Pernitrated metalloporphyrins as catalysts in oxidation with magnesium monoperoxophthalate
Part II. Epoxidation of linear olefins

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Abstract

The system composed of manganese (2,6)-dichlorotetraphenyl- or pentafluorotetraphenyl-porphyrins, bearing nitro groups at the β-pyrrolic positions as catalysts and monoperoxyphthalic acid magnesium salt (MMPP) as oxidant is an efficient model system for epoxidation of dodecene-1 and propene. A comparison with the corresponding system based on iron and cobalt complexes as well as the influence of the addition of a nitrogenous base are also described. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metalloporphyrin-based model systems for oxidation of hydrocarbons in a liquid phase under mild conditions commonly contain such terminal oxidants as hydrogen peroxide, organic hydroperoxides, hypochlorites, monopersulphates and peroxyacids or its salts [1,2]. Magnesium monoperoxyphthalate, alternatively used in organic synthesis instead of hazardous peroxyacids [3,4], is also known as the effective and selective oxidant in epoxidation of olefins or hydroxylation of hydrocarbons catalyzed by metalloporphyrins [5–10]. Among the metalloporphyrins bearing substituents at their periphery, very important class containing atoms of halogens or organic or inorganic groups attached at β-pyrrolic positions as well as other substituents at phenyl rings, were recently synthetized and investigated as catalysts for oxidation of organic substrates [11–15]. The yield of products and the selectivity of such a system appeared to be dependent on the character of a metal center, structure of the porphyrin ligand

used, as well as the oxidant applied. Moreover, that it has been claimed by many authors [16–18], the reaction medium containing strongly coordinating molecules present is capable of modifying the catalytic efficiency of porphyrin complexes. However, effective systems containing halogenated porphyrins with β-nitro groups, in which the presence of organic bases in the reaction medium is not necessary, are also known [19].

Here, we report the catalytic applications of certain manganese, iron and cobaltous porphyrins to epoxidize linear, rather inert olefins: dodecene-1 and propene. Catalytic epoxidation of dodecene-1 or propene with magnesium monoperoxyphthalate (MMPP) in ethyl acetate–water solution, containing Bu_4NCl as the phase transfer agent, has been investigated. Manganese, iron and cobalt tetraarylporphyrins with partially or completely halogenated phenyl rings, having nitro substituents introduced into pyrrole rings, have been used as catalysts. Contrary to similar catalytic systems containing metalloporphyrins with less substituted peripheric positions, the influence of the presence of N-base used: 4-*tert*-butylpyridine was generally found to be negative or not significantly modifying the yield of the products.

2. Experimental

Epoxidation of dodecene-1 was performed in a thermostated (25°C) glass reactor of 10 ml volume equipped with a magnetic stirrer. Organic phase consisting of 1 ml ethyl acetate as a solvent, 3.45×10^{-4} M of olefin, 6.24×10^{-5} M or none of 4-*tert*-butylpyridine and 2.5×10^{-6} M of porphyrin catalyst was mixed for 1 h with 2 ml of water containing 7.0×10^{-4} M of oxidant MMPP and 1.0×10^{-5} M of tetrabutyl-ammonium chloride as a phase transfer agent. In order to replace the dodecene-1 by gaseous propene, the reactor was branched to an electronic system of valves maintaining the constant, atmospheric pressure over a reaction mix-

ture containing the described components. After 1 h of stirring, products were analyzed by gas chromatography. Porphyrin ligands, TDCPP and TPFPP were prepared according to a Lindsay method [20], and nitrated by fumic nitric acid [19]. Manganese, iron and cobalt ions were then introduced by a standard metal insertion method [21]. 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

The results obtained are summarized in Tables 1 and 2. The investigated manganese–porphyrin complexes appeared suitable catalyst for epoxidation of both olefins under mild conditions. As is shown in Table 1, the corresponding iron complexes were less active in epoxidation of dodecene-1, whereas cobaltous porphyrins were totally inactive. The addition of the N-base such as 4-*tert*-butylpyridine decreases the activity of all investigated systems. This effect is most evident in the case of both iron porphyrins employed.

When propene is used as a substrate of the reaction (Table 2), nitrated pentafluoroporphyrins of manganese and iron were found to be the most active catalysts. Still, the addition of a pyridine derivative, negatively influenced the catalytic activity of manganese and iron complexes, with exception of cobaltous ones, which demonstrate rather small, but significant activity, compared to the system in which none of metalloporphyrin was present.

