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Influence of manganese tetraarylporphyrins substituents on the selectivity of cycloalkanes oxidation with magnesium monoperoxyphthalate

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Abstract

The catalytic properties of manganese porphyrins of the second and third generation and magnesium monoperoxyphthalate (MMPP) as oxidant have been studied in oxidation of cyclohexane or cyclooctane under mild conditions. We have found that the structure of manganese porphyrin has an influence on selectivity of the investigated reaction. Apart from main cycloalkanes oxidation products (alcohol and ketone), olefins and epoxides resulting from oxidative dehydrogenation of substrates in the course of reaction, were surprisingly found. This represents the first example of the oxidative dehydrogenation of cycloalkanes with MMPP as oxygen donor. The reaction mechanism is discussed and proposed.

Keywords: Metalloporphyrins; Cycloalkanes oxidation; Oxidative dehydrogenation

1. Introduction

Metalloporphyrins with electron-withdrawing substituents in macrocyclic rings have been extensively used as precursors of stable catalysts for epoxidation of olefins and hydroxylation of alkanes in a liquid phase under mild conditions [1–5]. These investigations allow to understand the factors that influence the yields and selectivity of metalloporphyrins catalyzed oxidations and should inspire the development of more active and selective hydrocarbon oxidation catalysts. The most efficient systems involve manganese or iron porphyrins bearing halogen groups on the phenyl or pyrrole rings. Electron-withdrawing substituents bring about an increase of the half-wave potential of the metalloporphyrins and thus protect the macrocyclic ligand from oxidative self-destruction. This strategy can prevent also μ-oxo dimer formation and improve catalytic efficiency of metalloporphyrins. Most of the studies have been focused on the application of these compounds as catalysts with different oxygen donors like iodosylbenzene [6], hydrogen peroxide [7], hypochlorites [8], monopersulphates [9], and molecular oxygen with sacrificial co-reductant [10]. There are only a few papers concerning the application of the magnesium monoperoxyphthalate (MMPP), which is commercially available, inexpensive and relatively new oxygen donor [11]. MMPP displays low toxicity and is safe to use in larger scale reaction. This versatile oxygen donor is capable of effecting many types of oxidation reactions. It has been used with metalloporphyrins for alkene epoxidation [12–16], benzene and alkylbenzene oxidation [17], hydroxylation of alkanes [18,19] and variety of organic molecules [20].

In our previous papers [14,15], we have shown that metalloporphyrins of the third generation with several nitro groups in β-position were active in epoxidation of linear and cyclic olefins without requiring the addition of any nitrogen base. We have found surprisingly that the activity of catalysts increases with the electronegativity of the axial ligand, although the presence of these ligands decreases the half-wave reduction potential of metalloporphyrins.

In this paper, we will continue our study on the application of metalloporphyrins with different electron-withdrawing substituents on the macrocycle ring in the oxidation of cycloalkanes using MMPP as oxygen donor. We have found that the presence of different groups in porphyrin rings modifies the yield and selectivity of the investigated reactions.

2. Experimental

Oxidation of cycloalkanes was carried out in a glass reactor of 10 mL volume. In a typical experiment, organic phase

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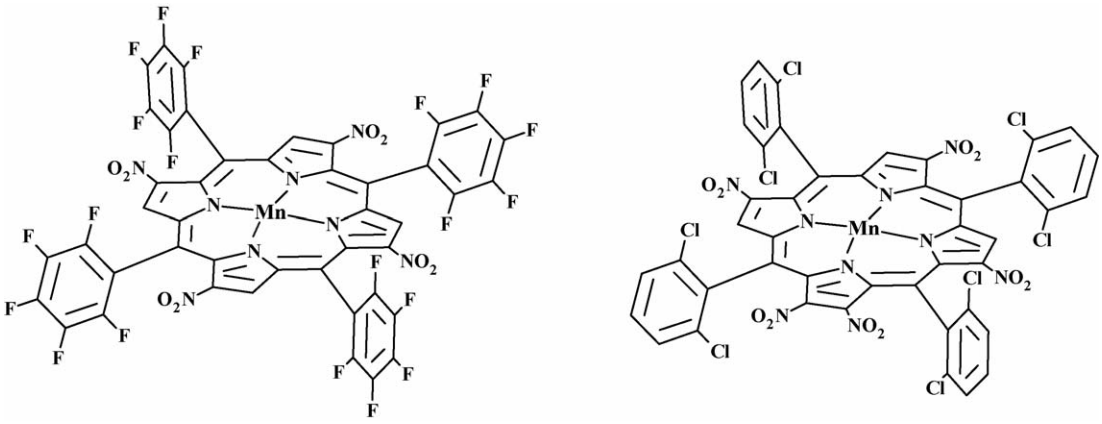

