

# Latex Supported Manganese(III) Porphyrin Catalysts for Oxidations of Alkenes by Hydrogen Peroxide and *tert*-Butyl Hydroperoxide in the Aqueous Medium

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Cationic polymer latexes were prepared by emulsion copolymerization of vinylbenzyl chloride and divinylbenzene followed by quaternization with trimethylamine and used as catalyst supports for 5,10,15,20-tetrakis(2, 6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) chloride and 5,10,15,20-tetra(4-sulfonatophenyl)porphinatomanganese(III) chloride. The supported catalysts and water soluble analogues were used for oxidation of styrene, 1-decene and *cis*-cyclooctene by hydrogen peroxide and *tert*-butyl hydroperoxide in the aqueous phase. The oxidation of 1-decene and *cis*-cyclooctene failed. In the oxidation of styrene, the porphyrin catalysts in the latex were more active than in solution. The relative molar ratios of oxidant: styrene: Mn porphyrin were 1250: 750: 1, and about 25% styrene conversion in 4 h was obtained. When hydrogen peroxide was employed as oxidant, styrene oxide and benzaldehyde were the major and minor products, respectively, and in the case of *tert*-butyl hydroperoxide, it was vice versa. The reaction depended on pH, the porphyrin ligand, type of oxidant used and presence of imidazole.

## Introduction

There has been great progress since the 1980s in the design and use of metalloporphyrins as oxidation catalysts for alkanes and alkenes<sup>1</sup>. Metalloporphyrins have structural resemblance to the cytochromes P-450, a class of enzymes that mediate a wide variety of oxygenations and the oxidative metabolism of exogenous compounds<sup>2,3</sup>. The active site of P-450 contains a single iron(III) protoporphyrin IX prosthetic group, which binds, reduces and activates molecular oxygen<sup>2</sup>.

During attempts to mimic the activity of P-450, a wide variety of substituted metalloporphyrins and metalloporphyrin-catalyzed oxidation reactions have been discovered<sup>1,3-5</sup>. Iron(III) and manganese(III) porphyrins have been used most commonly as oxidation catalysts, and iodosylbenzene, hypochlorites, hydrogen peroxide, alkyl peroxides, amine *N*-oxides, *m*-chloroperbenzoic acid, dioxygen with a reducing agent, perchlorate, periodate and ozone have been employed as oxygen sources<sup>1</sup>. These studies have been carried out under various conditions; for example, polymer supported or bound metalloporphyrin catalysts have been used in the reactions to take separation and/or catalyst protection advantages of the supported catalysis<sup>6-13</sup>. Usually large polymer beads have been employed as support. Clearly, these systems are het-

erogeneous and the drawbacks of this type system are mass transfer and intraparticle diffusional limitations. However, polymer latexes, due to very small particle sizes ( $< 1 \mu\text{m}$ ) and extremely large surface areas, can overcome mass transfer and intraparticle diffusional limitations of the conventional supported catalysis. So far, few investigations about latex-supported metallo complex catalysts<sup>14-26</sup> and only two investigations about latex-supported metalloporphyrin catalysis<sup>22,24</sup> have been reported. The latex-supported metallo complex catalysts have had higher catalytic activities than the homogeneous analogues. In the reactions catalyzed by latex-supported metalloporphyrins, sodium hypochlorite has been employed as an oxygen source and the destruction of metalloporphyrins have been evidenced<sup>22</sup>.

In this study, hydrogen peroxide and *tert*-butyl hydroperoxide, which are less powerful oxidants than sodium hypochlorite, were used in the epoxidation of styrene, 1-decene and *cis*-cyclooctene catalyzed by latex bound and soluble 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrinatomanganese(III) chloride and 5,10,15,20-tetra(4-sulfonatophenyl)porphyrinatomanganese(III) chloride.

