

Epoxidation of alkene in water catalyzed by metalloporphyrin

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Received: August 2023; Revised: September 2023; Accepted: October 2023

Abstract: The majority of solvents that are utilized for homogeneous industrial catalysis are volatile organic compounds, which present risks due to toxicity, volatility and flammability. The discovery of surrogates which offer reduced environmental impact and safer process which is based on the principles of green chemistry is of great importance. An efficient biomimetic epoxidation reaction based on association of sodium periodate as oxidant to water soluble manganese and iron meso-tetrakis(p-sulfonatophenyl)porphyrin (MnTPPS, FeTPPS) as catalysts in water was reported. We have been able to omit organic solvent and do epoxidation reaction in water accompanied by phase transfer catalyst agent/ or minimum amount of organic solvent/ or high axial ligand ratio. FeTPPS was more active and more unstable than MnTPPS. The factors which affect the stability and efficiency of catalysts were investigated. The influence of acetonitrile or axial ligands on the epoxidation reactions catalyzed by water soluble metalloporphyrins could be due to the fact that they act as a phase transfer agent that affect the substrate- catalyst interactions during the oxygen transfer step.

Keywords: Biomimetic epoxidation reaction, MnTPPS, FeTPPS, Sodium periodate, Green chemistry.

Introduction

The majority of solvents that are utilized for homogeneous industrial catalysis are volatile organic compounds, which present risks due to toxicity, volatility and flammability. The discovery of surrogates to traditional organic solvents which offer reduced environmental impact and safer process is of great importance. Biomimetic epoxidation reactions with synthetic metalloporphyrin complexes have been attracting much attention in the last two decades [1-5]. Most of synthetic p-450 analogues are soluble in organic solvents and their activities with water soluble oxidizing agents depend upon phase transfer catalysis. However the organic solutions in with most p-450 mimics are studied doesn't resemble physiological condition [6]. It is preferable that oxidation reactions be based on the principles of green chemistry and avoids heavy metal reagents, toxic solvents and generation of hazardous wastes as well as aqueous reaction condition.

We wish to report an epoxidation reaction catalyzed by manganese and iron meso-tetrakis (p-sulfonatophenyl) porphyrin (MnTPPS, FeTPPS) [7-12] (Figure 1) in water as inexpensive and environmental benign solvent under sodium periodate as an effective, inexpensive and nontoxic oxidant. MnTPPS and FeTPPS was synthesized and purified according to the literature [13-17]. Omitting of organic solvent and presenting very simple, cheap and clean methods are our major goals in this paper.

Results and Discussion

The epoxidation reactions in water were carried out at room temperature with the alkene as substrate, sodium periodate as oxidant, sodium acetate as cocatalyst and for constant ionic strength, imidazole as axial ligand and MnTPPS and FeTPPS as catalyst in 1:2:0.73:0.06:0.006 ratio respectively. Five different factors of this biomimetic epoxidation of alkenes those were investigated in this communication are: 1) The comparative efficiency of MnTPPS and FeTPPS as catalyst 2) Influence of acetonitrile associated

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with water in a single phase system. 3) Influence of imidazole as axial ligand 4) Complete omitting of organic solvents. and 5) Influence of tetra n-butylammoniumbromide as phase transfer agent on the yield of oxidation products. The potential of manganese (III) porphyrin catalyst for epoxidation was initially investigated with cyclooctene in the presence of sodium periodate. The optimum condition used for the epoxidation of cyclooctene can be applied to styrene (Table 1).

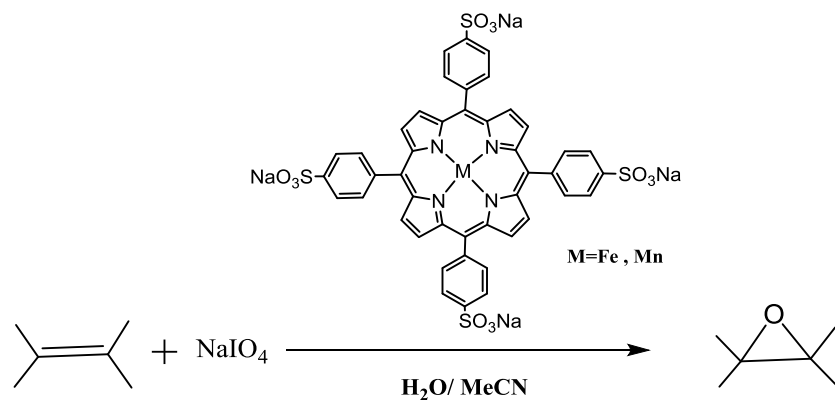


Figure 1. Epoxidation procedure.