Fig. 1. Structures of the third generation polynitrated manganese porphyrins Mn(TPFPβ(NO_2)$_4$P) and Mn(TDCPβ(NO_2)$_5$P).

consisting of 1 mL ethyl acetate as a solvent, 3.45×10^{-4} m of hydrocarbon to be oxidized and 2.5×10^{-6} m of metalloporphyrin catalyst were mixed with 2 mL of aqueous solution containing 7.0×10^{-4} m of oxidant MMPP and 1.0×10^{-5} m of tetrabutylammonium chloride as phase transfer agent. The reaction mixture was stirred with a magnetic bar and the temperature was maintained constant. After 1 h of the reaction at room temperature the products were analyzed by gas chromatography. In a blank experiment no reaction was observed when the manganese porphyrin catalyst was not present in the reaction mixture.

Porphyrin ligands, TDCPP and TPFPP (with substituents on phenyl rings, called sometimes the second generation porphyrins) were prepared according to a Lindsay method [21] and nitrated by fuming acid to obtain TPCPβ(NO_2)$_5$P and TPFPβ(NO_2)$_4$P (called sometimes third generation porphyrins with substituents on phenyl and pyrrolic rings) [22] (Fig. 1). Careful purification on Al_2O_3 and SiO_2 permitted to obtain the ligand substituted with five nitro groups. Ligand of the third generation porphyrin TDCPβCl_8P was obtained as described by Lyons et al. [23]. Manganese complexes were prepared by DMF metalation procedure with Mn(OAc)$_2$ [24].

Metalloporphyrins and ligands were purified by successive chromatography on silica gel or alumina columns. The purity of final products was checked by UV–vis and NMR spectroscopy.

Magnesium monoperoxyphthalate was purchased from Aldrich and titrated iodometrically prior to use.

3. Results and discussion

A series of manganese porphyrins of the second and third generation were applied as catalysts in the oxidation of two model unreactive cycloalkanes (cyclohexane and cyclooctane) with MMPP as oxygen donor at room temperature. All these complexes turned out to be active catalysts for oxidation of cycloalkanes. Table 1 shows the results of the oxidation of cyclohexane. For the manganese porphyrins of second generation: Mn(TPFPP) and Mn(TDCPP) with electron-withdrawing substituents on phenyl rings, the main products are cyclohexanone and cyclohexanol. It is interesting to notice that in biological systems alcohol is always the main product. No other products were detected in the organic phase, although the ketone and alcohol were found at selectivies of about 50–60%. This suggests that some other products were formed which were soluble in water. These were probably polyhydroxylation compounds. Formation of such products was postulated by Querci and Ricci [18] for the same reaction with MMPP. Halogenation of pyrollic ring performed for the Mn(TDCPβCl_8P), increases its catalytic activity. For this porphyrin with electron-withdrawing substituents on phenyl and pyrrole rings the conversion of cyclohexane and the yield to cyclohexanone increase while the yield to cyclohexanol decreases. In contrast to chlorinated and perchlorinated metalloporphyrins, ring-polinitrated metalloporphyrins have received little attention [14,15,22]. Polinitration of pyrollic rings also causes an increase of the catalytic activity of manganese porphyrin similarly to halogenation but we observed the formation

Table 1
Oxidation of cyclohexane catalyzed by manganese porphyrins with MMPP as oxygen donor[a]

Catalyst	Cyclohexane conversion (%)	Cyclohexanone yield (%)	Cyclohexanol yield (%)	Cyclohexene yield (%)	Epoxide yield (%)
Mn(TDCPP)	84.3	30.7	26.9	–	–
Mn(TPFPP)	95.5	32.5	21.3	–	–
Mn(TDCPβCl_8P)	100	38.8	20.8	–	–
Mn(TPCPβ(NO_2)$_5$P)	100	39.4	18.1	2.2	7.1
Mn(TPFPβ(NO_2)$_4$P)	97.2	40.3	15.2	1.4	5.9

[a] See conditions in the text.