## Experimental

### Reagents and Instrumentation

Pyrrole (Merck) and borontrifluoride etherate (Sigma) were vacuum-distilled before use and stored under nitrogen at 4-5 °C. 2,6-Dichlorobenzaldehyde (Merck), benzaldehyde (Merck), hydrogen peroxide (3% w/v, Çağdaş Lab.) *tert*-butyl hydroperoxide (Bu<sup>t</sup>OOH, Merck), silica gel (70-230 mesh, Merck), Dowex 50X8 (Aldrich) were used as received. Vinylbenzyl chloride (70/30 m/p, Aldrich), divinylbenzene (m/p mixture, 55%, rest of ethylvinylbenzene), styrene (Aldrich) were used after the extraction of the inhibitors with 0.1 N NaOH and vacuum distillation. Chloroform was distilled over K<sub>2</sub>CO<sub>3</sub> and stored under N<sub>2</sub> over the 4 Å molecular sieve. The other reagents used were research grade.

Elemental analyses and <sup>1</sup>H NMR spectra were performed or taken by the Marmara Research Center of TÜBİTAK. GLC analyses of the reaction mixtures were performed on a Shimadzu GC-9AM equipped with a 2 mx3 mm ID 25% Carbowax 20M glass-packed column on 60/80 Chromosorb W<sup>®</sup> column support and an FID detector. The UV-visible spectra were taken using Shimadzu 2101 PC Ultraviolet-visible spectrophotometer, and TEM micrographs of the latex particles were taken at 19000-48000 magnification using JEOL- 100 CX2 transmission electron microscope at Ankara University. The average of the diameters of 8-10 non-aggregated particles measured from the photographic print of the micrographs was given as the particle size of the latexes.

### Preparations of Sulfonated Manganese Porphyrins

#### Preparation of 5,10,15,20-Tetrakis(2,6-dichloro-3-sulfonatophenyl)-porphyrinatomanganese(III) chloride (1, Mn TDCSPPNa<sub>4</sub> (Cl))

First, the porphyrin ligand 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (H<sub>2</sub>TDCPP) was prepared according to Linsey et al.<sup>27,28</sup>. In order to produce a sufficient amount H<sub>2</sub>TDCPP for catalysis, the synthesis was carried out six times and 1.05 g H<sub>2</sub>TDCPP was obtained. The sulfonation of H<sub>2</sub>TDCPP and its metallation after sulfonation were carried out as in the literature<sup>22,29</sup>. The structures in every steps were confirmed by using UV-visible and <sup>1</sup>H NMR spectroscopies and elemental analyses.

### **Preparations of 5,10,15,20-Tetra(4-sulfonatophenyl)porphinatomanganese(III) Chloride (MnTSPPNa<sub>4</sub>(Cl))**

First, 5,10,15,20-tetraphenylporphyrin (H<sub>2</sub> TPP) was prepared using the Adler method<sup>30</sup>. The procedures of the sulfonation and the metallation of the sulfonated porphyrin were similar to the ones used for the preparation of MnTDCPPNa<sub>4</sub>(Cl)<sup>29</sup>.

### **General Procedure for Preparations of Latexes**

The preparations of latexes were done in two steps using the emulsion polymerization technique of Campbell et al.<sup>31</sup>. In a typical preparation, a 250 mL round-bottomed flask was equipped with an overhead stirrer, a condenser and an addition funnel. The reaction flask was charged with hexadecyltrimethyl ammonium bromide (CTAB, 170 mg, 0.47 mmol) and distilled water (40 mL) and heated to 65 °C under N<sub>2</sub>. During the entire polymerization process, the flask content was stirred at 1100 ± 50 rpm. The addition funnel was charged with CTAB (457 mg, 1.30 mmol), vinylbenzyl chloride (VBC, 10.13 g, 66.4 mmol), divinylbenzene-ethylvinylbenzene (DVB-EVB, 863 mg, 3.65 mmol DVB, 2.94 mmol EVB), sodium bisulfite (22 mg, 0.21 mmol) and distilled water (30 mL). By shaking this mixture, a white pre-emulsion was obtained. After potassium persulfate (85 mg, 0.32 mmol) and sodium bisulfite (4 mg, 0.04 mmol) were added to the reaction flask at 65 °C, the pre-emulsion in the addition funnel was added dropwise to the stirred solution in the flask over fifteen minutes. After addition was completed, new fractions of potassium persulfate (10 mg, 0.027 mmol) and sodium bisulfite (2 mg, 0.02 mmol) were added and the polymerization was carried on for an extra 1.5 hours at 65 °C to completion.

