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Journal of Molecular Catalysis A: Chemical 198 (2003) 215–221

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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The effect of peripheral substituents in metalloporphyrins on their catalytic activity in Lyons system

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Received 11 September 2002; accepted 2 December 2002

Abstract

Manganese porphyrin catalysts with different number of halogens atoms substituted at the phenyl and pyrrole rings were investigated in the Lyons system in oxidation of cyclooctane with molecular oxygen (as air) to cyclooctanone and cyclooctanol without the use of sacrificial co-reductant. The catalytic activity of metalloporphyrins increases with the increase of the redox potential of metalloporphyrins in the investigated system and shows almost linear relationship with the number of the halogens on porphyrin macrocycle. On the basis of obtained results the new reaction mechanism is discussed and proposed.

Keywords: Metalloporphyrins; Hydrocarbon oxidation; Cyclooctane

1. Introduction

Metalloporphyrins have in recent years attracted much interest, as they are able to perform selectively various oxygenation reactions of hydrocarbons in liquid phase under mild conditions. They are also models for studying monooxygenases based on cytochrome P-450. Great advances have been made in understanding the mechanism of these processes through studies with different oxygen donors such as iodosylbenzene, hydrogen peroxide, organic hydroperoxides, hypochlorites, monopersulfates, magnesium monoperoxophthalate and molecular oxygen with sacrificial co-reductant [1–4]. One of the most interesting trends in oxidation of hydrocarbons with metalloporphyrins as catalysts is oxidation of acyclic alkanes in Lyons system with molecular oxygen (as air), which is an inexpensive, abundant and readily available oxidant. These complexes, in particular bearing electron-withdrawing substituents at the porphyrin macrocycle, are efficient catalysts for the direct reaction of hydrocarbons with molecular oxygen to give alcohol and/or carbonyl compounds at unprecedented rates [5–11]. The mechanism of the catalytic oxidation of hydrocarbons that utilizes molecular oxygen without the use of sacrificial co-reductant is still a matter of discussion [8,12,13].

Recently [14], we have described how changing the axial ligand of the metalloporphyrin complex can considerably enhance the catalytic activity of these catalysts in the oxidation of the cycloalkanes with molecular oxygen.

Using metalloporphyrins with the same axial ligand but with different substituents on the macrocycle ring, we will continue in this work our study on the application of metalloporphyrins in the oxidation of cyclooctane with molecular oxygen (as air) and in the absence of a reducing agent. The activity of such

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1381-1169/02/$ – see front matter
doi:10.1016/S1381-1169(02)00688-X

catalysts appeared to be dependent on the character of the metal center and on the structure of the porphyrin ligands by influencing the rate of chain propagation. We have found that the yield of products in hydroxylation reaction shows an almost linear relationship with the number of the halogens on porphyrin macrocycle.

2. Experimental

The liquid-phase oxidation of cyclooctane was performed in a stainless steel batch reactor system at the optimum temperature of 120 °C and under the air pressure of 10 atm, with the molar ratio of cyclooctane to oxygen set at 6.5. The Teflon lined reactor of 1 l volume equipped with magnetic stirrer was used.

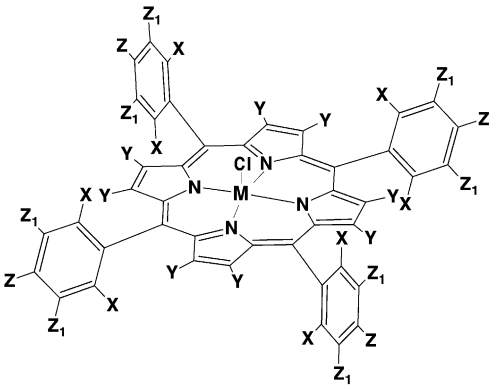
In the typical experiment, the catalyst at the concentration of 3.3×10^{-4} M of metalloporphyrin dissolved in 1 ml of benzene, was introduced into the reaction medium composed of cyclooctane and air, when the required reaction conditions were obtained. After 6 h of reaction time the oxidation was stopped by immersing the hot reactor in a cold water bath. The products were analyzed by means of SRI 8610B gas chromatograph equipped with MXT-200 (15 m) column. The ligands TPP, TTP, T(*p*-Cl)PP (see Fig. 1 for notation) were synthesized according to the procedure described previously [15]. The ligands TDCPP, TPFPP and TPClPP were made by the procedure used by Lindsay et al. [16]. The ligands TDCPβCl_8P and TPFPβBr_8P were obtained as described by Lyons et al. [8]. The metallocomplexes were prepared by DMF metalation procedure [17]. Metalloporphyrins and ligands were purified by successive chromatography on a silica gel or alumina columns. The purity of the ligands and metalloporphyrins was checked by UV-Vis, IR and mass spectroscopy.