Table 2
Oxidation of cyclooctane catalyzed by manganese porphyrins with MMPP as oxygen donor[a]

Catalyst	Cyclooctane conversion (%)	Cyclooctanone yield (%)	Cyclooctanol yield (%)	Cyclooctene yield (%)	Epoxide yield (%)
Mn(TDCPP)	89.6	32.2	26.3	–	–
Mn(TPFPP)	92.3	35.1	25.8	–	–
Mn(TDCPβCl_8P)	100	39.8	22.9	–	–
Mn(TPCPβ$(NO_2)_5$P)	100	41.6	20.2	5.5	9.7
Mn(TPFPβ$(NO_2)_4$P)	100	45.4	18.2	3.1	8.4

[a] See conditions in the text.

of two new products: olefin and epoxide in small yields. Olefin is the product of the oxidative dehydrogenation of cycloalkanes. It becomes then oxidized to the epoxide. The oxidation of the olefins to epoxides by single oxygen donors was discussed in our earlier study [14,15] It is worth noting that the character of the substituents has significant influence on the activity and selectivity of catalysts. Thus, by varying the structure of the porphyrin ligand we are able to change the selectivity of the reaction and its mechanism. The use of Mn(TDCPβCl_8P) bearing chloro substituents, moderately electron-withdrawing groups, results in ketone and alcohol while the pernitro manganese porphyrins Mn(TPCPβ$(NO_2)_5$P) and Mn(TPFPβ$(NO_2)_4$P) with bulky and strongly electron-withdrawing substituents produce additionally olefin and epoxide. The most active among studied catalysts were two polynitrated manganese complexes: Mn(TPCPβ$(NO_2)_5$P) and Mn(TPFPβ$(NO_2)_4$P) showing the highest yields and the highest selectivity.

The formation of products of the oxidative dehydrogenation of cycloalkanes was also observed by Nappa and Tolman [25] in oxidation of cyclohexane with iron porphyrins and iodosobenzene as oxygen donor. Moreover, oxidative dehydrogenation was also present in oxidation of terpene derivative with metalloporphyrins and sodium hypochlorite or potassium monopersulfate as oxygen donors [26], but this reaction pathway was suggested to be rather unusual when using metalloporphyrins as catalysts [26]. Oxidative dehydrogenation was also observed in oxidation of cyclohexane with iodosobenzene and manganese porphyrins [27]. The addition of tin Lewis acids, $Ph_3SnO_2C_8F_{15}$ and $Ph_3SnO_3SC_6F_{13}$ as axial ligands increase the yield of products in this reaction by reducing the electron density on metallic center.

The catalytic results of the oxidation of cyclooctane in the presence of the same manganese porphyrins as catalysts are shown in Table 2. The nature and location of the substituents in porphyrin rings have a major influence on the yields and products distribution in the oxidation of cyclooctane. Comparison of the results obtained for cyclohexane (Table 1) with those observed in case of cyclooctane quoted in Table 2 indicates that the latter is more reactive and gives higher yields of products. In the case of cyclooctane oxidation with polynitrated manganese porphyrins, the yields of olefin and epoxide increases in comparison with cyclohexane oxidation. The most efficient catalytic system in this reaction, similarly to the cyclohexane oxidation, involves polynitrated manganese porphyrins of the third generation: Mn(TPCPβ$(NO_2)_5$P) and Mn(TPFPβ$(NO_2)_4$P) bearing electron-withdrawing substituents on the phenyl and nitro groups on pyrrole rings.