After the temperature of the crosslinked poly (vinylbenzyl) chloride emulsion was brought to around 40 °C in thirty minutes, a solution of aqueous trimethylamine (45%, 8.7 g, 66.3 mmol) diluted with distilled water (30 mL) was added. This quaternization reaction was continued for six hours at 40 °C. To calculate the number of quaternary ammonium sites in the emulsion, the solid content of the emulsion and the amount of liberated chloride ions were determined using the Volhard titrimetric method<sup>32</sup>.

### **General Procedure for Epoxidation of Styrene**

In a typical experiment, a 25 mL round-bottomed flask was charged with styrene (130 mg, 1.25 mmol), toluene (115 mg, 1.25 mmol) as internal standard for GLC analyses, and latex (1.0 mL) which contains 59 mg polymer and 0.210 mmol N<sup>+</sup> group. While this mixture was being stirred magnetically, MnTDCSPPNa<sub>4</sub>(Cl) (1.0 mL, 1.63 × 10<sup>-3</sup> M), NaOH (0.60 mL 3.8 N) and H<sub>2</sub>O<sub>2</sub> (2.30 mL, 0.88 M) or Bu<sup>t</sup>OOH (0.28 mL, 7.3 M) were added sequentially and the flask contents were stirred for four hours at ambient temperature.

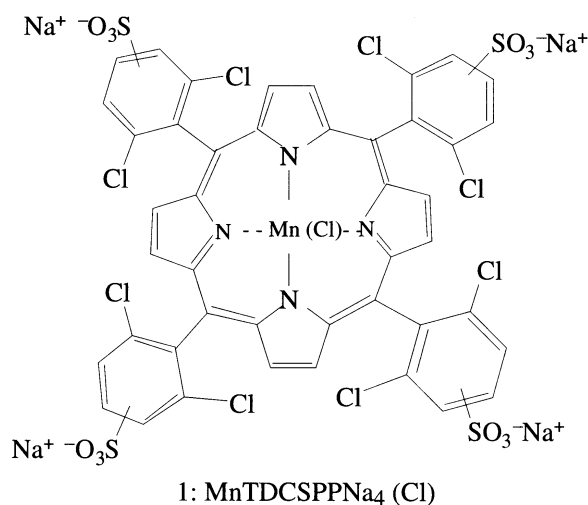
After the reaction time was over, the reaction mixture was transferred in a capped centrifuge tube. A few milliliters of diethylether was added, and the tube was shaken vigorously and centrifuged with a bench top centrifuge. The organic phase was transferred in a tube and the extraction process was repeated 7-8 times to ensure no organics were left in the aqueous phase. The extract was analyzed quantitatively by GLC.

## **Results and Discussion**

### **Preparation and Properties of the Metalloporphyrins**

In the literature, a wide variety of metalloporphyrins, which have resemblance to the active sites of the cytochrome P-450 enzymes, have been synthesized and used as catalysts for oxidations of alkanes and alkenes<sup>1</sup>.

