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Manganese porphyrins as catalysts for oxidation of cyclooctane in Lyons system

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Abstract

Oxidation of cyclooctane with molecular oxygen (as air) in the presence of first generation manganese porphyrins $\text{XMn}^{\text{III}}(\text{TTP})$, where $\text{X} = \text{F}^-$, Cl^- , Br^- , I^- , OH^- , CH_3COO^- , as catalysts was investigated in the Lyons system. The catalytic activities of the metalloporphyrins in the oxidation of cyclooctane to cyclooctanone and cyclooctanol are covariant with electronegativity of halides as axial ligands and increase with the decrease of the redox potential of metalloporphyrins. It was concluded that axial ligands are involved in the reaction initiating the reaction by generating the radicals with simultaneous reduction of the manganese porphyrin. Relatively high yields of products were obtained without the use of sacrificial co-reductant. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Metalloporphyrins; Hydrocarbon oxidation; Cyclooctane

1. Introduction

Metalloporphyrins have been the subject of many studies because of their potential application as selective catalysts. They are also model systems for oxidation of hydrocarbons in the liquid phase under mild conditions. Different oxygen donors such as iodosobenzene, hydrogen peroxide, organic hydroperoxides, hypochlorites, monopersulphates and molecular oxygen with sacrificial co-reductant or photochemical or electrochemical activation of the dioxygen were applied [1–3]. A lot of information has been accumulated regarding both the mechanism and the reactivity for the systems with oxygen donors but, in contrast, little is known regarding the catalytic oxidation of hydrocarbons with the utilization of molecular oxygen. There are only a few papers

concerning the direct oxidation of hydrocarbons with molecular oxygen and metalloporphyrins as catalyst [1,4–10]. They have shown that changing the axial ligand of the metalloporphyrin or phthalocyanine complexes can convert a catalytically inactive compound into an active catalyst for the oxidation of light alkanes with molecular oxygen. This so called Lyons system is very promising mainly for economic reasons, since molecular oxygen (as air) is an ideal inexpensive and readily available oxidant and the necessity of using a sacrificial co-reductant is eliminated [11]. We now report new results which demonstrate that the manganese porphyrins $\text{X}^{\text{III}}\text{Mn}(\text{TTP})$ with different axial ligands, where $\text{X} = \text{F}^-$, Cl^- , Br^- , I^- , OH^- , CH_3COO^- are active catalysts in the reaction of cyclooctane and dioxygen (as air) without addition of any co-reductant. The yield of products in such a system appeared to be dependent on the character of the axial ligand. We have found that the

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yields of products in hydroxylation reaction show an almost linear relationship with the electronegativity of the axial ligands.

2. Experimental

In the standard procedure, the liquid-phase oxidation of cyclooctane was carried out for 6 h at 120°C and under the air pressure of 10 atm. The teflon lined stainless steel batch reactor of 1 L volume equipped with magnetic stirrer was used. It was filled with cyclooctane and oxygen then was introduced, the molar ratio of cyclooctane to oxygen being set at 6.5. The catalyst at the concentration of 3.3×10^{-4} M of metalloporphyrin in 1 ml of benzene was introduced into the reaction mixture at the moment when the chosen reaction temperature was reached. The constancy of the reaction temperature was controlled by a thermocouple. After 6 h of stirring, the products were analyzed by means of SRI 8610 B gas chromatograph equipped with a MXT-20 (15 m) column. The syntheses of the metalloporphyrin complexes (OAc)Mn(TTP) and ClMn(TTP) were performed according to the procedure of Adler et al. [12]. The complexes XMn(TTP), where X = F⁻, Br⁻, I⁻ were made from the corresponding chloroform solution of (OAc)Mn(TTP) by the ligand-exchange procedure used by Ogoshi et al. [13]. The purity of the final products was checked by UV–VIS, IR and mass spectroscopy.

Cyclic voltametric measurements were carried out with an EP-21 potentiostat and a glassy carbon disk as a working electrode.

