane catalyzed by different XMnIII(TTP) metalloporphyrins<sup>a</sup>

Metalloporphyrins	Cyclooctanone		Cyclooctanol		Ratio c-one/c-ol
	Yield (%)	TON <sup>b</sup>	Yield (%)	TON <sup>b</sup>	
FMn(TTP)	13.9	30580	2.3	5060	6.0
CH <sub>3</sub> COOMn(TTP)	11.1	24420	1.4	3080	7.9
ClMn(TTP)	10.7	23540	1.3	2860	8.2
ClMn(TTP)+2,6-di - <i>tert</i> -butyl- <i>p</i> -cresol	Traces		Traces		–
OHMn(TTP)	10.7	23540	1.5	3300	7.1
BrMn(TTP)	8.9	19580	1.1	2420	8.1
Imn(TTP)	5.9	12980	0.7	1540	8.4

<sup>a</sup> See conditions in text.

<sup>b</sup> Mol product  $\times$  mol catalyst<sup>-1</sup>  $\times$  h<sup>-1</sup>.

was obtained. Thus, the following order of reactivity was observed:



Several effects are usually considered in the discussion of the correlation between the properties of metalloporphyrins and their catalytic activity in oxidation processes: electron and geometric effects of ring substituents and the influence of the axial ligand. Depending on the type of the substituent they may exert also a steric influence. It has been found that in the case of iron porphyrins introduction of electron-withdrawing substituents at the ring increases the redox potential of Fe(III)/Fe(II) porphyrin system and increases the catalytic activity of XFe(TTP) [8]. It has been explained by the assumption that stabilization of the Fe(II)

state makes easier the decomposition of alkyl hydroperoxide accelerating thus unfolding of the chain reaction. Contrary to that effect the same atoms, which were used as the electron-withdrawing rings substituents, when present in ionic form as axial ligands behaved as electron donors and decreased the redox potential of the Fe(III)/Fe(II) porphyrin due to the stabilization of the high oxidation state of the metal, but the catalytic activity in the oxidation of alkanes was also found to increase. In order to explain this observation we had to assume that the axial ligand takes part in the initiation step of the chain reaction, reacting with the hydrocarbon molecule to form the radical.

We observed the high yields of products in the case of fluoride complex and a low catalytic efficiency in cyclooctane hydroxylation with IMn(TTP). The large axial ligand like iodide gives rise to an out-of-plane structure, while small ligands like fluorine give an in-plane configuration. The values for the displacement of the manganese from the plane of the porphyrin are found to be 0.09 Å for F<sup>-</sup> but 0.35 Å for I<sup>-</sup> [26]. It means that in the iodide complex, the metal is hidden under the plane of the porphyrin. The displacement is related to electronegativity of the halide ions, which influence also the redox potential of the porphyrin. Thus, for the halides as axial ligands, the reaction yield increases with the rise of ligand electronegativity and decrease of the redox potential and it is nearly a linear relationship (Fig. 1).

The relatively high activity was observed for hydroxo and acetate anions as the axial ligands. For the hydroxo ion the same effect was observed in the case of the oxidation of isobutane with molecular oxygen, where the metalloporphyrin complexes having axial chloride were found to be

