OXIDATION OF PHENOLS AND STYRENES IN WATER CATALYZED BY METAL COMPLEXES BOUND TO COLLOIDAL PARTICLES

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PREFACE

The aim of this research is to develop polymer colloid supported transition-metal catalysts for oxidations of organic compounds in water. The colloid supported metal complexes are a new type of heterogeneous catalysts. A stable colloid, such as milk, paint or ink, is one in which the dispersed particles do not precipitate.

In this work, polymer colloids, also called latexes, were prepared by the same techniques used to make polymers for latex paints, coatings, and rubber. The colloidal particles were spherical and <0.1 μm in diameter. Metal complex catalysts were bound to these colloidal particles and reactions of organic compounds were performed in water. Conventional heterogeneous catalysts are 0.1-5 mm in diameter and their activities are limited by the transport of the reactants to the catalytically active sites. Decreasing the particle diameter increases the surface area per unit weight of catalyst and shortens the diffusion path length of the reactants to the active sites.

Anionic water-soluble cobalt(II) phthalocyanine and manganese(III) porphyrin complexes were bound to the polymer colloids. These transition-metal complexes are related to the active sites of the cytochrome P-450 enzymes which catalyze a wide variety of oxygenations in living organisms.

The latex-bound cobalt(II) complex catalyzed the oxidation of a water-insoluble phenol by molecular oxygen in water faster than the water-soluble analogue did. The latex-bound manganese porphyrin catalyzed the oxidation of water-insoluble styrene by sodium hypochlorite from commercial laundry bleach and gave 2.5 times more product than did the soluble catalyst. The higher activities of latex-bound transition-metal catalysts

compared with soluble analogs are attributed primarily to absorption of the substrates by the latexes.

This research developed a new type of catalysis in aqueous colloids, investigated oxidations of water-insoluble organic compounds in water and in a colloidal medium, brought some understanding of how chemical reactions occur in a colloidal medium. In the long run this type of catalysis might be developed to manufacture water-insoluble organic compounds. This type of process promises lower cost, and less pollution due to reduced use of solvent.

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CHAPTER I

INTRODUCTION

A catalyst is a substance that increases the rate of a chemical reaction, is not changed by the reaction, and does not change the position of equilibrium of a reversible reaction. It is normally used in small amount compared with the reactant.

Catalysts are essential for most chemical transformations to take place in living cells as well as in industrial chemical processes. Enzymes, which are structurally complex, efficient and specific in transformations, are the catalysts nature uses. They mediate reactions in heterogeneous environments such as on the surfaces of membranes. Enzymatic activities are quantified in many different ways. Commonly used are *specific activity* and *molecular activity.*[1] *Specific activity* is expressed as the number of μmoles of substrate reacting per min per mg of enzyme. *Molecular activity*, that is often called *turnover number*, is defined as the number of molecules of substrate reacting per min per molecule of enzyme.

Catalysts employed in industrial processes are much simpler than enzymes and can be as simple as mineral acids. They can be homogeneous or heterogeneous. Their catalytic activities are often reported differently from enzymatic activities with terms such as *turnover number*, which is the number of moles of product(s) formed per mole of catalyst used and *turnover frequency* which is the number of moles of product(s) formed per mole of catalyst per unit of time. Although heterogeneous catalysts are usually less active and less specific than their homogeneous analogues, they are heavily used in industrial scale reactions due to ease of separation from reaction mixtures and practicality of use in flow systems and of packing in columns. The lower activities of heterogeneous catalysts are due in part to diffusional limitations of the reactants to the active sites and utilization of only catalytic sites on or near the surfaces.[2,3] The chemistry of heterogeneous catalysts is not understood as well as that of homogeneous catalysts.

Most heterogenous catalysts are bound to inorganic supports such as alumina and silica gel[4,5] and to organic supports such as polymers.[6-10] A variety of polymeric supports with organic and organometallic functional groups has been prepared. Crosslinked and insoluble polystyrene is most often used as the support, and several methods have been developed to functionalize the polymer for catalyst attachments.[6-10]

In addition to homogeneous and heterogeneous catalysts, other catalysts in microheterogeneous environments have found applications in hydrolysis of a wide range of organic compounds.[11-14] These microheterogeneous systems can be broadly classified into molecular aggregated systems, polymeric systems, and adsorbed systems. Surfactants and lipids aggregate in water. Organic polymer colloids, polyelectrolytes, and ion-exchange membranes, inorganic polysilicates such as clays and zeolites, and polysaccharides such as starch are heterogeneous at the molecular level.[11]

The chemical literature contains a large volume of information about transition-metal containing compounds as catalysts for oxidations,[15-20] reductions, and other transformations. Among the most common are macrocycle-metal compounds. For example, metallophthalocyanines and metallotetraarylporphyrins have been found efficient catalysts for transfer of oxygen to certain substrates. Catalytic activity depends on the central metal ion. Cobalt(III) is the most generally active metal ion catalyst for autoxidation of organic compounds.[15] Co(III) complexes catalyze oxidation of phenols and thiols, and even aliphatic hydrocarbons and benzene under certain conditions. The oxidant often is dioxygen and the reactions are understood to proceed by a Co(III)-oxo intermediate which either donates oxygen to or removes hydrogen from substrate.

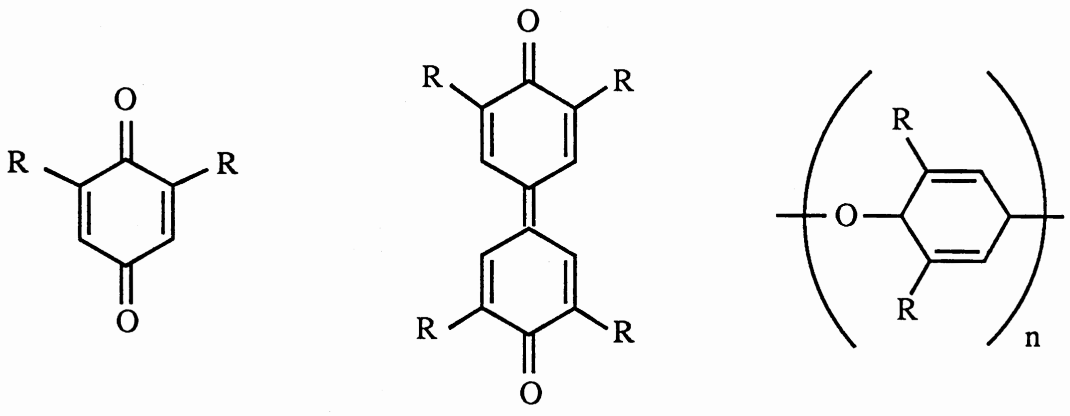
Manganese(III) and iron(III) tetraarylporphyrins, which have structural resemblance to the active sites of the cytochrome P-450 enzymes, catalyze epoxidation of alkenes and hydroxylation of alkanes.[18-20] Although nature uses dioxygen as the oxidant, iodosobenzenes, hypochlorite, alkyl peroxides, hydrogen peroxide, persulfates, amine *N*-oxides, perchlorate, and periodate also have been used in oxidations catalyzed by metallotetraarylporphyrins. The active intermediate of manganese(III) tetraarylporphyrin catalyzed oxidations was proposed as a Mn(V)=O species, which donates an oxygen atom to an alkene or abstracts a hydrogen atom from an aliphatic carbon to introduce a hydroxyl group to an alkane. Homogeneous as well as heterogeneous catalytic applications of these transition metal compounds have been employed in many oxidations.

Transition Metal Catalyzed Oxidations of Alkylphenols with Dioxygen

In biological systems, dioxygen is activated and utilized in oxygen insertion reactions catalyzed by oxygenases and in oxidations of organic substrates catalyzed by oxidases. Dioxygen also is essential for electron flow to produce adenosine triphosphate (ATP) for aerobic metabolism.[16] The active sites of these enzymes contain a transition metal such as iron, copper, manganese, or cobalt which complexes and activates the dioxygen before transfer. Manganese and cobalt are not involved in oxygen transfer reactions as much as iron and copper are. A manganese porphyrin is an oxygen transport agent in photosynthesis. Cobalt is believed to utilize oxygen in free radical reactions of vitamin B_{12}.[16]

The use of model systems to mimic the utilization of dioxygen in biological systems has been subject of numerous sudies. Transition-metal ligand complexes that can activate and transfer dioxygen to alkylphenols include metal-Schiff base complexes, metallotetraarylporphyrins, and metallophthalocyanines. Among the transition metals which can complex with dioxygen and undergo one electron oxidation are Fe(II), Mn(II), Co(II), Cu(II), and Cr(II) complexes.[16] For example, many Co(II) complexes with nitrogen bases reversibly react with dioxygen to give dioxygen adducts.

The relatively easy oxidation of 2,6-dialkylphenols and the industrial importance of oxidized phenolic products have led to numereous studies of phenol oxidation in a search for better catalysts for dioxygen activation and for better knowledge of the mechanisms. The oxidation of 2,6-dialkylphenols may give low molecular weight products, such as benzoquinones (**1**) and diphenoquinones (**2**), and a polymeric product (**3**) where R is a less bulky alkyl group such as methyl (Figure 1). The oxidation potentials of phenols decrease as the number of alkyl substituents on the aromatic ring increases. As shown in Table I, dialkylated phenols have lower oxidation potentials than monoalkylated ones and phenol. Steric and electron donating ability of these alkyl substituents make changes in the oxidation potentials of phenols.[21,22]



1a R : $C(CH_3)_3$ **2a** R : $C(CH_3)_3$ **3** R : CH_3

1b R : CH_3 **2b** R : CH_3

Figure 1. Oxidation products of 2,6-dialkylphenols.