The stability of porphyrins in the course of the catalytic reaction was checked by UV-Vis spectroscopy. It was found that in the case of the second and third generation porphyrins (TDCPP, TPFPP, TPClPP, TDCPβCl_8P and TPFPβBr_8P) practically no changes of the concentration of the porphyrin after the reaction could be detected. Only in the case of the first generation porphyrins (TPP, T(*p*-Cl)PP and TTP) their partial decomposition was observed and after the reaction the amount of porphyrin decreased to 30–70% of the initial value.

Cyclic voltammograms were recorded with the EP-21 potentiostat and a glassy carbon working electrode.

3. Results and discussion

In our previous paper [14], we have found surprisingly that the activity of catalysts composed of manganese porphyrins with different axial ligands increases with the electronegativity of this ligand, although their presence decreases the half-wave reduction potential of metalloporphyrins. On the other hand, the literature data reported that substitution of electron-withdrawing substituents in the porphyrin ring increases the redox potential and increases the



Ligand	X	Y	Z	Z_1
TPP	H	H	H	H
TTP	H	H	CH_3	H
T(p-Cl)PP	H	H	Cl	H
TDCPP	Cl	H	H	H
TPFPP	F	H	F	F
TPClPP	Cl	H	Cl	Cl
TDCPβCl_8P	Cl	Cl	H	H
TPFPβBr_8P	F	Br	F	F

Fig. 1. Structures of the investigated porphyrins.

catalytic activity in oxidation of isobutane [13]. This was explained by assuming that reduction of Fe(III) to Fe(II) is involved in the initiation of the chain reaction and the increase of the redox potential makes this process easier by stabilizing the Fe(II) state.

The cathodic shift of the redox potential of metalloporphyrins with increasing electronegativity of the counter ion has been explained by the stabilization of the oxidized state of the metal [18]. This is in line with the observation that the redox potential of Co(II)/Co(III) system can be correlated with the value of the ligand field stabilization energy [19]. The stronger the ligand field, the more favored is the low spin configuration, in which Co(III) is much more stabilized than Co(II) and the more negative is the redox potential. Thus, we have assumed that a different mechanism operates in the initiation of the chain reaction in which axial ligands are involved:

$$\mathrm{M(III)PorX + RH \rightarrow M(III)PorX \cdots HR} \quad (1)$$

$$\mathrm{M(III)PorX \cdots HR \rightarrow M(II)Por + HX + R^{\bullet}} \quad (2)$$

The overall rate of the catalytic oxidation of a hydrocarbon molecule in the liquid phase can be expressed by the equation:

$$-\mathrm{d}O_2/\mathrm{d}t = k_p[\mathrm{RH}][R_i/2k_t]^{1/2} \quad (3)$$

where R_i is the initiation rate, k_p the propagation rate constant and k_t the termination rate constant.