3. Results and discussion

Manganese meso-tetraphenyl porphyrins X Mn^{III}(TTP) with different axial ligands like F⁻, Cl⁻, Br⁻, I⁻, OH⁻, CH₃COO⁻ were used as catalysts in the hydroxylation of the cyclooctane, which is a rather poorly reactive substrate. 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. Table 1 summarizes the data obtained from our catalytic experiments. It may be seen that the investigated manganese porphyrin complexes appeared suitable catalysts for the oxidation of cyclooctane under the chosen conditions. The complexes were active in this reaction at temperatures above 100°C. As is shown in Table 1, the reaction yield varies with the change of the axial ligand, but the ratios of ketone to alcohol are nearly the same. We found that FMn^{III}(TTP) complex is the best catalyst in hydroxylation 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 was obtained. We observed the following order of reactivity: F⁻ > CH₃COO⁻ > Cl⁻ ≥ OH⁻ > Br⁻ > I⁻.

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 lig-

Table 1
Oxidation of cyclooctane catalyzed by different XMn^{III}(TTP) metalloporphyrins^a

Metalloporphyrins	Cyclooctanone yield (%)	Cyclooctanol yield (%)	Ratio (-one/-ol)
F Mn (TTP)	13.9	2.3	6.0
CH ₃ COOMn (TTP)	11.1	1.4	7.9
Cl Mn (TTP)	10.7	1.3	8.2
Cl Mn (TTP) + 2,6-di- <i>tert</i> -butyl- <i>p</i> -krezol	Traces	Traces	–
OH Mn (TTP)	10.7	1.5	7.1
Br Mn (TTP)	8.9	1.1	8.1
I Mn (TTP)	5.9	0.7	8.4

^a See conditions in text.

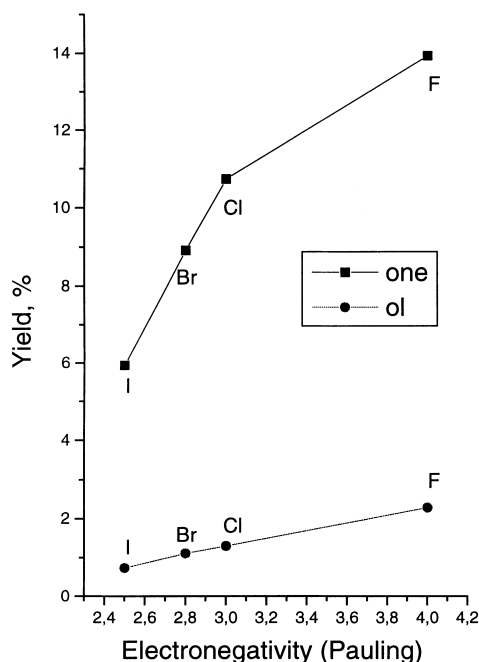


Fig. 1. The yield of cyclooctanone and cyclooctanol in the oxidation of cyclooctane in the presence of $\text{XMn}^{\text{III}}(\text{TTP})$ as a function of the electronegativity of axial ligand X (where $\text{X} = \text{F}^-$, Cl^- , Br^- , I^- , OH^- , CH_3COO^-).

and. It has been found that in the case of iron porphyrins, introduction of electron-withdrawing substituents at the ring increases the redox potential of $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ porphyrin system and increases the catalytic activity of $\text{XFe}(\text{TTP})$ [8]. Depending on the type of the substituent, they may also exert a steric influence. Contrary to that effect, the electron-withdrawing axial ligands decrease the redox potential of the $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ 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. This has been explained by assuming that stronger bond between the metal and the axial ligand make the catalyst more resistant to the oxidative attack.

We observed the high yields of products in the case of fluoride complex and a low catalytic efficiency in cyclooctane hydroxylation with $\text{IMn}(\text{TTP})$. 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 \AA for F^- but 0.35 \AA for I^- [14]. 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. Thus, for the halides as axial ligands, the reaction yield increases with the rise of ligand electronegativity 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 active catalysts in this reaction [7], 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 Battioni that the system which uses metalloporphyrin as catalyst and ammonium acetate ($\text{CH}_3\text{COONH}_4$) as cocatalyst or the axial ligand is especially efficient for alkanes oxidation [15,16]. The exchange of the axial ligand had the similar effect on the catalytic activity of metalloporphyrins as was observed by Tatsuno [17] and Nappa [18] for iron porphyrins with iodosobenzene (PhIO) as the oxygen atom donor. The effect of axial ligand on the metal centre in our manganese porphyrins is demonstrated in Table 2.