Table I. Oxidation Potentials of Selected Phenols[a],[21]

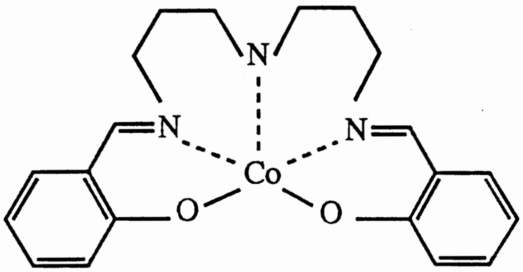
phenol	$(OP)_0$
phenol	0.92
2-methylphenol	0.85
4-methylphenol	0.84
4-*tert*-butylphenol	0.84
2-ethylphenol	0.81
2-*tert*-butylphenol	0.81
2,6-dimethylphenol	0.76
2,6-di-*tert*-butylphenol	0.68
2,4,6-trimethylphenol	0.67
2,4,6-tri-*tert*-butylphenol	0.69

[a] Relative to a saturated calomel reference electrode and extrapolated to zero pH.

A general introduction to the most commonly used transition-metal complexes in alkylphenol oxidation is presented below.

Cobalt-Schiff Bases

Monomeric and polymeric cobalt-Schiff bases (**4**, **5**, **11**, **16**, **17**, **21**, **26**) activate dioxygen and transfer it to alkylphenols. Some of the Schiff bases prepared from salicylaldehydes and amines and used in the oxidation of alkylphenols are **4** and **5**. Nishinaga reported[23] that the product distribution in the catalytic oxygenation of 2,6-di-*tert*-butyl-4-alkylphenols (**6a-d**) and 2,6-di-*tert*-butylphenol (**7**) with cobalt-Schiff base ligands depends on the structure of the catalyst as well as the structure of the phenol. Bis(3-salicylideneaminopropyl)aminecobalt(II) (**4**), which forms a 1:1 (O_2:metal) adduct with dioxygen, led preferentially to the formation of *p*-quinols **8** from corresponding phenols (**6a-d**). On the other hand, bis(salicylidine)ethylenediamine cobalt(II) (**5a**), which gives 1:2 (O_2:metal) adduct with dioxygen, gave predominantly formation of peroxides **9** from phenols (**6a, c, d**). Depending on the catalyst, phenol, and solvent, *p*-benzoquinones, *o*-benzoquinones, diphenoquinones, and phenols with oxidized alkyl groups, and *p*-quinols were obtained from the reactions.



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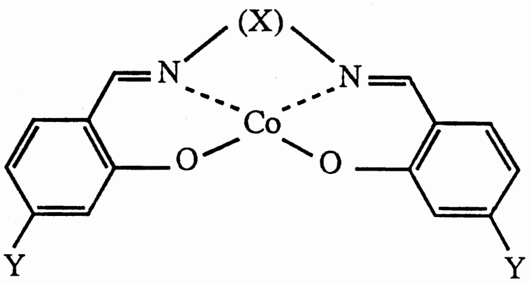
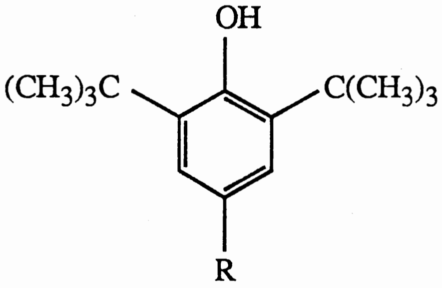
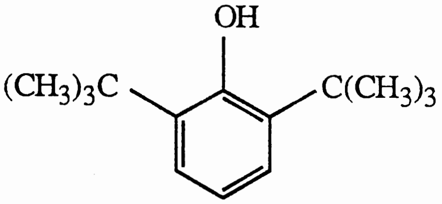


5a	X = $-(CH_2)_2-$	Y = H
5b	X = $-(CH_2)_2-$	Y = OH
5c	X = $-(CH_2)_3-$	Y = H



6a	$C(CH_3)_3$
6b	CH_3
6c	C_2H_5
6d	$CH(CH_3)_2$



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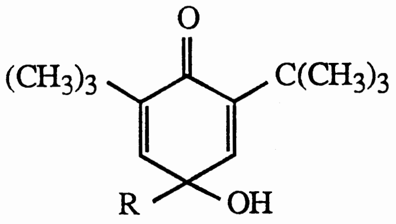
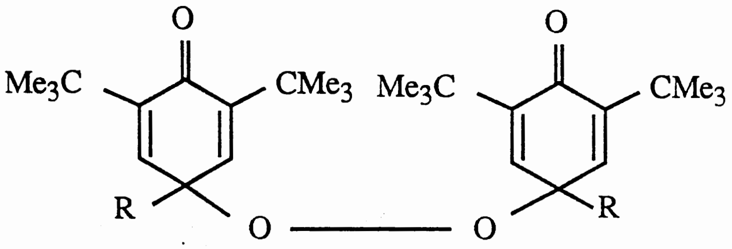
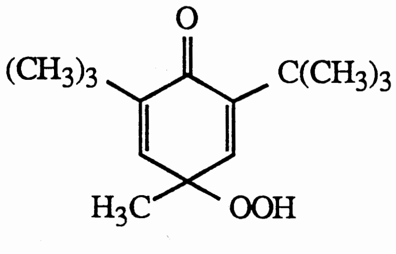




8a	$C(CH_3)_3$	**9a**	$C(CH_3)_3$
8b	CH_3	**9b**	CH_3
8c	C_2H_5	**9c**	C_2H_5
8d	$CH(CH_3)_2$	**9d**	$CH(CH_3)_2$

The oxidation of **6b** catalyzed by **4** in methanol (below 10 °C) gave hydroperoxide **10** (yield ~80%), which was converted to quinol **8b** at higher temperature. On the other hand, in $CHCl_3$ and in benzene complex mixtures of oxidation products were obtained.



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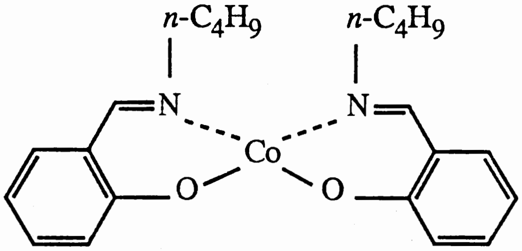
A cobalt-Schiff base complex as homogeneous catalyst for the oxidation of 2,6-di-*tert*-butylphenol (**7**) in methanol and water was reported by Fullerton.[24] The catalyst, *N,N′*-ethylenebis(4-hydroxysalicylideneiminato) cobalt(II) (**5b**), was slightly soluble in water and readily soluble in 1N sodium carbonate or sodium hydroxide solution. Oxidation of 2,6-di-*tert*-butylphenol (**7**) either in a 9:1 methanol-water mixture or in methanol alone proceeded at a much faster rate in base than under neutral conditions. In a typical reaction, a mole ratio of ten to one of phenol **7** to catalyst was employed. No unreacted phenol **7** was found after 2 h at 20 °C when the oxygenation was carried out in a basic solution of methanol-water, whereas there was 40% unreacted phenol **7** when the reaction was carried out in neutral solution. The product distributions were 44% of **1a** and 56% of **2a** under basic conditions and 50% of **1a** and 10% of **2a** under neutral conditions. The effect of base on the reaction and product distribution was not discussed. Also 4-hydroxysalcomine (**5b**) was a more effective catalyst for the oxidation of phenol **7** than the unsubstituted salcomine **5a**.

Autoxidation of certain phenols may give polymeric product rather than benzoquinone or diphenoquinone. When bis(n-butyl-*N*-salicylideneiminato) cobalt(II) (**11**) was used as a catalyst in the oxidation of 2,6-dimethylphenol (**12**) in toluene, 3,5,3',5'-tetramethyl-4,4'-diphenoquinone (**2b**) and poly(2,6-dimethyl-1,4-phenylene oxide) (**3**) were obtained in roughly the same quantities.[25] The oxidation of 9.76 mmol of phenol **12** was carried out under one atmosphere of pure dioxygen in a stirred glass reactor in the presence of 0.22 mmol of catalyst **11** at temperatures of 20-40 °C. During 24 h reaction, 4.82 mmol of dioxygen was consumed which gives the stoichiometric ratio of 2,6-dimethylphenol to dioxygen 2.03:1. The irreversible oxidation of the cobalt(II) chelate was observed as well.



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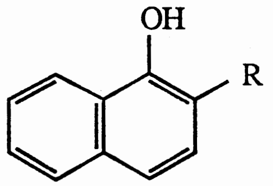
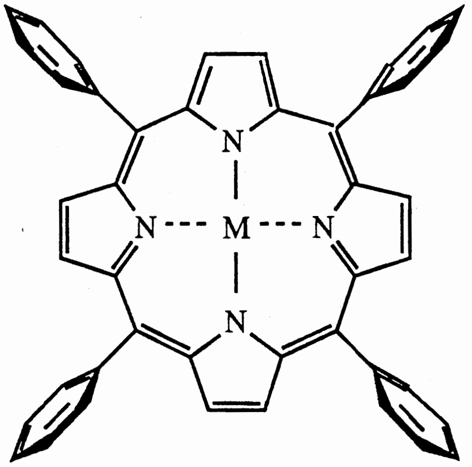
Oxidations of 2,6-di-*tert*-butylphenol (**7**), 2,4,6-tri-*tert*-butylphenol (**6a**), 1-naphthol (**13**), and 2-methyl-1-naphthol (**14**) by dioxygen in the presence of monomeric and polymeric cobalt-Schiff base complexes, cobalt and manganese(III) tetraphenyl-porphyrins and (pyridine)cobaltoxime were investigated by Frostin-Rio.[26] The rates and selectivities of these reactions were found very dependent on the catalyst and on the solvent. The catalyst-substrate ratios were 0.1 for cobalt complexes and 0.01 for manganese(III) tetraphenylporphyrin. In some reactions, 1 equivalent of $(n\text{-}C_4H_9)_4NBH_4$, pyridine, or NaOH per mol of phenol was added. Manganese(III) tetraphenylporphyrin chloride (**15**) catalyzed the oxidation of phenol **7** to benzoquinone **1a** (0-40%) and diphenoquinone **2a** (60-100%) in 1.2 atm of dioxygen in the presence of the reducing agent $(n\text{-}C_4H_9)_4NBH_4$ and / or NaOH. In toluene, 70-100% yields were achieved in 4 h whereas in CH_3CN, the yield was 100% in 0.5 h when manganese(III) tetraphenylporphyrin (**15**)-NaOH was used.