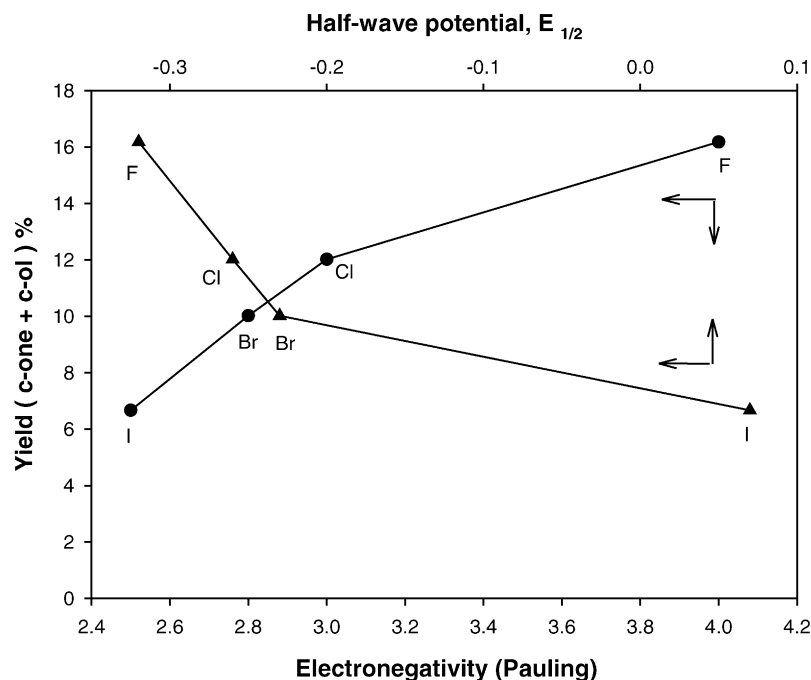


Fig. 1. The yield of cyclooctanone and cyclooctanol in the oxidation of cyclooctane in the presence of XMnIII (TTP) as a function of the electronegativity of axial ligand X and the redox potential of the porphyrin (where X = F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, OH<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>).

Table 3  
Spectroscopic and electrochemical properties of manganese porphyrins

Metalloporphyrins	Soret band (nm) <sup>a</sup>	Half-wave reduction potential $E_{1/2}$ (V) <sup>b</sup>
FMn(TTP)	459	-0.32
CH <sub>3</sub> COOMn(TTP)	472	-0.28
ClMn(TTP)	476	-0.26
OHMn(TTP)	479	-0.26
BrMn(TTP)	486	-0.23
Imn(TTP)	501	+0.07

<sup>a</sup> UV-vis absorption measurements in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> All potentials are reported vs. AgCl/Ag in 1 M KCl.

active catalysts in this reaction [4], but for high activity it was necessary to use the hydroxo form of the catalyst. For the acetate ion, it was shown by Mansuy and co-workers [27,28] that the system which uses metalloporphyrin as catalyst and ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) as cocatalyst or the axial ligand is particularly efficient for alkanes oxidation. The exchange of the axial ligand had a similar effect on the catalytic activity of metalloporphyrins as that observed by Tatsuno et al. [29] and Nappa and Dolman [30] for iron porphyrins with iodobenzene (PhIO) as the oxygen atom donor. The effect of axial ligand on the metal centre in our manganese porphyrins is demonstrated in Table 3. In agreement with earlier observations [30] the half-wave reduction potential of the metalloporphyrins decreases with the increasing electronegativity of the axial ligand. It is interesting to note that simultaneously the increase of the catalytic activity with a decreasing half-wave reduction potential of the metalloporphyrins is observed. The complex with the most negative Mn(III)/Mn(II) potential gives the highest yield. Like other metalloporphyrins the frequencies of the visible absorption maxima (Soret band) are dependent on the axial anion (Table 3). Ions with higher electronegativity give rise to a blue shift. It is related to the increase in the negative charge in the macrocycle and corresponds to the lower redox potential. It is known that the introduction of the electron-withdrawing substituents at the meso and/or  $\beta$ -position remarkably increases both the catalytic activity and the reduction potential. Surprisingly, in our case the situation is opposite. The met-

alloporphyrins with the lower reduction potential are more active catalysts in the investigated system. Apparently, the character of bonding between the axial ligand and the metal centre has a more pronounced influence on the catalytic properties than the electronic effect due to the introduction of ring substituents. One of the factors maybe the change of geometry of the metal centre, the other—a mechanism of the reaction different from that proposed for cytochrome P-450, the initiation step of the chain reaction being the abstraction of hydrogen from the organic molecule by the axial ligand of the porphyrin and injection of the electron to the latter.