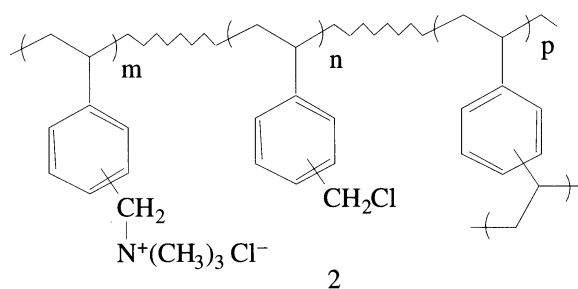
However, metalloporphyrins are easily destroyed or deactivated by oxidants such as iodosylbenzene, hypochlorites, alkyl peroxides, hydrogen peroxide so on<sup>1</sup>. The stability of the porphyrins is enhanced more by electron withdrawing and bulky substituents attached especially to the ortho positions of the phenyl groups of tetraarylporphyrins<sup>33-36</sup>. In order to have a water soluble, destruction resistant and oxygen transfer active metalloporphyrin, 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinat manganese(III) chloride (1, MnTDCSPPNa<sub>4</sub>(Cl)) was prepared according to the literature methods<sup>22,27,28</sup>. For comparison, the catalytic activity of MnTDCSPPNa<sub>4</sub>(Cl), 5,10,15,20-tetra(4-sulfonatophenyl)porphinat manganese(III) chloride (MnTSPPNa<sub>4</sub>(Cl)) was prepared as well. The latter is known to be destroyed easily by some oxidants.



(MnTSPPNa<sub>4</sub>(Cl)) was prepared in three steps: 1. Formation of porphyrin ligand from pyrrole and 2,6-dichlorobenzaldehyde; 2. Sulfonation of the porphyrin ligand with concd. H<sub>2</sub>SO<sub>4</sub>; 3. Metallation of the sulfonated porphyrin ligand. The UV-visible, <sup>1</sup>H NMR spectroscopic techniques and elemental analyses were used to prove the structures in every steps. The synthesis of the porphyrin ligand was carried out six times and the average yield obtained was 7.3% based on pyrrole. The sulfonation of H<sub>2</sub>TDCPP was found to be incomplete, and from <sup>1</sup>H NMR spectrum, 3.8 sulfonate groups per porphyrin ligand were seen. Nevertheless, the metalloporphyrin gained enough solubility in water and attachment site to the quaternary ammonium groups of the latexes. (MnTSPPNa<sub>4</sub>(Cl)) was prepared using similar synthetic routes as in the case of MnTDCSPPNa<sub>4</sub>(Cl). The structures in every steps were checked by UV- visible spectrophotometer.

## Preparations of Cationic Polymer Latexes

Latexes, which can be called colloidal anion exchange resins, were prepared via a two-stage process. In the first stage, emulsion polymerization of mixtures of DVB, VBC and styrene gave latexes containing chlorobenzyl moieties in polymer chains crosslinked with DVB. In the second stage, trimethylamine treatment converted most of the chloromethyl groups into quaternary ammonium groups, resulting in a latex in the form of a colloidal anion exchange resin (2). The number of quaternary ammonium groups was determined by analysis of the chloride ion content with the Volhard titrimetric method and by determination of the solid content of every latex. The particles sizes (diameter) of the latexes were determined with TEM micrographs.



The number of quaternary ammonium groups of the prepared seven latexes ranged from 3.5% to 81%. Four of the latexes containing styrene moieties (65.9-80.9%) lost their stabilities and coagulated in 1-2 months, so they were not used as catalyst support. Table 1 gives the compositions and properties of the stable latexes.

**Table 1.** Compositions and Properties of the Latexes

Latex	DVB mol%	EVB mol%	VBC mol%	$R_4N^+Cl^-^a$		Solid content mg/mL	Particle Size, nm
				mol%	eq/g		
QL6	10.2	8.2	1	81	$4.13 \times 10^{-3}$	49	$471 \pm 123$
QL7	5.0	4.1	23	68	$3.58 \times 10^{-3}$	59	$66 \pm 16$
QL8	1.0	0.8	22	76	$3.86 \times 10^{-3}$	73	$63 \pm 13$