One could expect that if the reaction is carried out in the absence of oxygen the alkyl radical will either dimerise to R–R or react with HX and form the derivative RX. In order to confirm this hypothesis, a separate experiment was carried out, in which cyclohexane was used as the substrate instead of the cyclooctane under argon atmosphere with 100-fold excess of manganese porphyrin catalyst Mn(TTP)Cl, which did not contain chlorine atoms in the porphyrin macrocycle. Chlorine was present only as the axial ligand. After 6 h of reaction, chlorocyclohexane was indeed detected showing that interaction with the axial ligand is responsible for the initiation step. This step (R_i in Eq. (3)) will be the easier the more electronegative is the porphyrin counter ion (axial ligand). The results obtained by Therien and co-workers [20] also support the proposed mechanism. The authors demonstrated by in situ high pressure NMR studies of isobutane oxidation, that on interaction of iron porphyrin (OH)Fe(III)Por and hydrocarbon the radical chain is initiated, yielding the radicals, water and porphyrin species Fe(II)Por.

Table 1
Oxidation of cyclooctane catalyzed by metalloporphyrins M(TTP)Cl with different metals[a]

Catalyst	Cyclooctanone yield (%)	Cyclooctanol yield (%)	Cyclooctanone/cyclooctanol ratio
Mn(TTP))Cl	10.72	1.30	8.25
Fe(TTP))Cl	8.90	1.44	6.18
Co(TTP))Cl	7.28	1.24	5.87

[a] See conditions in the text.

Using metalloporphyrins with the same axial ligand and assuming that initiation rate remains constant, we have studied the application of metalloporphyrins with different substituents on the macrocycle ring in the oxidation of cyclooctane with molecular dioxygen (as air) and in the absence of a reducing agent. The activity of such catalysts appeared to be dependent on the character of the metal center and on the structure of the porphyrin ligands by influencing the rate of chain propagation.

At the beginning, we have examined the influence of the character of the metal center on the activity and selectivity of catalysts. Oxidation reactions were carried out with the metalloporphyrins having the same ligand TTP but different metals. The results are reported in Table 1. We used metalloporphyrins of the first generation: Mn(TTP)Cl, Fe(TTP)Cl and Co(TTP)Cl.

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. No other products were detected. 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 [13]. The most active among studied catalysts was a manganese complex showing the highest yields and the highest ketone/alcohol ratio. Therefore, manganese porphyrins with different substituents on macrocyclic ligands were chosen and their catalytic properties were investigated. We have examined the oxidation of cyclooctane with metalloporphyrins with structures presented in Fig. 1. We used the first generation of porphyrins with one or without substituents

Table 2
Oxidation of cyclooctane catalyzed by manganese porphyrins Mn(P) with different substituents[a]

Catalyst	Cyclooctanone yield (%)	Cyclooctanol yield (%)	Cyclooctanone/ cyclooctanol ratio	Number of halogen atoms	Half-wave reduction potential ($E_{1/2}$, V)
Mn(TPP)Cl	6.40	1.26	5.08	0	−0.23
Mn(T(*p*-Cl)PP)Cl	10.23	1.83	5.59	4	−0.18
Mn(TDCPP)Cl	12.12	2.11	5.74	8	−0.12
Mn(TDCPβCl_8P)Cl	15.38	2.96	5.20	16	+0.11
Mn(TPClPP)Cl	15.85	2.93	5.34	20	+0.01
Mn(TPFPP)Cl	17.21	3.22	5.41	20	+0.04
Mn(TPFPβBr_8P)Cl	20.11	3.87	5.20	28	+0.27

[a] See conditions in the text.

(TPP, T(*p*-Cl)PP), the second generation—those with more halogen substituents at the phenyl rings (TDCPP, TPFPP, TPClPP) and third generation with substituents at the phenyl and pyrrole rings (TPFPβBr_8P, TDCPβCl_8P). Results of our study are presented in Table 2. As it is seen, the yields of products are high and the cyclooctanone/cyclooctanol ratio varies within the range of 5–6 for the studied catalysts.