13 R : H

14 R : CH_3

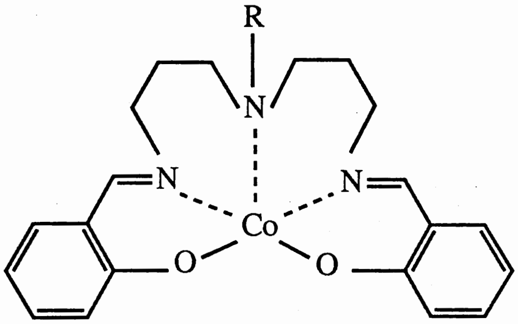


MTPP

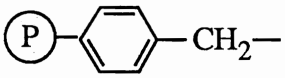
15 Mn(III)TPP (L) L : Cl, OAc

19 Co(II)TPP

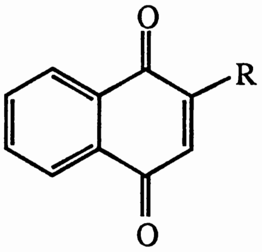
Co complex **16** in CH_3CN was the most effective catalyst among the penta-coordinated cobalt complexes for autoxidation of 2,6-di-*tert*-butylphenol (**7**) to give 2,6-di-*tert*-butylbenzoquinone (**1a**) as the major product. The polystyrene bound analogue of Co complex **16** (**17**) gave better yield (100% in 6 h) when toluene was the solvent. However the yield was only 30% in 24 h when $CHCl_3$ was the solvent. Without any appreciable loss in the catalytic activity, the polymeric catalyst was reemployed ten times.



16 R : CH_3

17 R : 

Both the rate and selectivity of 1-naphthol (**13**) autoxidation depend on the catalyst and on the solvent. The oxidation was achieved with Co complex **5c** in $CHCl_3$ in 3.5 h but did not give the 1,4-naphthoquinone (**18**). The products obtained were proposed as dimers from oxidative coupling of phenoxy radicals, based on the elemental analysis and spectroscopic data. On the other hand in the presence of Co complex **16**, the oxidation of 1-naphthol (**13**) gave 50% quinone **18** and 50% dimeric products in $CHCl_3$ in 3 h and 100% quinone **18** in CH_3CN in 0.5 h. $CHCl_3$ was a less suitable solvent, and the polymeric Co complex (**17**) showed much lower activity than the corresponding monomeric catalyst. Cobalt(II) tetraphenylporphyrin (**19**) gave only 85% conversion to oxidation products including 30% quinone **18** in the presence of pyridine in CH_3CN in 24 h.

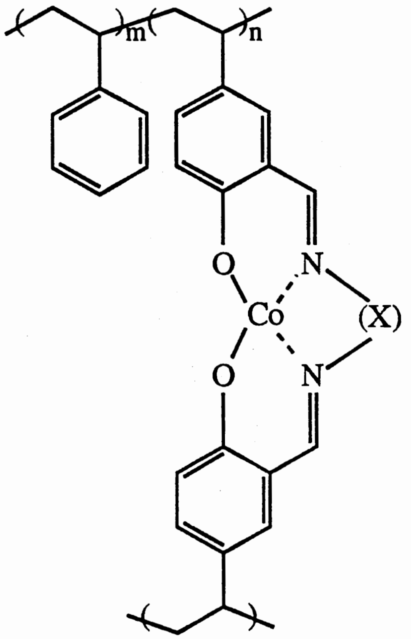


18 R : H

20 R : CH_3

In contrast, the autoxidation of 2-methyl-1-naphthol (**14**) was specific and 2-methyl-1,4-naphthoquinone (**20**) was the only product. Quantitative conversions were obtained in 0.5 h in toluene and CH_3CN when Co complex **16** was the catalyst. The polymeric analogue of the catalyst (**17**) also gave quantitative conversions in toluene in 0.5 h and in CH_3CN in 2.5 h. However when manganese(III) tetraphenylporphyrin chloride (**15**) catalyst was used in the presence of $(n\text{-}C_4H_9)_4NBH_4$ in CH_3CN, quantitative conversion was achieved in 12 h, but only 20% of the product was quinone **20**. Co(II) tetraphenylporphyrin (**19**) in the presence of pyridine gave quantitative conversions of 2-methyl-1-napthol to 2-methyl-1,4-naphthoquinone in 2.5 h. 2,4,6-Tri-*tert*-butylphenol (**6a**) gave a more complex product mixture and a slower rate than those of 2,6-di-*tert*-butylphenol (**7**) under similar conditions and in the presence of Co complexes. On the other hand when porphyrin **15** was employed, quantitative conversions were achieved in 0.5-4 h depending on the solvent, ligand, and reducing agent. The proposed mechanism of oxidation of 2,4,6-tri-*tert*-butylphenol (**6a**) involves peroxy intermediates to give the final oxidation products.[26]

Copolymerization of various divinyl-Schiff bases and styrene led to polymers containing covalently bound ligands. After introduction of Co(II) to the polymeric Schiff bases (**21a-d**), their catalytic activities were tested for the autoxidation of 2,6-di-*tert*-butylphenol (**7**). The polychelates showed lower activity in comparison with the low molecular weight chelate. 2,6-Di-*tert*-butylbenzoquinone (**1a**) was obtained in 97% yield in 2 h at 20 °C with the low molecular weight chelate **5a**. The yields were 9 to 64% with Co(II) polymer-bound chelates in DMF for 20 h.[27]



21a X = $-(CH_2)_2-$

21b X = $-(CH_2)_3-$

21c X = $-(CH_2)_2NH(CH_2)_2-$

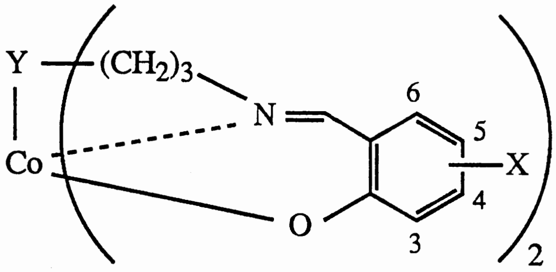
21d X $=(CH_2)_3NH(CH_2)_3-$

A bis(3-aminopropyl)amine ligand attached covalently to 20% cross-linked macroreticular and gel polystyrene resins with a CH_2 spacer was first reacted with salicylaldehyde, and the polymeric Schiff base ligand obtained was used to bind Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions.[28] The polymeric cobalt-Schiff base complexes (**17**) were active catalysts for autoxidation of 2,6-dimethylphenol (**12**) in benzene. Both the gel and macroreticular resin bound catalyst had lower activity than the homogeneous catalysts at comparable conditions. The Co complex **16** gave 87.4-100% conversion, whereas the reaction catalyzed by macroreticular bound catalyst under comparable conditions gave 42.8-46.5%. The gel resin containing cobalt(II) complex caused significant change in product distribution. Lowering the microreticular resin loading increased production of 3,5,3',5'-tetramethyl-4,4'-diphenoquinone (**2b**), but 2,6-dimethylbenzoquinone (**1b**) was still the major product. Probably the lower concentration of cobalt in the polymer increased the probability of two phenoxy radicals combining to give 3,5,3',5'-tetramethyl-4,4'-diphenoquinone (**2b**).[28]

Mechanistic studies of the autoxidation of hindered phenols with cobalt(II) bis[3-(salicylideneamino)propyl]methylamine (**16**) showed that the reaction is first order in dioxygen, substrate, and cobalt concentrations.[29] The turnover frequency [mol of dioxygen consumed/(mol of Co x h)] for 2,6-di-*tert*-butylphenol (**7**) was 4.8 at 30 °C under 60 psi dioxygen initial pressure in benzene. However the catalytic activity dropped after 70 turnovers, which was attributed to formation of peroxides and $HO_2^{\cdot}$ during the oxidation. Externally added hydrogen peroxide in methanol decreased the number of turnovers. When H_2O_2 was used as the only oxygen source, catalysis of conversion of H_2O_2 to H_2O and O_2 and simultaneous irreversible oxidation of the cobalt center were observed, and no benzoquinone formed.

The autoxidation of substituted phenols was catalyzed by a series of substituted tetradentate and pentadentate cobalt Schiff base complexes (**22**) in toluene or methanol to find the electronic and steric factors affecting the reaction rate.[30] The most dramatic effect on the catalytic activity was observed when the donor atoms (Y) about cobalt were varied (Table II). Electron donating ability of Y affected the initial rates of the oxidation about 100-fold. Variation of the substituents on the phenyl ring led to minor variations in the rate of the reaction.

Autoxidation of (E)-4-stilbenols (**23a-d**) catalyzed by Co complex **16** in the presence of dioxygen gave the aldehydes **24** and **25** from oxidative cleavage of the olefinic C-C double bond.[31] In a typical oxidation experiment, substrate (10 mmol) and Co-Schiff base complex (1 mmol) in 1,2-dichloroethane were purged with dioxygen and stirred at 25 °C for 5 h. The conversions were 31% for **23a**, 70% for **23b**, and 100% for **23c** and **23d**. The mechanism proposed requires first abstraction of phenolic hydrogen, then addition of $Co\text{-}O_2$ adduct to benzylic position of the phenyl moiety, and finally cyclization of the peroxy Co(III) species to form a dioxetane intermediate, which decomposes to give aldehydes **24** and **25**.