<sup>a</sup> $P - N^+(CH_3)_3Cl^-$

## Epoxidation of Styrene Catalyzed by Polymer-Supported and Soluble Manganese Porphyrins

In the literature, metalloporphyrins, especially Mn and Fe derivatives, were used as catalysts for the epoxidation of alkenes by an oxidant<sup>1,2,4</sup>. These reactions were usually carried out in two-phase aqueous-organic mixtures due to the insolubility of alkene and metalloporphyrins in water where an oxidant such as  $OCl^-$ ,  $H_2O_2$ , ROOH etc. is present, and usually a phase transfer agent was employed to carry the oxidant into the organic phase. This two-phase system has the advantage of protecting metalloporphyrin to a large quantity of the oxidant, which is primarily responsible for the oxidative destruction of the metalloporphyrin. When water soluble metalloporphyrins are used as epoxidation catalysts, the oxidative destruction of metalloporphyrins becomes more important due to the presence of both metalloporphyrin and oxidant in the same phase. To overcome or limit the oxidative degradation problem and the formation of catalytically inactive  $\mu$ -oxo dimers, sterically hindered porphyrin  $MnTDCSPPNa_4(Cl)$  was used as a soluble and supported catalyst<sup>37</sup>. The aim of the binding of the sulfonated Mn porphyrins to latexes was to improve the catalytic activity by creating an organic medium with latexes to attract water insoluble alkenes and further preventing the formation of catalytically inactive porphyrin  $\mu$ -oxo dimers<sup>8,22,24</sup>. As a result, latex was expected to lead in concentrating water insoluble alkene within the polymer matrix, where a high concentration of the catalyst was present due to electrostatic binding. If this is true, the local concentrations of both reactant and catalyst should be higher than the overall concentrations in the aqueous solution, and this formation is expected to give a higher catalytic activity than the system without latex.

To see the experimental results of this argument, soluble and latex supported  $MnTDCSPP(Cl)$  catalysts were used as epoxidation catalysts for styrene by  $H_2O_2$  and  $Bu^tOOH$ . Epoxidations were carried out at room temperature in a mixture containing 1.25 mmol styrene, water soluble or supported Mn porphyrin, 2.03 mmol  $H_2O_2$  or  $Bu^tOOH$  at  $pH > 13$  for 4 h. The total volume of the mixtures was usually 5-6 mL.

The relative molar ratios of oxidant: styrene: MnTDCSPPNa<sub>4</sub>(Cl) were 1250: 750: 1. When the soluble and supported Mn porphyrin were not present in the reaction mixture, no reaction was observed, which shows that the catalyst is essential for the transfer of oxygen to the alkene.

**Catalytic Activities of Soluble and Latex Supported Manganese Porphyrins:** When latex bound MnTDCSPP (Cl) (except the one bound to QL6) was used as catalyst, higher conversions of styrene were observed than when soluble MnTDCSPPNa<sub>4</sub>(Cl) was used (Table 2). In the reaction, styrene oxide and benzaldehyde were the major and minor products, respectively, in the presence of both soluble MnTDCSPPNa<sub>4</sub>(Cl) and latex bound MnTDCSPP (Cl). The activities of the catalysts bound to QL7 and QL8, which differ in the degree of crosslinking and have somewhat similar size and degree of functionalization, were similar. However, the activity of the catalyst bound to QL6 was even lower than that of water soluble MnTDCSPPNa<sub>4</sub>(Cl) (Table 2). The size of QL6, which has a diameter seven times greater than that of QL7 and QL8, may be responsible for lower catalytic activity.

**Table 2.** Epoxidation of Styrene with H<sub>2</sub>O<sub>2</sub> Catalyzed by Soluble and Latex Bound Mn Porphyrins<sup>a</sup>

Reaction	Mn Porphyrin	Latex (mg)	GLC Analysis, %	
			Styrene oxide	Benzaldehyde
1	-	QL7 (59)	-	-
2	MnTDCSPPNa <sub>4</sub> (Cl)	-	11	1
3	MnTDCSPPNa <sub>4</sub> (Cl)	QL7 (59)	20	7
4	MnTDCSPPNa <sub>4</sub> (Cl)	QL8 (60)	18	6
5	MnTDCSPPNa <sub>4</sub> (Cl)	QL6 (60)	3	3
6	MnTSPPNa <sub>4</sub> (Cl)	QL7 (59)	10	5
7 <sup>b</sup>	MnTSPPNa <sub>4</sub> (Cl)	QL7 (59)	1	1

<sup>a</sup> Styrene (1.10-1.30 mmol), Mn Porphyrin (1.63x10<sup>-3</sup> mmol), H<sub>2</sub>O<sub>2</sub> (2.03 mmol) were present in the reaction mixtures. Volume 5.0-5.3 mL, pH > 13 and reaction time 4 h. <sup>b</sup> Reaction time 0.25 h.