Comparison of the results obtained with Mn(TTP)Cl (Table 1) with those observed in case of porphyrins quoted in Table 2 indicates that catalysts with electron-donating substituents on porphyrin ligand like TTP give higher ketone/alcohol ratio than the porphyrins with electron-withdrawing substituents. The activity of metalloporphyrins varies to a large extent as a function of the degree of halogenation of the porphyrin ligand. The most efficient catalytic system involves manganese porphyrins of the third generation—Mn(TPFPβBr_8P) bearing electron-withdrawing substituents on the phenyl and pyrrole rings, but another metalloporphyrin of this generation Mn(TDCPβCl_8P)Cl shows lower catalytic activity than the second generation metalloporphyrins like Mn(TPClPP)Cl and Mn(TPFPP)Cl. It is a well-known fact, that introducing the electron-withdrawing substituents by halogenation of the phenyl rings and especially of the pyrrole rings exerts a significant effect on the reactivity of the metalloporphyrin complexes although this is not always true [21–24]. Fig. 2 shows the effect of the degree of metalloporphyrins halogenation on the catalytic activity of porphyrinato complexes. As the number of halogen substituents around the periphery of the porphyrin macrocycle increases, the yield of products also increase. This figure demonstrates linear relationships between the number of halogen substituents and the yields of both products: cyclooctanone and cyclooctanol.

In Table 2, the half-wave reduction potentials ($E_{1/2}$) of manganese porphyrins are given. The halogenation of the manganese porphyrins causes the large positive shift in the redox potential of manganese(III)/manganese(II) redox couple in comparison to their unsubstituted analogous. In the investigated system a linear relationship between half-wave potentials and the activity of the metalloporphyrins is observed, except the case of Mn(TDCPβCl_8P)Cl which should be more active than Mn(TPClPP)Cl and Mn(TPFPP)Cl because of its higher redox potential. Its lower activity may be due to steric hindrance of the access of a large cyclooctane molecule by bulky chlorine substituents at the pyrrole rings. Thus, 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. On the other hand, a linear correlation between catalytic activity and electronegativity of different axial ligands for the same simple metalloporphyrin system was obtained as it was described in the previous paper [14].

Fig. 3 presents our proposal for the reaction mechanism. 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 [8,14]. 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 molecular oxygen activation and oxo complex or via the activation of

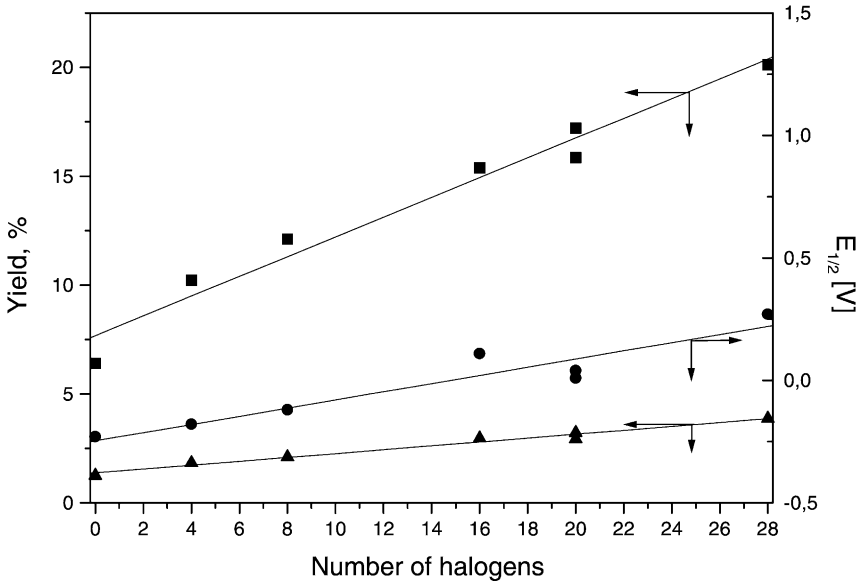


Fig. 2. Yields of cyclooctanol (■), cyclooctanone (▲) and half-wave potential (●) as a function of the number of halogens.

hydrocarbons. The first mechanism involves activation of molecular oxygen to form peroxo or superoxo complex which reacts with the second metalloporphyrin yielding oxo complex. The metal oxo-group abstracts hydrogen atom from the hydrocarbon molecule and generates alkyl radical. It was shown [12], that the perhalogenated metalloporphyrins are inert in the presence of molecular oxygen and it is unlikely that oxygenated species M(Por)–O_2 are involved in oxidation mechanism. We suggest that the oxidation of alkanes by metalloporphyrins occurs through a radical-chain mechanism, whose initiation step is the reaction of hydrocarbon with axial ligand, which yields the radicals and leads to the reduction of Mn(III)Por to Mn(II)Por as described by reactions (1) and (2).