Table 1. Epoxidation of alkene by NaIO₄ catalyzed by MTPPS^a in Water containing 20% Acetonitrile.

Catalyst	Substrate	Product	Yield (%) ^b
MnTPPS	Cyclooctene	Cyclooctene oxide	98
		Benzaldehyde	70
	Styrene	Styrene oxide	2.5
		Phenyl acetaldehyde	2.5
FeTPPS	Cyclooctene ^c	Cyclooctene oxide	35(100)
		Benzaldehyde	85
	Styrene	Styrene oxide	2.5
		Phenyl acetaldehyde	2.5

^a Reaction condition: alkene (100μmole), NaIO₄ (200μmole), Im (6μmole), catalyst (0.6μmole), H₂O / MeCN (4 / 1).

^b GC yield based on starting alkene.

^c Reaction condition: alkene (100μmole), NaIO₄ (200μmole), Im (15μmole), catalyst (0.6μmole), H₂O / MeCN (2 / 1).

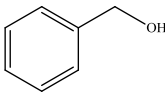
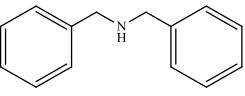
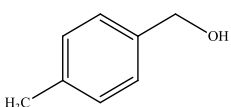
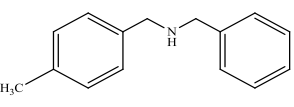
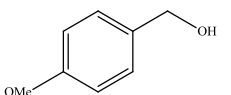
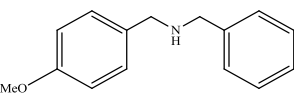
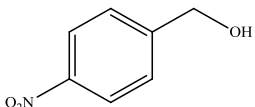
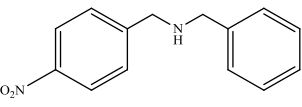
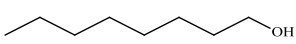
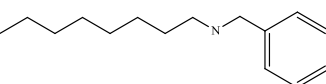
We have been able to apply a selective method for oxidation of alkene, for example styrene was

converted 75 percent to benzaldehyde and only 2.5 percent to styrene oxide and 2.5 percent to

phenyl acetaldehyde because, sodium periodate itself oxidized styrene oxide to benzaldehyde in water at room temperature. The conversion of cyclooctene decrease when the percentage of acetonitrile in the reaction medium increases, i.e. when the hydrophobicity of the medium increases. The maximum catalytic activity is obtained for 20 percent of acetonitrile (Figure 2).

Sodium acetate was applied for constant ionic strength. It didn't have cocatalytic effect in the epoxidation of cyclooctene in water containing 30 percent acetonitrile. However, in the water containing 20 percent acetonitrile addition of sodium acetate is an effective factor to increase the yield of epoxidation of cyclooctene from 60 to 98 percents.

Table 2. Conversion of various alcohols in terms of structure in the reaction with benzylamine to second-type amines in the presence of the NCM@EDTA-Cu(II) catalyst.

Entry	substrate	Product	Yield (%)
1			90
2			92
3			94
4			75
5			65

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For 20% of acetonitrile, axial ligands in MnTPPS didn't affect the rate and the yield of epoxidation, but in aqueous condition axial ligands in MnTPPS become important whereas the yield of cyclooctene oxide increased when the molar ratio of axial ligand increased (6% for Im/Cat = 10 and 75% for Im/Cat = 75) (Figure 3).