In agreement with earlier observations [18] 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

Table 2
Spectroscopic and electrochemical properties of manganese porphyrins

Metalloporphyrins	Soret (nm) ^a	Half-wave reduction potential $E_{1/2}$ (V) ^b
F Mn (TTP)	459	-0.32
CH_3COO Mn (TTP)	472	-0.28
Cl Mn (TTP)	476	-0.26
OH Mn (TTP)	479	-0.26
Br Mn (TTP)	486	-0.23
I Mn (TTP)	501	+0.07

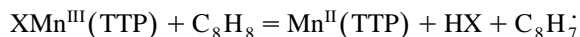
^a UV-VIS absorption measurements in CH_2Cl_2 .

^b All potentials are reported vs. AgCl/Ag in 1M KCl.

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 2). 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 β -position remarkably increases both the catalytic activity and the reduction potential. Surprisingly, in our case the situation is opposite. The metalloporphyrins 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 reaction mechanism is still not well established. Among the several pathways that could lead to hydroxylation, two are proposed for oxidation of alkanes in Lyons system. The first pathway proposed by Lyons et al. requires dioxygen binding to the reduced metalloporphyrin and formation of the peroxo-bridged M–O–O–M dimer. The active oxo species is formed by homolysis of the latter. The next step is an abstraction of hydrogen by M=O complex related to the accepted mechanism of the alkane hydroxylation by cytochrome P-450. The second mechanism proposed by Gray and coworkers [19] 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 decomposed efficiently by metalloporphyrins. In the first mechanism, the metalloporphyrin takes part in the initiation of the reaction by dioxygen activation, in the second, the metalloporphyrin participates in the propagation of the alkyl hydroperoxide chain reaction. The partial decomposition of the manganese porphyrins occurs concomitantly with the catalytic oxidation of cyclooctane under these conditions, which can be followed by electronic absorption spectroscopy. In both mechanisms the catalytic activity is expected to in-

crease with rise of the redox potential of the metalloporphyrin. We observed an opposite correlation between the redox potential and the catalytic activity which indicates a different mechanism to operate. Namely, our results suggest that the axial ligand plays an important role in the investigated reaction: it participates in the reaction and initiates it by generating the radicals with simultaneous reduction of the metalloporphyrin:



This reaction would be more favoured the lower the redox potential will be of the Mn^{III}/Mn^{II} couple, as indeed observed. In our system the reaction was almost perfectly quenched by the addition of such a typical radical inhibitor as 2,6-di-*tert*-butyl-*p*-cresol (Table 2). Results obtained by in-situ high pressure NMR studies of iron porphyrin catalyzing isobutane oxidation with the dioxygen [20] support the proposed mechanism. Namely, the authors demonstrated that alkyl radicals that initiate the radical chain may derive from a reaction involving OHFe^{III}(P) and producing water and Fe^{II}(P) species.

In the case of the oxidation in the system consisting of the second or third generation of iron(III) porphyrins with OH⁻ as axial ligand, Mansuy [1] postulates the homolytic cleavage of the iron-axial ligand bond resulting in the formation of $\cdot\text{OH}$ free radicals which initiate the chain reaction by abstraction of hydrogen from the hydrocarbon molecules. In view of the similarity in the behaviour of the series of XMn^{III}(TTP) porphyrins described here, in which X = F⁻, Cl⁻, Br⁻, I⁻, OH⁻, CH₃COO⁻, it seems plausible to assume that the chain reaction is initiated by a concerted reaction of the hydrocarbon molecule and the axial ligand with simultaneous transfer of an electron to the metal centre and its reduction.

4. Conclusions

The axial ligands effectively modulate the behavior of the first generation manganese porphyrins as catalysts in the cyclooctane oxidation by dioxygen. They initiate the chain reaction by generating the radicals with simultaneous reduction of manganese

porphyrin. In the series of manganese porphyrins $\text{XMn}^{\text{III}}(\text{TTP})$ where $\text{X} = \text{I}^-$, Br^- , Cl^- , OH^- , CH_3COO^- , F^- , the redox potential decreases which is accompanied by an increase in catalytic activity, cyclooctane being oxidized to ketone and alcohol in the ratio 6–8 with the relatively high yields, without the use of sacrificial co-reductant. The catalysts used in this process may be readily prepared by the conventional methods and they are relatively cheap in comparison to metalloporphyrins of the second and the third generations. Further experiments are required for a better understanding of the detailed mechanisms of alkane oxidation in such systems.

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