Changing the Mn porphyrin from MnTDCSPPNa<sub>4</sub>(Cl) to MnTSPPNa<sub>4</sub>(Cl) could provide useful information about the stability and effect of the porphyrin ligand on the reaction. MnTSPPNa<sub>4</sub>(Cl) is known to have more tendency toward oxidative destruction, and it has been previously reported that soluble and latex bound MnTSPP(Cl) was destroyed by NaOCl in seconds<sup>22</sup>. In this study, the oxidant was either H<sub>2</sub>O<sub>2</sub> or Bu<sup>t</sup>OOH and the destruction of MnTSPPNa<sub>4</sub>(Cl) seemed to be prevented by use of these oxidants. As given in Table 2, latex bound MnTSPP(Cl) showed catalytic activity in the first 15 minutes and continued activity in 4 h. If the destruction had been fast enough like in the NaOCl case, the conversion would have stopped in a short time. A 15% conversion catalyzed by latex bound MnTSPP(Cl) was lower than conversion catalyzed by latex bound MnTDCSPPNa<sub>4</sub>(Cl). The lower activity of the latex bound MnTSPP(Cl) catalyst may be caused by the formation of  $\mu$ -oxo dimer complexes of this Mn porphyrin. It is known that  $\mu$ -oxo dimer complexes of metalloporphyrins are inactive catalysts in the oxygen transfer reactions. On the other hand ortho-substituted metalloporphyrins such as MnTDCSPPNa<sub>4</sub>(Cl) can not form  $\mu$ -oxo dimers due to the steric hindrance of the substituents.

**Effect of Oxidant:** Table 3 reports the experiments carried out with different oxidants. In this study primarily H<sub>2</sub>O<sub>2</sub> and Bu<sup>t</sup>OOH were used as oxidant, and one reaction was carried out using NaOCl to compare the effect of the oxidant type. When NaOCl was used, the highest conversion in the shortest time (1 h compare to 4 h) was obtained, which agrees with the report in the literature<sup>22</sup>. When H<sub>2</sub>O<sub>2</sub> and Bu<sup>t</sup>OOH were used as oxidant, there were no significant difference in the conversion, but there was an important difference in the product distributions of the two reactions. In the Bu<sup>t</sup>OOH case, benzaldehyde became the

major product instead of styrene oxide. Another observation for reaction run with the peroxides was gas evolution, which was not observed when  $\text{MaOCl}$  was used. In addition to the formation of metalloporphyrin-oxo ( $\text{MP}=\text{O}$ ) complex, which is the active species for the transfer of oxygen to the substrate, apparently  $\text{H}_2\text{O}_2$  and  $\text{Bu}^t\text{OOH}$  were dismutated or decomposed by the metalloporphyrins to give a gas. It may be speculated that the extent of this competing reaction of the peroxides may affect the conversion of styrene as well. The decomposition of  $\text{H}_2\text{O}_2$  by soluble and resin bound Mn- and Co-TSPP was reported in the literature, but the authors did not report or speculate about the decomposition products<sup>7</sup>. In another report, the reaction between  $\text{Bu}^t\text{OOH}$  and 5,10,15,20-tetra (N-methyl-4-pyridyl)porphyrinatoiron(III) pentachloride in aqueous solution gave methane and ethane gaseous products as well as water soluble products<sup>38</sup>.