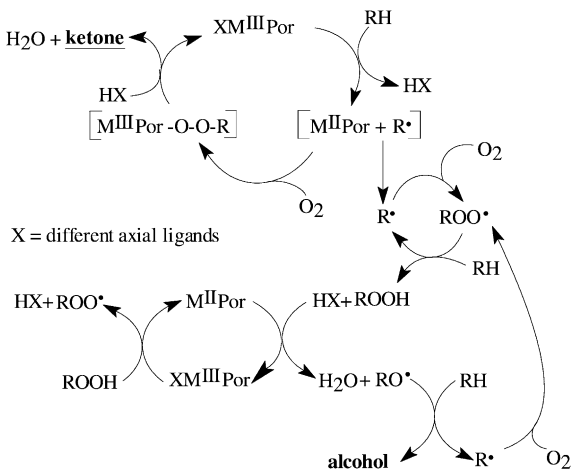


Fig. 3. Scheme of the oxidation of hydrocarbons with metalloporphyrins in Lyons system.

The next step in the mechanism proposed by us is the reaction between the cycloalkyl radical and molecular oxygen leading in the presence of the Mn(II) to the formation of Mn–O–O–cycloalkyl complex in the solvent cage [25–27]. The intermediate formed undergoes an intramolecular decomposition, giving selectively the corresponding ketone as a main product and the Mn(III) complex is restored with participation of HX, initiating a new catalytic cycle. The cycloalkylperoxo radical may also react along a parallel pathway, yielding first the cycloalkylhydroperoxide, which on interaction with Mn(II)Por and HX decomposes in a homolytic way to form $RO^{\bullet}$ radical and Mn(III)Por. The radical splits hydrogen from the hydrocarbon forming alcohol and propagating the chain reaction. The obtained results corroborate 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. A lot of papers concentrate [5–13] on the reaction of hydroperoxides with synthetic metalloporphyrins. However, no general agreement exists on the mechanism of the cleavage of the O–O bond. Lyons et al. [9] 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 who suggested that this step is homolytic and there is no evidence for the formation of an oxometal species complex [12]. We assumed that the cleavage of hydroperoxide is a homolytic process in which the radicals are generated and this decomposition leads to the alcohol as a main product. The reaction $2ROO^{\bullet} \rightarrow ROH + RO + O_2$ known to occur in the non-catalytic oxidation of hydrocarbons seems to play a minor role in view of fact that in our case the main product is ketone, the ratio of ketone to alcohol amounting to about 5–8 (see Tables 1 and 2).

In general, 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 hydrocarbons.

4. Conclusions

Metalloporphyrins with multiple electron-withdrawing peripheral substituents are suitable catalysts for cyclooctane oxygenation reaction producing cyclooctanone and cyclooctanol. The nature of the porphyrin ring has a remarkable effect on the activity of the metalloporphyrin. Their efficiency depends on the number of halogen substituents in the porphyrin ring rather than on their position. We have found that the yield of products in hydroxylation reaction shows an almost linear correlation with the number of halogen substituents and redox potential of the metalloporphyrins. The proposed reaction route is the radical process initiated by axial ligand of metalloporphyrins and proceeding through the formation of a metalloporphyrin–cycloalkylperoxo complex, which decomposed yielding ketone and through homolytic decomposition of a cycloalkylhydroperoxide yielding alcohol.

Acknowledgements

The financial support of the Polish Committee for Scientific Research within Grant 7 T09A 101 20 is gratefully acknowledged.

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