### 3.3. The effect of peripheral substituents

It is an established fact that introduction of electron-withdrawing substituents on the porphyrin ring increases the activity of metal complexes [11,12]. In order to elucidate the parameters determining this effect the oxidation of cyclooctane was investigated in the presence of three generations of manganese porphyrins with different substituents on macrocyclic ligands [2]. We used the simplest unsubstituted porphyrins or porphyrins with one substituent at the phenyl rings (TPP, TTP and T(p-Cl)PP), those with more substituents at the phenyl rings (TDCPP, TPFPP and TPCIPP) and the porphyrins with electron-withdrawing halogen groups at both the phenyl and pyrrole rings (TDCP $\beta$ Cl<sub>8</sub>P, TPFPP $\beta$ Br<sub>8</sub>P). Their structures are presented in Fig. 2. Results of our study are summarized in Table 4. As it is seen, the yields of products are high and the cyclooctanone/cyclooctanol ratio varies within the range of 5–6. Comparison of the results obtained with Mn(TTP)Cl (Table 1) and those observed in the case of porphyrins quoted in Table 4 indicates that catalyst with electron-donating substituents on porphyrin ligand like TTP gives higher ketone/alcohol ratio than the porphyrins with electron-withdrawing substituents. The activity of metalloporphyrins varies in a wide range as a function of the degree of halogenation of the porphyrin ligand. As the number of halogen substituents around the periphery of the porphyrin macrocycle increases, the yield of products also increases, the most efficient catalytic system being the man-

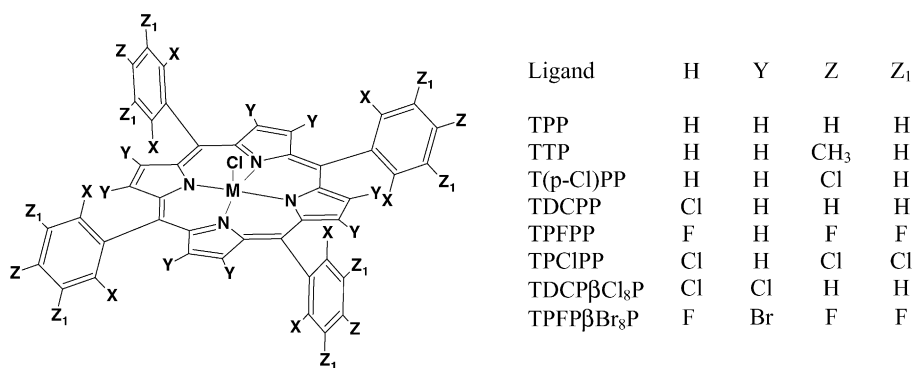


Fig. 2. Structures of the investigated porphyrins.

Table 4

Oxidation of cyclooctane catalyzed by manganese porphyrins Mn(P) with different substituents<sup>a</sup>

Catalyst	Cyklooctanone		Cyklooctanol		Ratio c-one/c-ol	Number of halogen atoms	Half-wave reduction potential $E_{1/2}$ (V)
	Yield (%)	TON <sup>b</sup>	Yield (%)	TON <sup>b</sup>			
Mn(TPP)Cl	6.4	14080	1.3	2772	5.1	0	-0.23
Mn(TPCIPP)Cl	10.2	22506	1.8	4026	5.6	4	-0.18
Mn(TDCPP)Cl	12.1	26664	2.1	4624	5.8	8	-0.12
Mn(TDCP $\beta$ Cl <sub>8</sub> P)Cl	15.9	33836	3.0	6512	5.2	16	+0.11
Mn(TPCIPP)Cl	17.2	34870	3.2	6446	5.4	20	+0.01
Mn(TPFPP)Cl	15.9	37862	2.9	7084	5.3	20	+0.04
Mn(TPFPP $\beta$ Br <sub>8</sub> P)Cl	20.1	44242	3.9	8514	5.2	28	+0.27

<sup>a</sup> See conditions in the text.<sup>b</sup> Mol product  $\times$  mol catalyst<sup>-1</sup>  $\times$  h<sup>-1</sup>.

ganes porphyrin of the third generation—Mn(TPFPP $\beta$ Br<sub>8</sub>P) bearing electron-withdrawing substituents on the phenyl and pyrrole rings. Fig. 3 shows the effect of the degree of metalloporphyrins halogenation on the catalytic activity of porphyrinato complexes. A linear relationship is observed between the yields of both products: cyclooctanone and cyclooctanol and the number of halogen substituents. In Table 4 the half-wave reduction potentials  $E_{1/2}$  of these manganese porphyrins are given. The halogenation of the manganese porphyrins causes a large positive shift in the potential of Mn(III)/(II) redox couple in comparison to their unsubstituted analogues. In the investigated system a linear relationship between the catalytic activity and the half-wave potentials of metalloporphyrins is observed. Analysis of the data summarized in Table 4 shows that one of the metalloporphyrins of the third generation Mn(TDCP $\beta$ Cl<sub>8</sub>P)Cl shows larger positive shift of the redox potential than could be expected from its catalytic activity lower than that of the second generation metalloporphyrins like Mn(TPCIPP)Cl and Mn(TPFPP)Cl. Apparently, a full correlation cannot be

expected when comparing various substituents like F, Cl and Br in the different places of the porphyrin macrocycle, in the phenyl or/and pyrrole rings.