Y = NCH_3 X = H, 3-*tert* -C_4H_9, 3,5-(*tert* -C_4H_9)$_2$, 3-OCH_3,
5-OCH_3, 3-OC_2H_5, 5-NO_2, 5-Br, 3,5-Br_2,
3-OH, 4-OH, 4,6-(OCH_3)$_2$, 4-OCH_3, 4-N(C_2H_5)$_2$

Y = NH X = H, 3-OCH_3, 5-NO_2

Y = O X = H

Y = S X = H

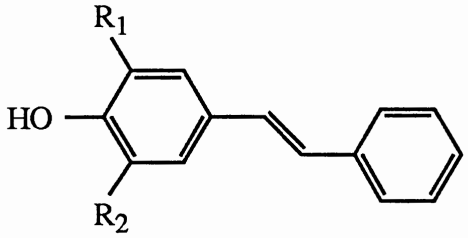
Y = PCH_3 X = H

22

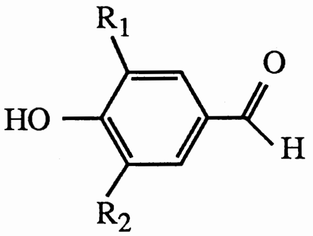
Table II. Autoxidation of 2,6-Dimethylphenol by Dioxygen-Cobalt Complexes **22**[a,30]

Y	initial rate[b]
NCH_3[c]	3.5×10^{-2}
NH	4.3×10^{-3}
S	2.1×10^{-3}
PCH_3[d]	8.1×10^{-4}
O	2.4×10^{-4}

[a] X is hydrogen in the complex **22**. All reactions were at room temperature, 75 psi initial O_2 pressure, 50 mL total volume of toluene solution, 0.1 g of catalyst, with 9.0 g of 2,6-dimethylphenol. [b] Initial rate expressed as moles of O_2 consumed divided by moles of cobalt used per second. [c] Reaction run in 50 mL of absolute methanol, 75 psi initial O_2 pressure, 6.0 g of 2,6-dimethylphenol at 25 °C, and 0.1 g of catalyst. [d] Catalyst is a slurry.



	R_1	R_2
23a	H	H
23b	OCH_3	H
23c	CH_3	CH_3
23d	$C(CH_3)_3$	$C(CH_3)_3$



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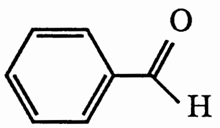
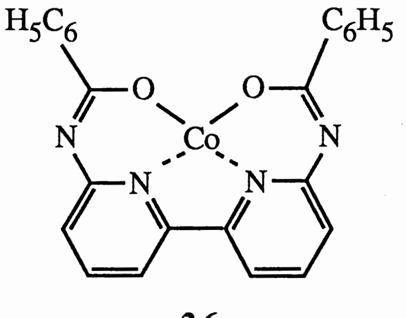


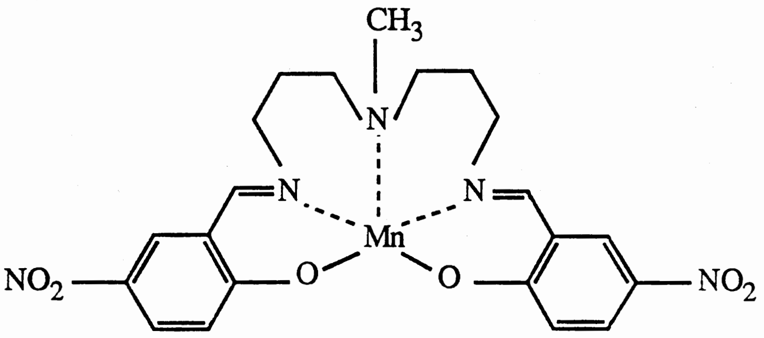
25

The cobalt(II) complex of a more stable salen analogue, 6,6'-bis(benzoylamino)-2,2'-bipyridine (**26**) showed high activity and stability in the autoxidation of 2,6-di-*tert*-butylphenol (**7**) to 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenoquinone (**2a**) in toluene-pyridine in 24 h.[32] The mole ratio of substrate to catalyst was 200 and the conversion was quantitative. The catalytic activity of Co complex **26** was retained after first reaction.



26

The effect of a magnetic field on the rate of catalytic autoxidation of 2,6-di-*tert*-butylphenol (**7**) to the corresponding diphenoquinone by [bis(3-((5-nitrosalicylidene)-amino)propyl)methylaminato]manganese(II) [**27**, $L_5Mn(II)$] complex was studied.[33,34] A 3-fold change in the rate of the reaction between 0 and 70 kG was observed, and it was concluded that the step in the catalytic process that is magnetic field dependent is the regeneration of catalyst $L_5Mn(II)$ from the reaction of μ-peroxomanganese $[L_5Mn(III)$-O-OH-$Mn(II)L_5]$ complex and 2,6-di-*tert*-butylphenol to form the 2,6-di-*tert*-butylphenoxy radical and hydrogen peroxide.[34]



27

In conclusion, tetradentate and pentadentate cobalt-Schiff bases are efficient catalysts for the oxidation of alkyl substituted phenols by dioxygen in homogeneous and heterogeneous reactions. The type of the chelating ligand affects the product distribution of the oxidation. Co-Schiff base complexes bound to organic polymer resins or gels showed lower activities than the homogeneous analogues, but reusabilty of the catalyst improved. The polymer matrix causes mass-transfer limitations of the reactants to the catalytic sites and may affect the product distribution. In some cases, the polymeric support protected the catalyst from fast deactivation.

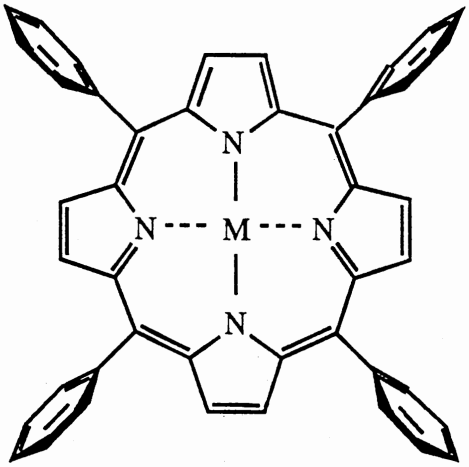
However there is no investigation in the literature about the oxidation of water-insoluble alkyl substituted phenols in water catalyzed by homogeneous and latex-bound Co-Schiff bases.

Copper-Amine Complexes

Owing to its industrial importance for production of poly(2,6-dimethyl-1,4-phenylene oxide), the metal-catalyzed oxidation of 2,6-dimethylphenol (**12**) with molecular oxygen has been studied in detail. Primary, secondary, and tertiary amines and pyridine derivatives associated with Cu(II) ion promoted the polymerization.[35-38] Koning[39-41] reported that Cu(II) complexes with *N,N,N',N'*-tetramethylethylenediamine, 4-(*N,N*-dimethylamino)pyridine, poly(amidoamines), and polystyrene-bound 4-(*N,N*-dimethylamino)pyridine, which was prepared from copolymerization of styrene and 4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine, catalyzed the polymerization of 2,6-dimethylphenol (**12**) to poly(2,6-dimethyl-1,4-phenylene oxide) (**3**) in short time at 25 °C with good specifity. 2,6-Dimethylphenol (**12**) was also oxidized in methanol by dioxygen catalyzed by basic copper(II) chloride[42] and in absolute ethanol by dioxygen catalyzed by anhydrous copper(II) chloride.[43] The copper(II) chloride catalyst in ethanol only gave 2,6-dimethyl-1,4-benzoquinone (**1b**) and 3,5,3',5'-tetramethyl-4,4'-diphenoquinone (**2b**).[43] Commercial poly(2,6-dimethyl-1,4-phenylene oxide) (**3**) is manufactured with a hydrolytically stable copper-diamine catalyst system. The polymerization is terminated by introducing nitrogen and by removing the copper with an aqueous chelating agent.[44]

Metallotetraphenylporphyrins

The catalytic activities of transition-metal tetraphenylporphyrin complexes (**15**, **19**, **28-30**) for the oxidation of 2,6-di-*tert*-butylphenol (**7**) by molecular oxygen were investigated.[45] Relative activities were Co(II)TPP (**19**) >Fe(III)TPP (Cl) (**28**) >Mn(III)TPP (Cl) (**15**) >V(IV)OTPP (**29**). Cu(TPP) (**30**) was inactive. A typical reaction containing 1% metalloporphyrin catalyst relative to the substrate was carried out at 55 °C for 60 h. When the oxidation was catalyzed by CoTPP (**19**), about 79% of phenol 7 was converted to the corresponding benzoquinone in 12 h.



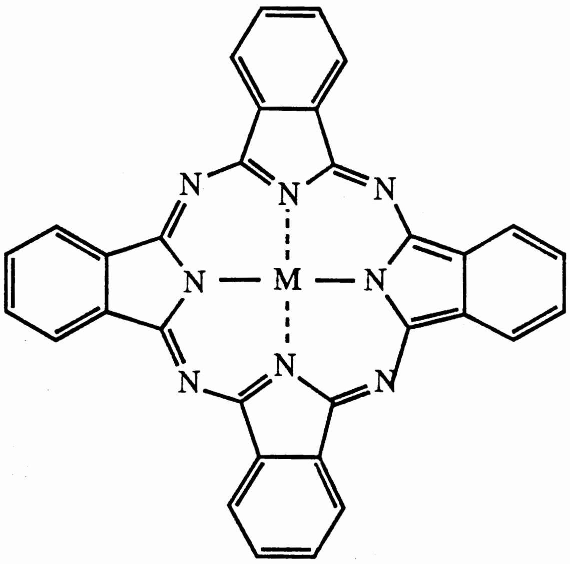
MTPP

15	Mn(III)TPP (Cl)
19	Co(II)TPP
28	Fe(III)TPP (Cl)
29	V(IV)OTPP
30	Cu(II)TPP

Metallophthalocyanines

Metallophthalocyanines are insoluble in most common solvents, so the oxidations catalyzed by metallophthalocyanines in organic solvents are indeed heterogeneous reactions.

Autoxidations of 2,6-dialkylphenols catalyzed by bis(salicylidine)etheylenediamine cobalt(II) (**5a**) (Table III) and by cobalt(II) phthalocyanine (**31**) (Table IV) were carried out under 50-80 psig dioxygen pressure.[22] When dimethylformamide (DMF) was used as solvent, the reaction required shorter time than when methanol and dimethylsulfoxide were used. Higher temperature favored the formation of diphenoquinones. Iron(II) phthalocyanine (**32**), copper(II) phthalocyanine (**33**) and manganese(II) phthalocyanine (**34**) showed lower activity than cobalt(II) phthalocyanine (**31**) under identical conditions.