**Table 3.** Effect of Oxidants on the Catalytic Activity of Latex Bound MnTDCSPP(Cl) for the Epoxidation of Styrene<sup>a</sup>

React.	Styrene	Mn P <sup>b</sup>	Oxidant (mmol)	Volume	Time	GLC Analysis, % <sup>c</sup>	
	mmol	mmol				mL	h
1	1.84	$2.15 \times 10^{-3}$	$\text{NaOCl}$ (3.90)	6.3	1	22	13
2	1.08	$1.63 \times 10^{-3}$	$\text{H}_2\text{O}_2$ (2.03)	5.0	4	20	7
3	1.26	$1.63 \times 10^{-3}$	$\text{Bu}^t\text{OOH}$ (2.03)	3.8	4	2	21

<sup>a</sup> Latex QL7 (59 mg) was present in the reaction mixtures and pH was  $> 13$ . <sup>b</sup> Mn P: MnTDCSPPNa<sub>4</sub>(Cl). <sup>c</sup> SO: Styrene oxide, BA: Benzaldehyde.

**Effect of pH:** To determine the pH dependence of the reaction, five reactions at different pHs were carried out using  $\text{H}_2\text{O}_2$  oxidant (Table 4). No reaction took place at pH 3.4, 6.3 and 8.6. At pH 10.1, only 7% conversion was observed. Considerable conversion was achieved at pH  $> 13$ , which is in agreement with the report in the literature<sup>22</sup>.

It is known that the addition of external ligands such as pyridine, imidazole and their derivatives shows very pronounced effect particularly on the catalytic activity of water insoluble metalloporphyrins<sup>39–44</sup>. In this study, addition of an external ligand (imidazole) to the reaction mixture did not increase the conversion of styrene, but helped reaction to take place in a wider pH range (from 5.7 to  $> 13$ ). At pH  $> 13$  the presence of imidazole had almost no effect on conversion and product distribution. On the other hand, there was about 36% conversion of styrene in the presence of imidazole at pH 7.4, at which no reaction took place at all in the absence of the external ligand. The presence of imidazole may be changing the epoxidation mechanism causing increase in the conversion and change in the product distribution at much lower pHs than pH  $> 13$  (Table 4). When  $\text{Bu}^t\text{OOH}$  was used as oxidant instead of  $\text{H}_2\text{O}_2$ , even at pH 4.3, the reaction was observed but the product distribution was altered (Table 4). Benzaldehyde became the major product instead of the expected product styrene oxide. In the presence of imidazole, again the conversion was higher at pH 8.6 than at pH  $> 13$ , which is a finding similar to that in the  $\text{H}_2\text{O}_2$  oxidant case.

**Effect of the Amounts of the Support and MnTDCSPPNa<sub>4</sub>(Cl):** Table 5 reports experiments carried out with increased amount of latex bound MnTDCSPP(Cl) or of latex or of styrene with all other amounts kept constant. When the amount of metalloporphyrin bound to a constant amount of latex was doubled, the conversion of styrene was increased about 25%. When the amount of latex increased, keeping the amount of metalloporphyrin constant, no significant increase in the conversion was observed. Increase in the amount of styrene did not affect the amounts of the products.

**Table 4.** pH, Imidazole and Oxidant Dependences of the Epoxidation of Styrene<sup>a</sup>

Reaction	pH	Oxidant	Imidazole mmol	Volume mL	GLC Analysis, % <sup>b</sup>	
					SO	BA
1	3.4	H <sub>2</sub> O <sub>2</sub>	-	5.0	-	-
2	6.3	H <sub>2</sub> O <sub>2</sub>	-	5.0	-	-
3	8.6	H <sub>2</sub> O <sub>2</sub>	-	5.0	-	-
4	10.1	H <sub>2</sub> O <sub>2</sub>	-	7.0	7	-
5	>13	H <sub>2</sub> O <sub>2</sub>	-	5.0	20	7
6	3.3	H <sub>2</sub> O <sub>2</sub>	0.22	6.5	-	-
7	5.7	H <sub>2</sub> O <sub>2</sub>	0.22	6.3	4	6
8	7.4	H <sub>2</sub> O <sub>2</sub>	0.22	5.5	21	15
9	9.4	H <sub>2</sub> O <sub>2</sub>	0.22	6.9	7	7
10	>13	H <sub>2</sub> O <sub>2</sub>	0.22	6.0	18	8
11	4.3	Bu <sup>t</sup> OOH	-	5.1	3	12
12	7.9	Bu <sup>t</sup> OOH	-	5.1	7	28
13	>13	Bu <sup>t</sup> OOH	-	3.8	2	21
14	8.6	Bu <sup>t</sup> OOH	0.22	5.0	15	30
15	>13	Bu <sup>t</sup> OOH	0.22	5.2	4	23