### 3.4. The support effect

Two approaches to immobilize metalloporphyrins on the supports have been applied. The first was the immobilization of metalloporphyrins by binding them to organic or inorganic solid supports and the second was the encapsulation of metallocomplexes in the cavities of zeolite. The UV–vis spectra of the supported metalloporphyrins and metalloporphyrins in homogenous phase were almost identical which indicated that the porphyrin ring was not modified during the metallocomplex impregnation.

The effect of the support on catalytic activity of metalloporphyrins was investigated by carrying out the reaction of cyclooctane oxidation in the presence of the polyfluorinated manganese, iron and cobalt porphyrins covalently bound to 3-aminopropylmontmorillonite, aminopropylsi-

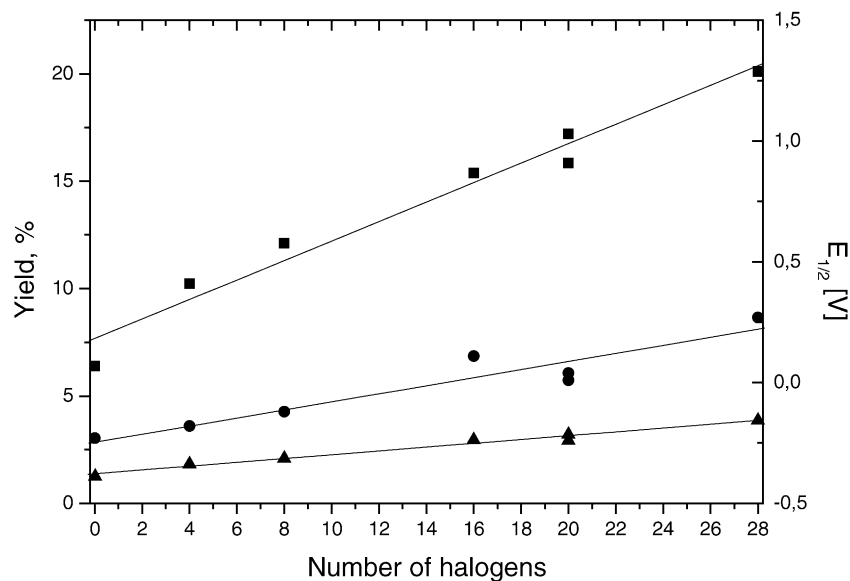


Fig. 3. Yields of cyclooctanone (■), cyclooctanol (▲) and half-wave potential (●) as a function of the number of halogens.



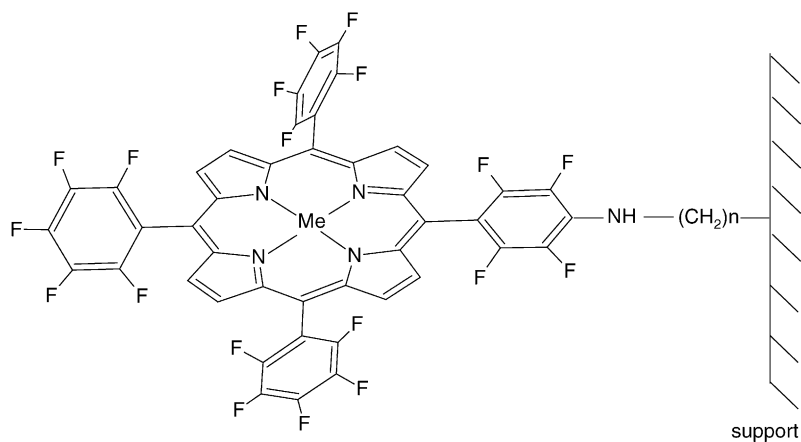


Fig. 4. Structures of the investigated supported metalloporphyrins (where M = Fe, Mn, Co, support = montmorillonite K10, silica or polystyrene,  $n = 1$  or 3).