MPc

31	Co(II)Pc
32	Fe(II)Pc
33	Cu(II)Pc
34	Mn(II)Pc
36	Ni(II)Pc

The autoxidations of 2,4,6-tri-*tert*-butylphenol (**6a**), 2,6-di-*tert*-butylphenol (**7**), and 2,4-di-*tert*-butylphenol catalyzed by iron(II) phthalocyanine (**32**) in methanol gave **9a** (87%), **2a** (100%), and **35** (57%) from the corresponding phenols. After exposure to dioxygen for 18 h at room temperature, the reactions gave almost exclusively oxidation product from coupling of two phenoxy radicals.[46] Phthalocyanines of Mn(II) (**34**), Co(II) (**31**), Ni(II) (**36**), and Cu(II) (**33**) were inactive. Under similar conditions, bis(salicylidine)ethylenediamine cobalt(II) (**5a**)-pyridine complex catalyzed oxidation of the above phenols preferentially to benzoquinones.

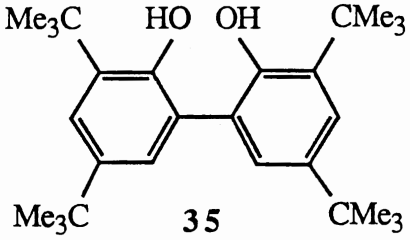


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Table III. Oxidation of 2,6-Dialkylphenols by Metal-Salcomines[22]

expt	phenol[a]	catalyst		solvent[d]	O_2, psig	temp., °C	time, h	phenol, conv. %	selectivity, %		
		[b]	%[c]						BQ[e]	DBQ[f]	others[g]
1	DBP	Pyr-Co-salen	5	Methanol	55	20	1.0	98	93.2	6.8	-
2	DBP	Pyr-Co-salen	2	DMF	55	24-50	0.5	100	99.0	1.0	-
3	DBP	Pyr-Co-salen	1	DMF	55	20-46	0.75	96	98.8	1.2	-
4	DBP	Pyr-Co-salen	1	DMF	atm	20-35	20.0	89	88.0	4.5	7.5
5	DBP	Pyr-Co-salen	0.5	DMF	54	20-35	3.0	92	88.2	10.6	1.2
6	DBP	Pyr-Co-salen	0.5	DMF	54	60-65[h]	1.0	99	46.5	54.5	-
7	DBP	Pyr-Co-salen	1	DMSO	55	15-40	2.5	49	84.0	1.5	14.5
8	DBP	Pyr-Co-salen	1	1-Me-2-Py	55	20-40	2.5	75	95.2	4.8	-
9	DBP	Co-salen	1	DMF	55	20-45	0.5	100	99.5	0.5	-
10	DMP	Pyr-Co-salen	1	DMF	55	25-45	2.5	95	98.0	2.0	-
11	DMP	Co-salen	1	DMF	55	20-45	0.75	100	100	-	-
12	DBP	Mn-salen	5	DMF	54	22-30	<0.2	100	<0.1	99.9	-

[a] DBP: 2,6-Di-*tert*-butylphenol, DMP: 2,6-Dimethylphenol. [b] Pyr: pyridine. Co-salen: bis(salicylidine)ethylenediamine cobalt(II). [c] Mole %/mole of phenol. [d] DMF: Dimethylformamide, DMSO: Dimethylsulfoxide. 1-Me-2-Py: 1-Methyl-2-pyrrolidinone. [e] Corresponding benzoquinone. [f] Corresponding diphenoquinone. [g] Unidentified higher molecular weight products. [h] Heat applied.

Table IV. Oxidation of Phenols by Metallophthalocyanines[22]

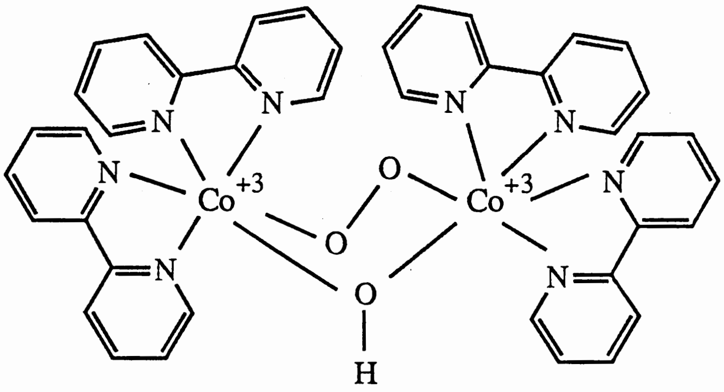
expt	phenol[a]	catalyst		solvent[c]	O_2, psig	temp., °C	time, h	phenol, conv. %	selectivity, %		
			%[b]						BQ[d]	DBQ[e]	others[f]
1	DBP	Co(II)Pc (**31**)	5	DMF	50	22-27	3.0	100	73	26	1
2	DBP	Co(II)Pc (**31**)	5	DMF	50-60	48-50[g]	1.5	100	51	49	-
3	DBP	Co(II)Pc (**31**)	5	DMF	50-60	68-70[g]	1.3	100	33	67	-
4	DBP	Co(II)Pc (**31**)	5	DMF	90	68-70[g]	1.3	100	33	67	-
5	DBP	Co(II)Pc (**31**)	5	DMSO	55	22-30	3.0	22	25	54	21
6	DBP	Co(II)Pc (**31**)	7	Methanol	55	22-32	6.0	16.4	51	49	-
7	DMP	Co(II)Pc (**31**)	5	DMF	53	22-28	3.0	96	100	-	-
							5.0	100	100	-	-
8	DBP	Cu(II)Pc (**33**)	5	DMF	55	22-27	3.0	10.5	41	59	-
9	DBP	Cu(II)Pc (**33**)	5	DMF	55	71-73[g]	2.0	100	12	88	-
10	DBP	Mn(II)Pc (**34**)	4	DMF	52	20-30	3.0	95	0.5	99.5	-
11	DBP	Fe(II)Pc (**32**)	4	DMF	55	23-30	2.0	18	22	78	-
12	BP	Co(II)Pc (**31**)	5	DMF	55-60	75-80[g]	3.0	17	12	-	-
13	Phenol	Co(II)Pc (**31**)	4	DNF	90	72-75[g]	2.0	-	-	-	-

[a] DBP: 2,6-Di-*tert*-butylphenol, DMP: 2,6-Dimethylphenol, BP: 2-*tert*-butylphenol. [b] Mole %/mole of phenol. Pc: phthalocyanine. [c] DMF: Dimethylformamide, DMSO: Dimethylsulfoxide. [d] Corresponding benzoquinone. [e] Corresponding diphenoquinone. [f] Unidentified higher molecular weight products. [g] Heat applied.

In conclusion; Co and Fe phthalocyanines, which are more stable toward oxidative degradation than Co-Schiff bases and metalloporphyrins, catalyze the autoxidation of alkylsubstituted phenols in organic solvents. Reactions are solvent and temperature dependent. No water-soluble phthalocyanine metal complex either monomeric or bound to water-soluble and insoluble polymers has been employed as catalyst for autoxidation of alkyl-substituted phenols. However autoxidations of 2-mercaptoethanol and 1-decanethiol catalyzed by homogeneous Co(II) phthalocyaninetetra(sodium sulfonate) and water-soluble and colloidal polymer-bound cobalt(II) phthalocyaninetetrasulfonate were reported. This catalyst system can be extended to the autoxidation of alkyl-substituted phenols.

Other Transition Metal Complexes

Catalytic oxidation of 2,6-di-*tert*-butylphenol (**7**) by molecular oxygen in the presence of bis(bipyridyl)cobalt(II) was reported.[47,48] The active catalyst was the dioxygen complex of tetrakis(bipyridyl)(μ-peroxo)(μ-hydroxo)dicobalt(III) (**37**) formed from the reaction of dioxygen (1 atm) and (bipyridyl)cobalt(II) in 95% methanol-water mixture containing 0.5 equiv. of KOH.



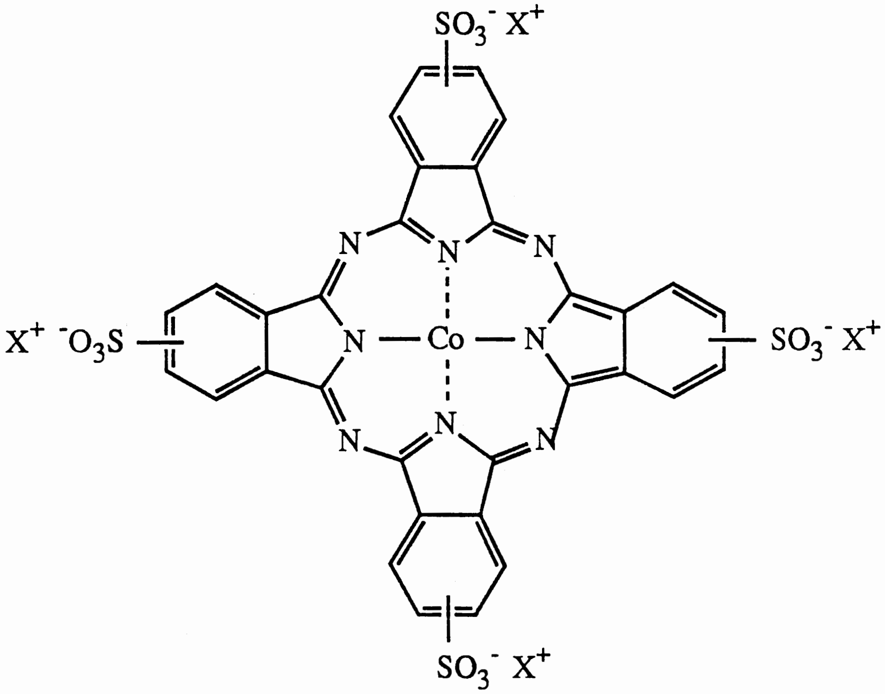
37

2,6-Di-*tert*-butyl-4-methylphenol (**6b**) was oxidized by dioxygen with a catalyst composed of $[Fe(CN)_6]^{-4}$ anchored to the surface sites of acid-modified γ–Al_2O_3.[49] A methanol suspension was irradiated with a Hg lamp at 550 nm with dioxygen bubbling for 12 h to convert 20% of the phenol to 66% of 2,6-di-*tert*-butyl-4-(methoxymethyl)phenol and 34% of 2,6-di-*tert*-butyl-4-methyl-4-methoxycyclohexa-2,5-dienone. In chloroform suspension, 20% of the phenol was converted to 3,3',5,5'-tetra-*tert*-butyl-4,4'-dihydroxybenzyl after 24 h.