For complete elimination of organic solvent, we applied tetra n-butylammoniumbromide in 10 molar ratio to the catalyst as phase transfer agent in 100% water solvent and to our surprise 100 percent conversion of cyclooctene was obtained. It seems for substrate which are more soluble in water there is no need for organic solvent or even phase transfer catalyst (Figure 4).

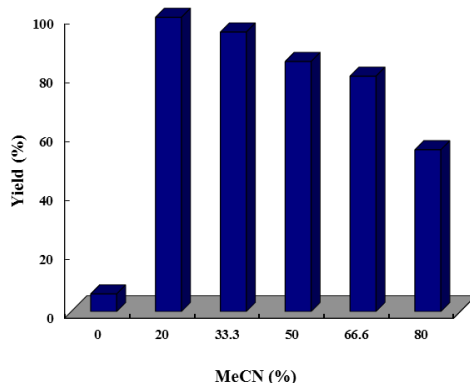


Figure 2. Influence of acetonitrile in epoxidation reaction catalyzed by MnTPPS, The ratio of catalyst: ligand: substrate: oxidant: 0.006:0.06:1:2.

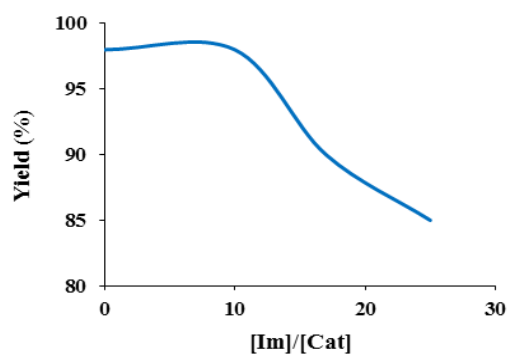


Figure 3. Influence of imidazole in epoxidation reaction catalyzed by MnTPPS in water containing 20 % MeCN

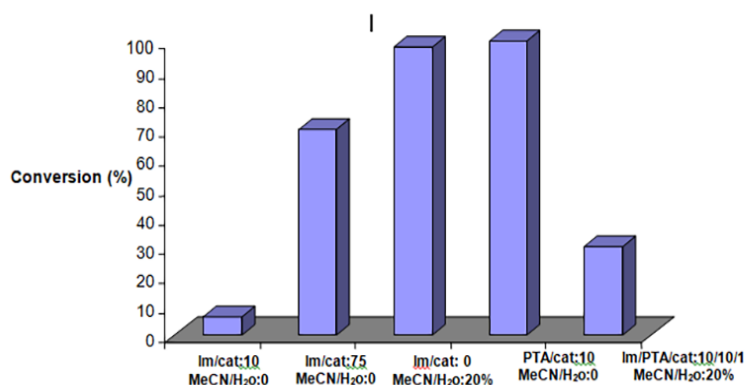


Figure 4: Influence of Acetonitrile, imidazole and phase transfer agent in epoxidation reaction catalyzed by MnTPPS

To our knowledge there are few reports of application of water soluble porphyrin as catalyst

for epoxidation of styrene and cyclooctene by water soluble oxidant. Our system is better than

Ford's system [23] in that MnTDCPPS was immobilized in colloidal anion exchange particles and catalyzed styrene epoxidation by NaOCl in 75%. He couldn't obtain epoxides for other alkenes. Attempts to improve the yield of cyclooctene oxide by addition of 50% methanol, 50% acetonitrile, and 22 % acetonitrile as co-solvent gave yields less than 1%, 4%, and 6% respectively. In aqueous medium containing high percentage of organic solvents that was reported by Yuan-Zong Li et al. (for styrene epoxidation by NaIO₄, NaOCl, and KHSO₅ catalyzed by MnTPPS the epoxidation yield was 5%, 25%, and 35% respectively) [24].

FeTPPS are more active than MnTPPS. Its stability in water highly depends on solubility of substrate in water. If the solubility of substrate

were low, the self-destruction of iron porphyrin became more important, therefore it shows much faster decomposition rate in aqueous solution containing oxidant (by observing the disappearance of the solution color) [25]. Improvement stability of FeTPPS in water solution was made by: 1) Increasing the percentage of acetonitrile, namely, the hydrophobicity of the reaction mixture (Table 1) 2) By addition of an extra ligand to FeTPPS especially for cyclooctene that is more insoluble in water than styrene (the solubility of styrene in water is 0.07g/L at room temperature). For example by increasing of axial ligand ratio to catalyst from 10 to 15 the yield of reaction was changed from 35 to 60 percent (Figure 5).