lica and 3-aminomethylpolystyrene (Fig. 4) without adding the sacrificial co-reductant and comparing the results with those obtained for metal complexes in homogeneous reaction under similar conditions [25]. In all the cases the only products observed were cyclooctanone and cyclooctanol. All the polyhalogenated metalloporphyrins and supported polyhalogenated metalloporphyrins were found to be active catalysts for cyclooctane oxidation. A summary of results can be found in Table 5. Among the liquid phase metalloporphyrins, the most active was manganese complex, showing the highest yields, whereas this complex bound to silica gel turned out to be the least efficient catalyst. It is interesting to note that after attachment of polyfluorinated metallocomplexes to silica gel, we have observed the inversion of the order of activity of the metalloporphyrins (Fig. 5). Among complexes supported on silica gel the most active was the cobalt porphyrin Co(TPFPP)Cl catalyst.

This complex deposited on montmorillonite appeared to be stable under oxidation conditions and it was possible

to re-use this catalyst with very similar ketone and alcohol yields and even with better selectivity (Table 5). The second catalyst series studied were polyfluorinated metalloporphyrins bound to the surface of polystyrene (PS). In the case of the supported catalysts MnTPFPP/PS and FeTPFPP/PS only small amounts of oxygenated products were detected and the activity of these catalysts was relatively low. Similarly, these metalloporphyrins deposited on montmorillonite also showed relatively low activity. As seen from Table 5 the selectivities and the yields of products were comparable to the results obtained for homogeneous catalysts only in the case of supported cobalt porphyrins. It is interesting to notice that in the case of cobalt supported metalloporphyrins as catalysts the yields of the products are independent of the kind of support. All these supported catalysts were found to be efficient catalysts also for the hydroxylation of cyclohexane and heptane and for epoxidation of cyclooctene with iodobenzene as oxygen atom donor [23]. It is not clear why the chosen supports have changed the catalytic properties

Table 5  
Oxidation of cyclooctane catalyzed by different metalloporphyrins in homogeneous system and supported on silica, polystyrene and montmorillonite K10<sup>a</sup>

Catalyst	Cyclooctanone		Cyclooctanol		Ratio c-one/c-ol	Loading of porphyrin (%, w/w)
	Yield (%)	TON <sup>b</sup>	Yield (%)	TON <sup>b</sup>		
MnTPFPPCl	17.2	37862	3.2	7084	5.3	–
FeTPFPPCl	12.3	27060	1.7	3740	7.2	–
CoTPFPPCl	10.3	22660	1.9	4180	5.4	–
MnTPFPP/SiO <sub>2</sub>	1.2	2640	0.2	440	6.0	5.5
FeTPFPP/SiO <sub>2</sub>	4.4	9680	0.6	1320	7.3	8.7
CoTPFPP/SiO <sub>2</sub>	7.6	16720	1.7	3740	4.5	7.1
MnTPFPP/PS	2.6	5720	0.4	880	6.5	2.2
FeTPFPP/PS	2.8	6160	0.4	880	7.0	2.7
CoTPFPP/PS	7.1	15620	1.5	3300	4.7	2.0
MnTPFPP/M-K10	5.2	11440	0.8	1760	6.5	1.9
FeTPFPP/M-K10	2.9	6380	0.4	880	7.3	2.2
CoTPFPP/M-K10	7.6	16720	1.6	3520	4.8	2.1
CoTPFPP/M-K10 <sup>c</sup>	8.4	18480	0.9	1980	9.4	2.1

<sup>a</sup> Conditions as in text.

<sup>b</sup> Mol product  $\times$  mol catalyst<sup>-1</sup>  $\times$  h<sup>-1</sup>.

<sup>c</sup> The second run.