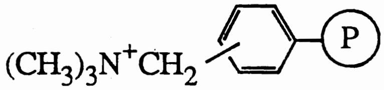
Cobalt(II) Phthalocyaninetetrasulfonate Catalyzed Oxidation of Thiols by Dioxygen

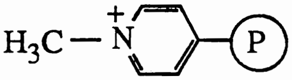
Oxidation of alkylphenols in water by dioxygen in the presence of soluble cobalt(II) phthalocyaninetetra(sodium sulfonate) (**38**) and polymer-bound cobalt(II) phthalocyaninetetrasulfonate (**39a**) is reported only in papers from our lab.[50,51] Water has been used as solvent for the autoxidation of 2-mercaptoethanol by Brouwer[52-54] and van Herk[55,56] and of 1-decanethiol by Hassanein[57,58] to the corresponding disulfides by dioxygen with homogeneous cobalt(II) phthalocyaninetetra(sodium sulfonate) (**38**), water soluble polymer-bound and latex-bound cobalt(II) phthalocyaninetetrasulfonate (**39b-f**) at pH 8-9.

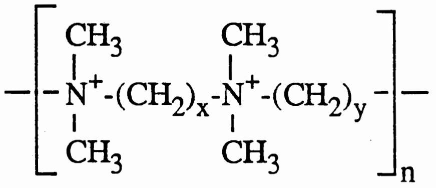
In the oxidation of 2-mercaptoethanol by dioxygen, water soluble basic polymers poly(vinylamine)[53] (**40**), poly(ethylenimine)[54] (**41**), poly(L-lysine)[54] and ionenes[54] promoted the catalytic activity of attached Co(II) phthalocyaninetetrasulfonate under homogeneous conditions. Poly(vinylamine) (**40**) increased the activity of Co(II) phthalocyaninetetrasulfonate (**38**) as much as 30 times.[52] The reaction produced hydrogen peroxide as side product, and addition of radical scavengers led to a decrease in the reaction rate, indicating the presence of radical intermediates during oxidation.[52] The pH dependence of the reaction rate was attributed to the thiol anions being reactive species in the system. The increased local concentrations of the thiol anions vicinity of the phthalocyanine attached-polymer was proposed as the cause of the rate increase of the reaction in the presence of cationic polymers.[54]

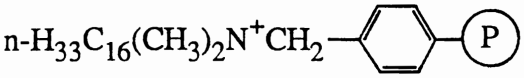


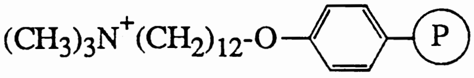
38 X+ : Na+

39a X+ :


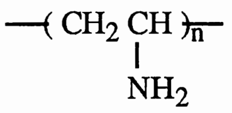
39b X+ :


39c X+ :

$$-\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}-(CH_2)_x-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}-(CH_2)_y-\right]_n-$$

39d X+ :


39e X+ :


39f X+ : n-H$_{37}$C$_{18}$(CH$_3$)$_2$N$^+$(CH$_2$)$_2$-OC(O)—Ⓟ



$-\!\left(CH_2\underset{\displaystyle NH_2}{CH} \right)_n-$

40 Poly(vinylamine)

$-\!\left(CH_2\,CH_2-NH \right)_n-$

41 Poly(ethylenimine)

Recently van Herk[56] extended the investigation of the autoxidation of 2-mercaptoethanol to a latex-bound phthalocyanine (**39b**) catalyst system. A two step synthesis shown in Figure 2 provided a 400 nm diameter water-insoluble support for phthalocyanine **38** with a hydrophilic surface and polymeric coil to expand and solubilize organic solutes. In the first step, a commercial block copolymer of 4-vinylpyridine and styrene (90:10 mol:mol) (**42**) was quaternized to **43** with methyl iodide. The latex **44** obtained from polymerization of surfactant **43** with styrene and divinylbenzene was extensively purified with a Dowex® 50-X4 cation exchange resin to remove unpolymerized polymeric surfactant molecules.

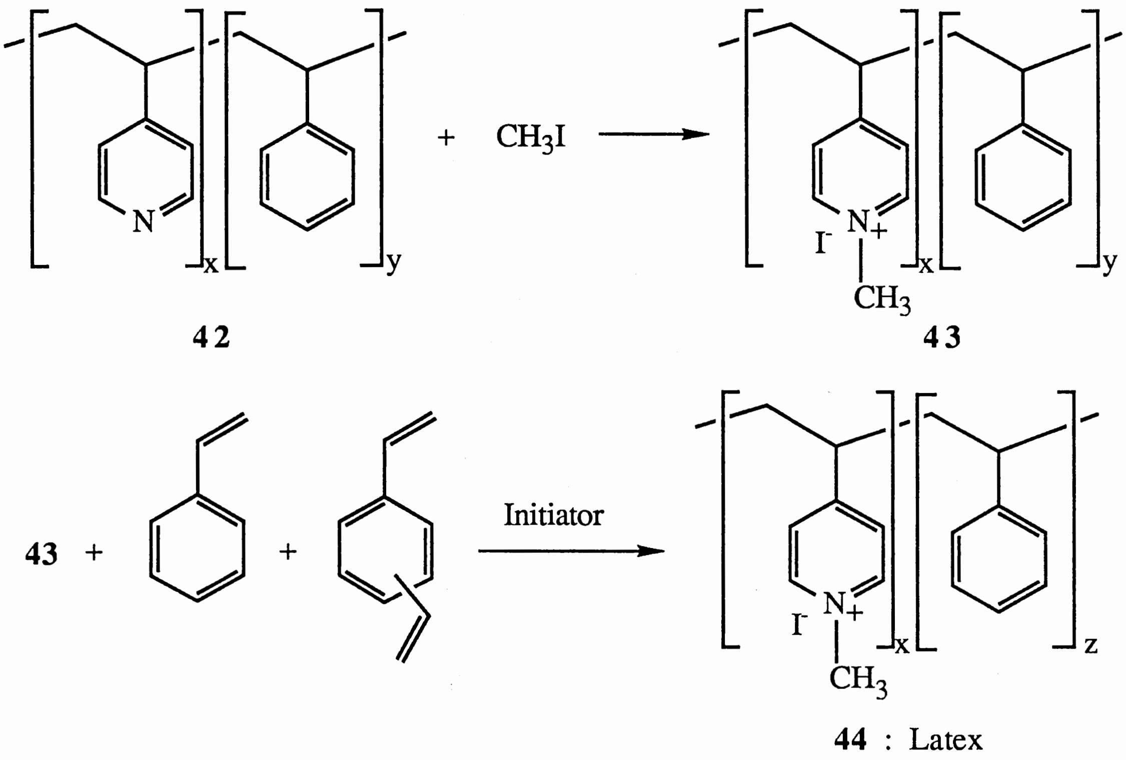


Figure 2. Preparations of polymeric surfactant **43** and poly(4-vinylmethylpyridinium-co-styrene) latex (**44**).[56]

Cobalt(II) phthalocyaninetetrasulfonate bound to latex **44** and dissolved in quaternized block copolymer **43** was used as a catalyst for autoxidation of 2-mercaptoethanol. Heterogeneous latex catalyst (**39b**) prepared from **44** was more active than the homogeneous block copolymer catalyst [**43**-cobalt(II) phthalocyaninetetrasulfonate]. The activities of both catalysts showed a linear dependence on the amount of catalyst indicating no mass transfer limitations, which were expected for latex catalyzed reaction. The lower activity of phthalocyanine attached to homogeneous block copolymer **43** was attributed to the hydrophobic part of the block copolymer which is catalytically inactive. Its function is to create latex or surfactant micelle-like structure. However a specific latex effect was also considered to promote the catalytic activity. In addition, the activity was largely lost when cobalt(II) phthalocyaninetetrasulfonate was bound to 2,4-ionene immobilized on 80 μm Amberlite® XAD-2 resin particles.

In the oxidation of 1-decanethiol,[57,58] colloidal cationic latex-bound phthalocyanines **39d-f** were used to catalyze the autoxidation of water immiscible 1-decanethiol at pH 9.0. Latex-bound phthalocyanine **39f** showed 11 times more activity than the homogeneous analogue (**38**).

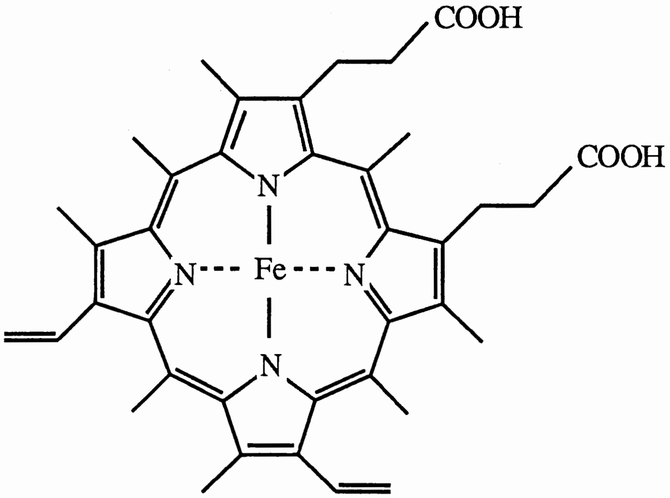
In conclusion water-soluble Co(II) phthalocyaninetetrasulfonate catalyzed efficiently autoxidations of 2-mercaptoethanol and 1-decanethiol in the aqueous phase. In both cases, latex-bound phthalocyanine gave faster reactions than water-soluble polymer-bound phthalocyanine and soluble phthalocyanine **38**. The autoxidation of alkylsubstituted phenols by soluble phthalocyanine **38** and latex-bound phthalocyanine **39** catalysts may be similar.