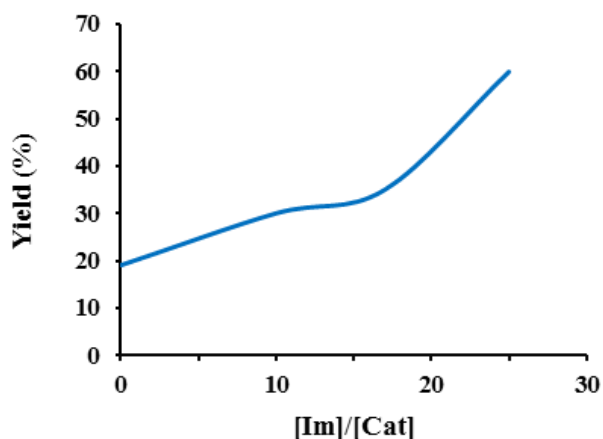


Figure 5. Influence of imidazole in epoxidation reaction catalyzed by FeTPPS in water containing 20 % MeCN

Turn over number (TON) of catalyst is determined by total concentration of products divided to the initial catalyst concentration in the presence of excess substrate. The ratio of catalyst, imidazole, substrate, oxidant that was applied in this study for manganese porphyrin was 1:10:1667:667 in water that contains 20% acetonitrile. The measured TON of MnTPPS for cyclooctene after 24h was 400.

For studying the durability of catalyst in the second 24h, we added 667 μ mol oxidant to that the above mixture and the same amount of oxidation product was obtained which shows this catalytic system is very efficient.

Conclusion

In conclusion, an efficient biomimetic epoxidation reaction based on association of

sodium periodate as oxidant to water soluble manganese and iron meso-tetrakis (p-sulfonatophenyl)porphyrin (MnTPPS, FeTPPS) as catalysts in water was reported. Because of our major goal in omitting organic solvent, we have been able to do epoxidation reaction in water accompanied by phase transfer catalyst agent/ or minimum amount of organic solvent/ or high axial ligand ratio. According to our results, the influence of acetonitrile or axial ligands on the epoxidation reactions catalyzed by water soluble metalloporphyrins could be due to the fact that they act as a phase transfer agent that affect the substrate- catalyst interactions during the oxygen transfer step. For studying it we applied tetra n-butylammonium bromide

(PTA/Cat = 10) as phase transfer agent in epoxidation of cyclooctene catalyzed by MnTPPS under in aqueous solution, 100 percent conversion was obtained.

Experimental

Materials

All materials were commercial reagent grade, and were obtained from Merck. The porphyrin ligand (tetraphenylporphyrin) was prepared according to the Adler et al. [18]. The sulfonation of H₂TPP and its metalation after sulfonation were carried out as in the literature [19-22]. The structures in every step were confirmed by using UV-visible and IR spectroscopies.

Analysis

IR and UV-vis spectra were recorded with a Shimadzu IR-470 spectrometer and UV-vis Shimadzu 2100. Gas chromatography was performed on a Varian CP-3800 equipped with DB-1 capillary column (0.3mm. 25m) and FID detector.

Epoxidation Reaction

All reactions were carried out at room temperature in a screw-capped vial with a magnetic stirring bar. 10 μmole n-decane as internal standard, 100 μmole of olefin and 0.18ml acetonitrile are added to a solution of 0.6 μmole MTPPS, 6 μmole imidazole and 37 μmole sodium acetate in 0.1ml water. 0.6ml of 0.33M NaIO₄ is then added to that mixture. The reaction was stirred for 24 h. 1ml of dichloromethane/n-hexane was added to the reaction medium and the tube was stirred vigorously with magnetic stirrer. The top organic phase was transferred to another flask. The extraction process was repeated until no alkene or product peak was seen on GC chromatogram.

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