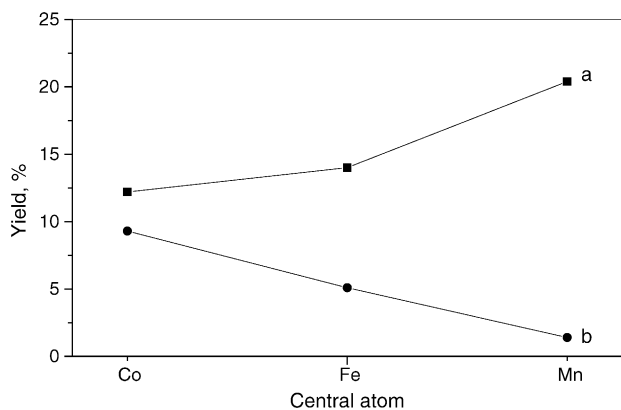


Fig. 5. Yield of products in the presence of porphyrins with different metals: (a) in homogeneous solution and (b) supported on silica.

of metalloporphyrins in our system but the same effect was observed in oxidation reaction of isobutane with supported metalloporphyrins as catalysts in Lyons system [10].

As mentioned all the supported catalysts have shown a lower catalytic activity in comparison with homogeneous systems. We suggest that this is due to a more restricted access for reagents to the metal centre in the heterogeneous system as compared to the homogeneous one, which could be caused by different positions of the macrocyclic ring in respect to the surface of the solid. The porphyrin ring may be positioned not only perpendicularly but also side-on to the surface of the support making the access to the catalytic centre more difficult.

In order to achieve a better isolation of the catalytic sites, metalloporphyrins were immobilized inside of zeolite cages using the ship-in-a-bottle procedure, described before as a method of preparation of the metalloporphyrins and their analogues inside the large pores of the zeolites [16,31,32]. The isolated complex immobilized in this way has special properties. It is unable to dimerize, which sometimes is a deactivating process in homogeneous catalysis and it is secured against other destructive reactions of catalysts under oxidizing conditions.

Here, we describe the study of the cationic metalloporphyrins encapsulated in NaX zeolite as ship in the bottle catalysts in oxidation of cyclooctane with molecular oxygen [24]. Three series of samples were used: pure metallocomplexes—manganese, iron and cobalt cationic 5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)porphyrins (MnTMPyP, FeTMPyP and CoTMPyP), zeolite X exchanged with the same metals and these metallocomplexes encapsulated in zeolite X. The structure of an encapsulated complex is shown in Fig. 6.

Results presented in Table 6 demonstrate that the catalytic activity of the system as well as the distribution of the reaction products depends on the nature of the metal centre. No reaction was observed in blank experiment when using parent NaX zeolite. The manganese exchanged zeolite shows some activity which is similar to pure manganese por-

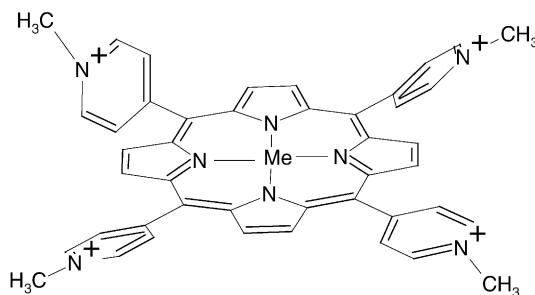


Fig. 6. Cationic metallo 5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)porphyrin entrapped inside of zeolite NaX (where Me = Fe, Mn, Co).

phyrin Mn(TMPyP) but is two times lower than that of the Mn(TMPyP) entrapped in NaX zeolite. Similarly, among the cobalt compounds, used in this reaction, the metallocomplex Co(TMPyP) encapsulated in NaX zeolite is also the most efficient catalyst. In the case of iron compounds, we have observed nearly the same activity for FeNaX, Fe(TMPyP) and Fe(TMPyP)/NaX catalysts. Generally, the lower activity of TMPyP porphyrins used in these experiments may be due to the fact that they are soluble in water but insoluble in cyclooctane used as the reaction medium. As regards the selectivities to the two products, almost all catalysts gave the same cyclooctanone/cyclooctanol ratio of about nine.

The results clearly show that cobalt complexes are considerably more active than manganese and iron catalysts. One of the possible reasons of this phenomenon may be the fact that cobalt complexes form superoxo compounds with molecular oxygen which are stable in comparison with iron and manganese complexes [16]. Moreover, this complex may be stabilized by the guest-host interaction in zeolite, zeolite matrix behaving like an electron-withdrawing substituent [33].