Metallotetraarylporphyrin Catalyzed Oxidations of Alkenes and Alkanes

In living organisms, the membrane-bound cytochrome P-450 dependent monooxygenases mediate a wide variety of oxygenations, among which are the biosynthesis and biodegradation of endogenous compounds such as steroids, fatty acids, prostaglandins, and leukotrienes, and the oxidative metabolism of exogenous compounds such as drugs and other environmental products by molecular oxygen[19,59,60] (eq 1).

$$RH + O_2 + 2H^+ + 2e^- \xrightarrow{P-450} ROH + H_2O \qquad (1)$$

The active sites of P-450 enzymes contain a single iron(III) protoporphyrin IX (**45**) prosthetic group and an axial thiolate anion contributed by a cysteine residue of the polypeptide. Dioxygen is bound, reduced, and activated at this iron site.[59] The catalytic cycle of cytochrome P-450 is given in Figure 3,[61] in which S represents substrates oxidized with catalysis by cytochrome P-450. The electrons required in the process are provided by NADPH via a coupled electron transferring enzyme system.



45 Protoporphyrin IX

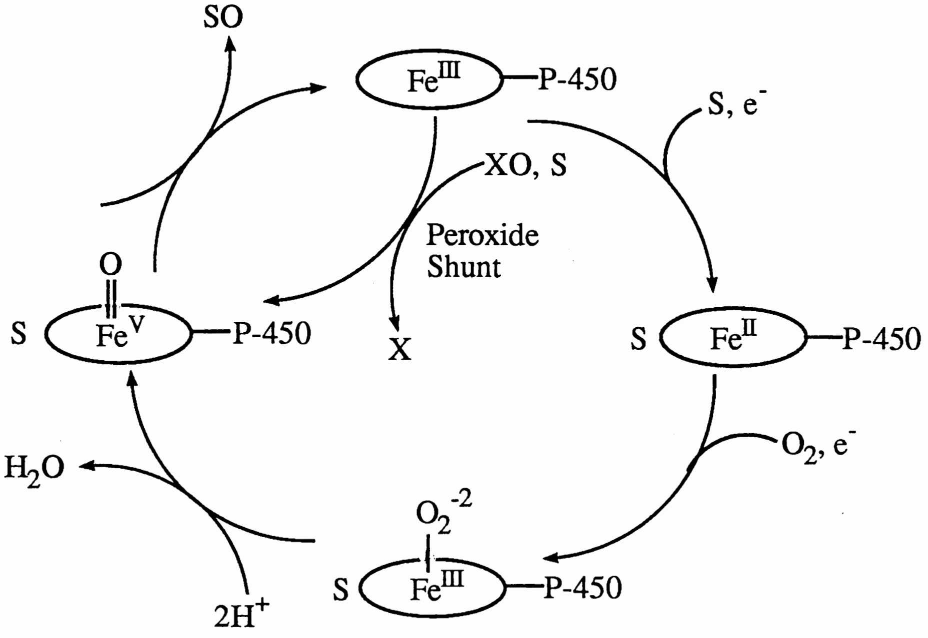
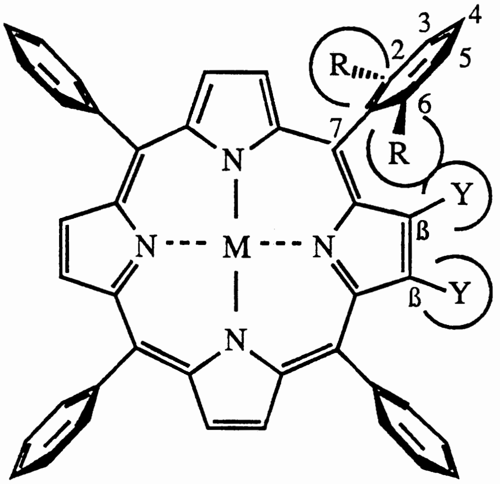


Figure 3. Catalytic cycle of cytochrome P-450.[61]

Also the use of exogenous oxygen sources, shown as XO in Figure 3, such as PhIO,[62] ROOH, $NaIO_4$[63] instead of dioxygen was reported with regard to the chemistry of oxygen activation by P-450. This is called the peroxide shunt pathway, which does not include the binding and reduction steps of dioxygen in the catalytic cycle of cytochrome P-450. Attempts have been made to mimic the activity of cytochrome P-450 with a wide variety of metalloporphyrins to catalyze oxidations of saturated and unsaturated hydrocarbons.[18-20,59,64,65] New porphyrins have been created to provide chemical selectivity at the metal binding site, to provide intramolecular ligands for axial coordination, and to protect the porphyrin from oxidative degradation. Bulky aryl substituents on the phenyl moieties of a porphyrin (**46**) help protect the *meso* carbons [C(7)] from oxidation.

The stability of tetraarylporphyrins is enhanced more by electron-withdrawing [66-69] and bulky substituents[66,69-75] especially in ortho positions [C(2) and C(6)] of the phenyl groups. The bulky groups inhibit the irreversible formation of μ-oxo dimers[76,77] and the *N*-alkylation of the pyrrole ring[78-80] by an olefin, and retard autocatalytic oxidative degradation.[66]



46

Dimeric μ-oxo manganese(IV) porphyrin complexes were obtained from the reaction of 5,10,15,20-tetraphenylporphinatomanganese(III) (X) (**15**) with iodosylbenzene, and complete characterizations of complexes, including X-ray crystal structures, were achieved.[76,77] The nature of the dimeric complexes is affected by the axial ligand X of porphyrin **15**. The structure and proposed mechanism of formation of dimeric μ-oxo manganese(IV) porphyrin is given in Figure 4 where X is N_3^- or OCN^-. However when X was Cl^- or Br^-, the dimeric complex obtained contains one iodosylbenzene per manganese.[77]

In aqueous medium, Carnieri[81] did not find any spectroscopic evidence of a reaction between oxo-5,10,15,20-tetrakis(4-carboxyphenyl)porphinatomanganese(V) and 5,10,15,20-tetrakis(4-carboxyphenyl)porphinatomanganese(III) acetate to form μ-oxo manganese(IV) porphyrin as proposed for 5,10,15,20-tetraphenylporphinatomanganese (III) X in Figure 4. The mechanisms of μ-oxo manganese porphyrin formation in organic and aqueous solutions are thought to be different.

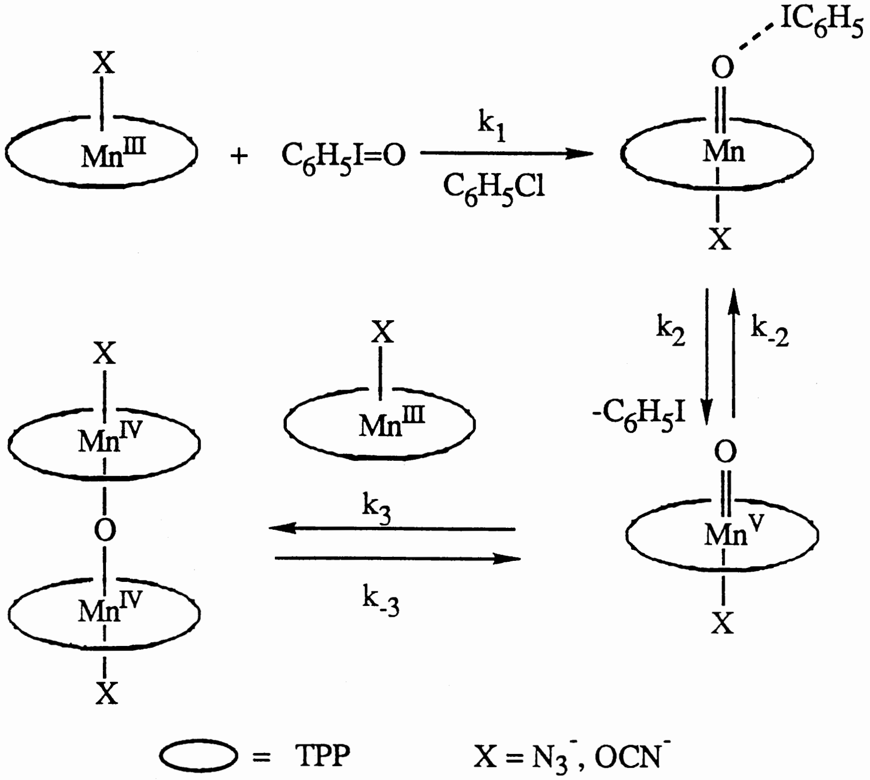


Figure 4. Mechanism of μ-oxo dimer formation from 5,10,15,20-tetraphenylporphinatomanganese(III) X with C_6H_5IO.[76]

Metalloporphyrin catalyzed epoxidation of alkenes with an oxidant could lead to the formation of a green-brown *N*-alkylporphyrin species (Figure 5). Usually at the end of reaction, the hemin was either destroyed, returned to its original form, or *N*-alkylated.[78]

Banfi studied the influence of structural factors on the stability, catalytic activity and selectivity of metallotetraarylporphyrins during epoxidation of cyclooctene by hypochlorite.[69,82,83] As shown in Table V, the hindered manganese porphyrins **47**, **48**, and **49** were stable in the presence of *N*-hexylimidazole at pH 9.0 and 0 °C. But the unhindered ones **15**, **50**, **51**, **52**, and **53** were not.