The introduction of halogen and nitro substituents, possessing electroaccepting abilities into porphyrin macrocycle, makes the metal center strongly electron deficient. The same properties acquire active oxo-like complexes with manganese or iron, generated in the course of the reaction and capable to epoxidize olefins. The organic N-base present in the reaction medium, upon coordination to the metal center,

Table 1

Epoxidation of dodecene-1 in the presence of β-pernitrated metalloporphyrins

[Catalyst] $= 2.5 \times 10^{-6}$ M, [dodecene-1] $= 3.45 \times 10^{-4}$ M, [4-*tert*-butylpyridine] $= 6.24 \times 10^{-5}$ M or none, [MMPP] $= 7.0 \times 10^{-4}$ M, [tetrabutylammonium chloride] $= 1.0 \times 10^{-5}$ M. Solvents: ethyl acetate $= 1$ ml, water $= 2$ ml. $T = 25°C$, $t = 1$ h.

Catalyst	4-tBuPy	Dodecene-1 conversion (%)	Epoxide yield (%)	Selectivity (%)	Epoxide/ catalyst (M/M)
None	−	0.0	0.0	−	−
None	+	0.0	0.0	−	−
Mn(Cl)TDCPβ-(NO$_2$)$_5$P	−	100.0	95.0	95.0	130.8
Mn(Cl)TDCPβ-(NO$_2$)$_5$P	+	82.5	78.0	95.0	108.0
Fe(Cl)TDCPβ-(NO$_2$)$_5$P	−	47.0	39.0	83.0	54.0
Fe(Cl)TDCPβ-(NO$_2$)$_5$P	+	19.0	14.0	73.0	19.2
CoTDCPβ-(NO$_2$)$_5$ P	−	0.0	0.0	−	−
CoTDCPβ-(NO$_2$)$_5$ P	+	0.0	0.0	−	−
Mn(Cl)TPFPβ-(NO$_2$)$_4$P	−	100.0	96.0	96.0	132.4
Mn(Cl)TPFPβ-(NO$_2$)$_4$P	+	100.0	94.0	94.0	130.0
Fe(Cl)TPFPβ-(NO$_2$)$_4$P	−	49.0	42.0	87.0	59.2
Fe(Cl)TPFPβ-(NO$_2$)$_4$P	+	28.6	22.0	80.0	31.7
CoTPFPβ-(NO$_2$)$_4$P	−	0.0	0.0	−	−
CoTPFPβ-(NO$_2$)$_4$P	+	0.0	0.0	−	−

serves as an electron source and reduces its electrophilicity. Therefore, the catalytic activity of such modified catalysts is decreased by the presence of this additive.

Distinct difference between the catalytic behavior of manganese and iron porphyrins in the presence of 4-*tert*-butylpyridine, may be explained in terms of different coordinating abilities of these metals. Iron achieves six coordinate geometry much easier than five coordinated manganese, which thus is better accessible for other molecules present in solution. Catalytic properties of cobaltous porphyrins, known to bind reversible dioxygen [22] rather, then react directly with ready-to-use oxidants, is under current investigation.

4. Conclusions

Nitrated and halogenated manganese porphyrins appeared to be effective catalysts for epoxidation of linear olefins studied with monoperoxyphthalic acid as oxidant. Pentafluoro manganese complex with nitro substituents at the β-pyrrolic positions showed the highest catalytic activity even in the presence of coordinating additive. Iron and cobalt porphyrins with the corresponding structure of the ligand are less active or inactive.

Table 2

Epoxidation of propene in the presence of β-pernitrated metalloporphyrins

[Catalyst] $= 2.5 \times 10^{-6}$ M, $p_{propene} = 1013$ hPa, [4-*tert*-butylpyridine] $= 6.24 \times 10^{-5}$ M or none, [MMPP] $= 7.0 \times 10^{-4}$ M, [tetrabutylammonium chloride] $= 1.0 \times 10^{-5}$ M. Solvents: ethyl acetate $= 1$ ml, water $= 2$ ml. $T = 25°C$, $t = 1$ h.

Catalyst	4-tBuPy	1,2-Epoxypropane/ catalyst (M/M)
None	−	−
None	+	−
Mn(Cl)TDCPβ-(NO$_2$)$_5$P	−	120.8
Mn(Cl)TDCPβ-(NO$_2$)$_5$P	+	91.6
Fe(Cl)TDCPβ-NO$_2$)$_5$P	−	49.0
Fe(Cl)TDCPβ-NO$_2$)$_5$P	+	18.5
CoTDCPβ-(NO$_2$)$_5$P	−	2.6
CoTDCPβ-(NO$_2$)$_5$P	+	35.0
Mn(Cl)TPFPβ-(NO$_2$)$_4$P	−	404.0
Mn(Cl)TPFPβ-(NO$_2$)$_4$P	+	320.8
Fe(Cl)TPFPβ-(NO$_2$)$_4$P	−	173.6
Fe(Cl)TPFPβ-(NO$_2$)$_4$P	+	110.8
CoTPFPβ-(NO$_2$)$_4$P	−	2.8
CoTPFPβ-(NO$_2$)$_4$P	+	41.2

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