The catalytic results show that supported metalloporphyrins could be potentially applicable to practical organic syntheses which utilize molecular dioxygen as the oxidant and in which sacrificial co-reductants are not required.

Table 6

Oxidation of cyclooctane catalyzed by cationic complexes in solution and cationic complexes encapsulated in zeolite

Catalyst	Cyclooctanone		Cyclooctanol		Ratio c-one/c-ol
	Yield (%)	TON <sup>a</sup>	Yield (%)	TON <sup>a</sup>	
NaX	–	–	–	–	–
CoNaX	0.9	1980	0.1	220	9.0
Co(TMPyP)	1.9	4180	0.2	440	9.5
Co(TMPyP)/NaX	4.1	9020	0.5	1100	8.2
MnNaX	1.0	2200	0.1	220	10.0
Mn(TMPyP)	1.0	2200	0.1	220	10.0
Mn(TMPyP)/NaX	1.9	4180	0.2	440	9.5
FeNaX	1.1	2420	0.1	220	11.0
Fe(TMPyP)	1.2	2640	0.1	220	12.0
Fe(TMPyP)/NaX	1.0	2200	0.1	220	10.0

<sup>a</sup> Mol product  $\times$  mol catalyst<sup>-1</sup>  $\times$  h<sup>-1</sup>.

#### 4. Mechanism of the reaction

Mechanism of the oxidation reaction of paraffinic hydrocarbons with gas phase oxygen in the presence of metalloporphyrins as catalysts must, among others, explain two important observations: (1) in the case of the oxidation of acyclic hydrocarbons the main product is alcohol (hydroxylation takes place) and (2) in the case of cycloalkanes the main product is ketone. While many investigations have been carried out on hydrocarbon hydroxylation, the mechanism of metalloporphyrin-catalyzed oxidation of hydrocarbons in Lyons system remains a subject of debate [4,9]. Certain details of this mechanism like formation of hydroperoxides and their decomposition by metalloporphyrins are generally agreed upon. However, it remains a point of contention whether the reaction proceeds by direct activation of molecular oxygen and formation of an oxo-complex or via the activation of hydrocarbon molecule. The first mechanism proposed by Lyons et al. involves activation of molecular oxygen by a metalloporphyrin molecule to form peroxy or superoxy complex which reacts with the second metalloporphyrin yielding an oxo-complex. The metal oxo-group abstracts hydrogen atom from the hydrocarbon molecule and generates alkyl radical, as assumed in the accepted mechanism of the alkane hydroxylation by cytochrome P-450. However, it was shown [9], that the perhalogenated metalloporphyrins are inert in the presence of molecular oxygen and it is unlike that metalloporphyrin–O<sub>2</sub> complexes are involved in oxidation mechanism. The second mechanism proposed by Gray and co-workers [9] suggests that oxygenation of alkanes is initiated by radicals present in the solution. Then a radical chain mechanism unfolds, in which alkyl hydroperoxide intermediates are formed and decomposed efficiently by metalloporphyrins. In the first mechanism, the metalloporphyrin takes part in the initiation of the reaction by dioxygen, in the second the metalloporphyrin participates in the propagation of the alkyl hydroperoxide chain reaction.

Results of experiments, in which manganese XMn<sup>III</sup>(TTP) porphyrin with different axial ligands was used (Table 2), showed that its catalytic activity in oxidation of cyclooctane strongly depended on the type of this ligand. Moreover, this activity increased with the decrease of the redox potential, whose shifts were due to the presence of axial ligands, which rules out the possibility that axial ligands act by accelerating the decomposition of the alkyl hydroperoxide and influence the unfolding of the chain reaction. In the last case, a opposite correlation of the activity and redox potential would be expected.