The mechanism of hydroxylation of the alkanes with metalloporphyrins as catalysts and oxygen donors was postulated by Groves as a "rebound mechanism" [28]. The first step involves reaction between metalloporphyrin and oxygen donor yielding oxo-complex. The oxo-species is strongly electrophilic in nature and may react with any electron rich region of a substrate. In the case of alkanes, reaction of substrate with oxo-complex leads to free radical and hydroxy metalloporphyrins in the solvent cage. Recombination of this intimate pair: radical with manganese intermediate would produce hydroxylated product and the starting metalloporphyrin. Alcohol is obtained by this pathway. Alternatively, the radical may diffuse out of the solvent cage to produce a free radical and hydroxy manganese porphyrin. In the next step free radical may react with substrate or metalloporphyrin giving other products.

Fig. 2 presents our proposal of the modification of the reaction mechanism. While, the oxidation of hydrocarbons with iodosylbenzene as oxygen donor mainly leads to the formation of alcohol as the main product with traces of ketone, in the case of MMPP the main products are the ketone and alcohol with little amounts of epoxide and olefin. Certain details of this mechanism like formation of an oxocomplex from metalloporphyrin and oxygen donor and its further reaction with alkane to radi-

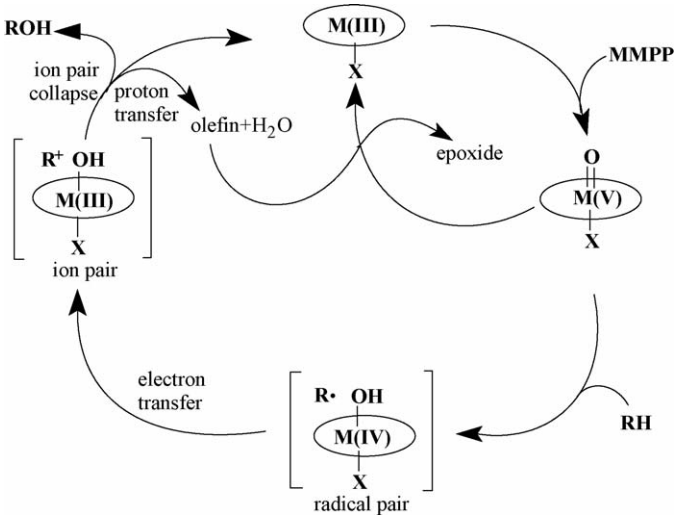

Fig. 2. Scheme of the oxidation of cycloalkanes with metalloporphyrin and MMPP.

cal and hydroxy metalloporphyrins are generally agreed upon. However, we suggest, on the grounds of our results, that in the case of polynitrated metalloporphyrin with bulky and strongly electron-withdrawing substituents the reaction may proceed by different mechanism because electron transfer is faster than a radical pair collapse. In other words, electron transfer mechanism is the predominant pathway with the subsequent ion pair collapse for alcohol formation. The same point of view was presented by Smegal and Hill [29]. Oxidation of alcohol usually occurs in our system, resulting in the formation of the corresponding ketone, the main product of our reaction [7,18,30]. A competing pathway produced olefin via the proton transfer. The result of the oxidation of olefin by oxo species is the epoxide formation.

Concluding, in the case of the oxidation of cycloalkanes with MMPP as oxygen donor the reaction may occur either via the mechanism proposed by us for polynitrated metalloporphyrins or via the rebound mechanism for other second and third generation metalloporphyrins depending on the nature of the metalloporphyrins and the type of oxygen donor.

4. Conclusions

Magnesium monoperoxophthalate (MMPP) is a very efficient oxygen donor in the oxidation of cycloalkanes catalyzed by manganese porphyrins with multiple electron-withdrawing peripheral substituents at room temperature and under phase-transfer conditions. We have found that the presence of different groups in porphyrin rings is capable of modifying the yield and selectivity of the investigated reaction. The system with polynitrated metalloporphyrins as catalysts, besides alcohol and ketone as the main oxidation products, gives olefin and epoxide which are the products of oxidative dehydrogenation of cycloalkanes.

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