<sup>a</sup> Styrene (1.10-1.30 mmol), MnDTCSPNa<sub>4</sub> (Cl) ( $1.63 \times 10^{-3}$  mmol), latex QL7 (59 mg), oxidant (2.03 mmol) were present in the reaction mixtures. Reaction time was 4 h. <sup>b</sup> SO: Styrene oxide, BA: Benzaldehyde.

**Table 5.** Effects of Concentrations of Porphyrin, Latex and Styrene on the Epoxidation of Styrene<sup>a</sup>

Reaction	Styrene mmol	MnDTCSPNa <sub>4</sub> (Cl) mmol	QL7 mg	GLC Analysis <sup>b</sup>	
				SO(mmol)	BA(mmol)
1	1.08	$1.63 \times 10^{-3}$	59	0.22	0.08
2	2.36	$1.63 \times 10^{-3}$	59	0.22	0.06
3	1.36	$3.26 \times 10^{-3}$	59	0.28	0.08
4	1.36	$1.63 \times 10^{-3}$	118	0.24	0.05

<sup>a</sup> H<sub>2</sub>O<sub>2</sub> (2.03 mmol) was present in the reaction mixtures. Volume 5.0-6.2 mL, pH > 13 and reaction time 4 h. <sup>b</sup> SO: Styrene oxide, BA: Benzaldehyde

**Effect of Time:** Time dependence of the styrene epoxidation catalyzed by latex bound MnTDCSPP (Cl) was investigated under typical conditions except time. The conversions were 4% in one hour 27% in four hours and 30% in seven hours. This result shows that the reaction slowed down after 4h. The decrease in the catalytic activity may be caused by the destruction of the porphyrin and the formation of catalytically inactive species.

**Repeated Use of the Catalyst:** In order to test the catalytic activity for the repeated use of the latex bound MnTDCSPP (Cl) catalyst, new portions of H<sub>2</sub>O<sub>2</sub> and styrene were added to a reaction mixture after four hours and eight hours. Before addition of new portions, the organics in the reaction mixture was extracted for GLC analysis. The first, second and third runs gave 24% (19% styrene oxide and 5% benzaldehyde), 7% (6% styrene oxide and 1% benzaldehyde) and < 2% (trace benzaldehyde) overall conversions, respectively. Apparently the catalytic activity diminishes gradually, which may be caused by the effects given above.



## Epoxidations of 1-Decene and *Cis*-Cyclooctene Catalyzed by Polymer-Supported and Soluble Manganese Porphyrins

It was attempted to oxidize 1-decene and *cis*-cyclooctene using soluble and the latex bound Mn porphyrin catalysts. These aliphatic alkenes were oxidized much slower than styrene. The usual conversions were less than 2% and the products were not identified.

## Conclusions

1. In the absence of Mn porphyrin, no oxidation of styrene was observed.
2. Latex supported MnTDCPP(Cl) catalyst showed higher catalytic activity than the soluble analogue.
3. Oxidation of styrene with H<sub>2</sub>O<sub>2</sub> and Bu<sup>t</sup>OOH catalyzed by Mn porphyrins yielded styrene oxide and benzaldehyde products.
4. The stabilities of MnTDCPPNa<sub>4</sub> and MnTSPNa<sub>4</sub> were better in the presence of peroxide type oxidants than NaOCl.
5. The yields and distributions of the products depended on pH, type of oxidant used and presence of imidazole.
6. The re-use of the supported and soluble MnTDCSPPNa<sub>4</sub> was limited.
7. Oxidation of 1-decene and *cis*-cyclooctene failed.

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