Thus, we have advanced a hypothesis that oxidation of alkanes in the presence of metalloporphyrins occurs through a radical-chain mechanism, in which a different mechanism operates in the initiation of the chain reaction (Fig. 7). The initiation step consists in the reaction of hydrocarbon molecule with the axial ligand, yielding a radical with simultaneous reduction of Mn<sup>III</sup>P to Mn<sup>II</sup>P. One could expect that if axial ligands are involved in the initiation of the chain, the

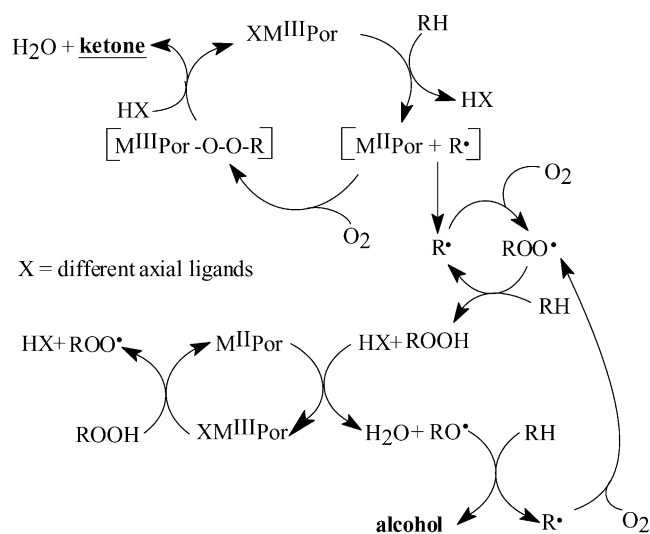


Fig. 7. Scheme of the oxidation of hydrocarbons with metalloporphyrins in Lyons system. (where X = different axial ligand).

reaction carried out in the absence of oxygen should lead either to dimerization of the alkyl radicals to R–R or to their reaction with HX and formation of the derivative RX. In order to confirm this hypothesis, an experiment was carried out, in which cyclohexane was reacted in the absence of oxygen under argon atmosphere. The formation of chlorocyclohexane was indeed detected confirming the hypothesis that interaction of the hydrocarbon molecule with axial ligand is responsible for the initiation step. The results obtained by Therien et al. [34] also support proposed mechanism. The authors demonstrated by in situ high pressure NMR studies of isobutane oxidation, that the reaction involving iron porphyrin OHFe<sup>III</sup>(P) and hydrocarbon initiates the radical chain yielding the radicals, water and porphyrin species Fe<sup>II</sup>(P).

The next step is the reaction between the radical, Mn<sup>II</sup> species and molecular oxygen leading to formation of Mn–O–O–cycloalkyl complex in the solvent cage. Formed intermediate further undergoes an intermolecular decomposition giving selectively the corresponding ketone as a main product and the Mn<sup>III</sup> complex initiating a new catalytic cycle. The experimental results described above are consistent with the proposed mechanism. The oxidation of acyclic hydrocarbons in Lyons system mainly leads to the formation of alcohols, which is a situation completely opposite to that found for the cyclic hydrocarbons. In this case, the escape of free radicals from the solvent cage which leads to the hydroperoxides is suggested. Lyons et al. [5] propose a heterolytic two-electron transfer from metalloporphyrin to the hydroperoxide, the mechanism which is analogous to that of cytochrome P-450. Another point of view was presented by Gray and co-workers [9] who suggested that this step is homolytic and there is no evidence for the formation of an oxometal species complex. We imply that the cleavage of hydroperoxides is a homolytic process in which the radicals are generated by oxidation and reduction of



hydroperoxides and this decomposition leads to the alcohol as a main product.

It may be concluded that in the case of the oxidation of hydrocarbons in Lyons system the reaction may occur either via the M–O–O–cycloalkyl complex route for cyclic hydrocarbons or by the hydroperoxides decomposition route for acyclic hydrocarbons or by both routes simultaneously depending on the nature of the hydrocarbon.

## 5. Conclusions

The catalytic results show that the activity of metalloporphyrin catalysts is dependent on the character of the metal center, type of axial ligand, nature of the porphyrin ring, number of halogen atoms substituted in this ligand and the kind of the support. It was demonstrated that the choice of the support influences the yields of the products: cyclooctanone and cyclooctanol and the selectivity. The results indicate that supported metalloporphyrin oxidation catalysts can be also used in flow reactors, in which dioxygen is utilized as the oxidant and in which the sacrificial co-reductants are not required.

## Acknowledgements

The financial support of the Polish Committee for Scientific Research within Grant 7 T09 A 10120 is gratefully acknowledged.

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