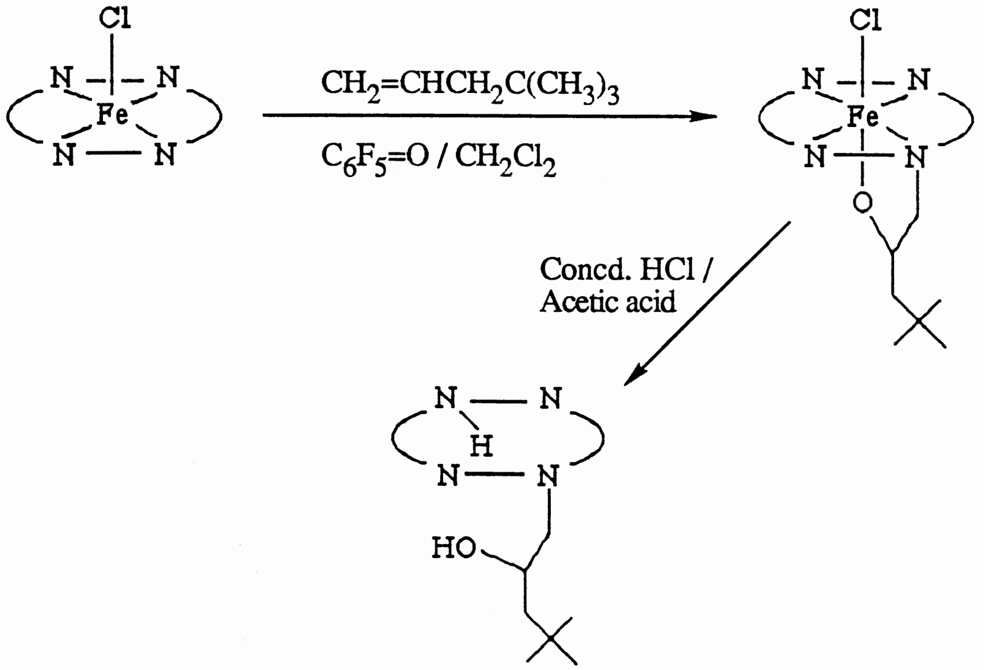
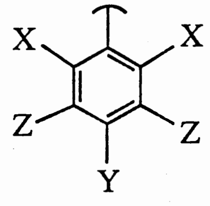


Figure 5. *N*-Alkylporphyrin formation from reaction of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphinatoiron(III) chloride and 4,4-dimethyl-1-pentene with C_6H_5IO.[78]

Table V. Modification of the Phenyl Groups of 5,10,15,20-Tetraarylporphinatomanganese(III) Acetate[69,82,83]

R =



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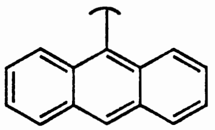
R =



2

	R	X	Y	Z	loss of the porphyrin %	time, min
15	1	H	H	H	total	<10
47	1	Cl	H	H	no	120
48	1	Cl	Cl	CH_3	no	120
49	1	Br	Br	CH_3	no	120
50	1	CH_3	CH_3	H	50	35
51	1	H	H	Cl	total	<10
52	1	F	F	F	total	<10
53	2	-	-	-	50	20

The stability of various substituted iron(III) porphyrins was studied in the presence of *tert*-butyl hydroperoxide by varying the substituents on the aromatic ring and the β-carbon of the pyrrole moiety systematically (Figure 6).[84] The combined steric and electron withdrawing effects of the substituents on the phenyl ring and at the *β*-positions of the pyrrole moiety increased the stability of the Fe(III) porphyrins (**46**, where M= Fe). The order of stabilty increased from 1 to 8 in Figure 6.

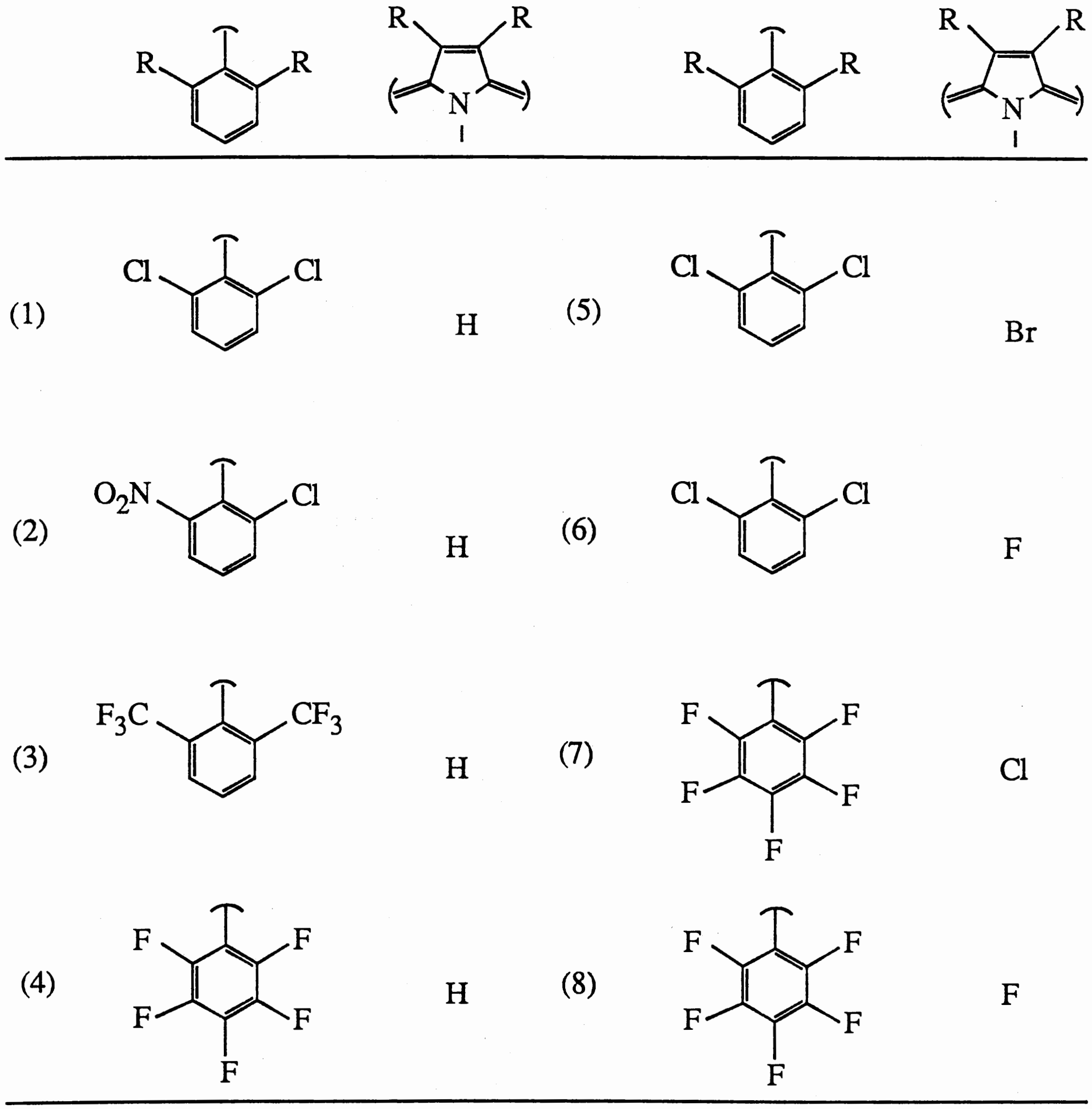


Figure 6. Systematic variation of substituents on phenyl and pyrrole groups of 5,10,15,20-tetraarylporphinatoiron(III) chloride (**28**).[84]

The remarkable stability of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphinatomanganese(III) chloride (**47**) toward oxidative destruction by iodosobenzene and by *m*-CPBA in the presence of norbornene in CH_2Cl_2 was reported elsewhere also.[66,85] In the *m*-CPBA case, 83% of the porphyrin was recovered after 8 days. Brominations of all eight β carbons of the pyrrole portion of 5,10,15,20-tetrakis(2,6-dichlorophenyl)-porphinatoiron(III) chloride gave more stable porphyrin than the unbrominated one.[85] The brominated porphyrin gave 75% yield of nonbornanols from nonbornane by 0.06 M pentafluoroiodosobenzene, and no porphyrin loss was observed. The unbrominated porphyrin was used under similar conditions, and 40% yield of nonbornanols was obtained which was accompanied by about 75% porphyrin destruction.

Metallotetraarylporphyrin Catalyzed Oxidations of Alkanes and Alkenes with Hypochlorite

Homogeneous Metallotetraarylporphyrin Catalysts. The cheap and readily available oxidizing agent, sodium hypochlorite, which has potential in industrial chemical processes, gave fast selective oxidations and showed high activity in the metalloporphyrin catalyzed oxidation of benzyl alcohol and benzyl ether to benzaldehyde[86] and in the epoxidation of alkenes.[69,82,83,87-91] These reactions are usually carried out with a phase transfer co-catalyst in a water-dichloromethane mixture.

In the catalytic oxidation of styrene with NaOCl, the porphyrin complexes of Cr, Mn, Co, and Fe gave much better yields than the complexes having Schiff base or acetylacetonate ligands (Table VI).[87,88] Only Mn(III) porphyrin complexes led to significant amounts of epoxide in the oxidation of styrene. The turnover frequencies were 30-40 moles of reactant per mol of catalyst per hour with 70-80% yield. The epoxidation rate is highly accelerated in the presence of pyridine (Table VI).

Table VI. Oxidation of Styrene with NaOCl in the Presence of Various Transition-Metal Complexes[a],88

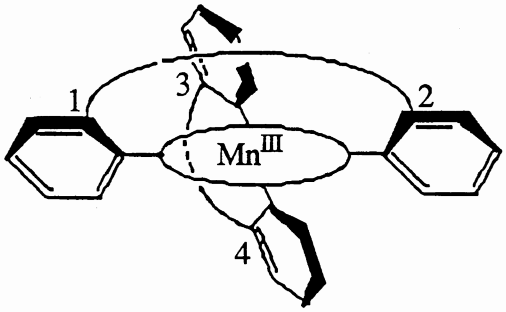
complex	conversion, %		yield of styrene oxide, %[b]	
Cr(TPP)Cl	24	(18)	8	(6)
Mn(TPP)OAc	80[c]	(68)	36[c]	(28)
Mn(TPP)Cl	75	(62)	35	(24)
Fe(TPP)Cl	33	(18)	2	(2)
Co(TPP)Br	53	(42)	6	(6)
Mn(Salpr)OAc[d]	22	(5)	0	(0)
Mn(Salphen)OAc[e]	17	(8)	4	(2)
Mn(Salphen)Br	28	(20)	6	(4)
Co(Salphen)(O_2)	38	(18)	8	(4)
VO(Acac)$_2$[f]	3-4		0	
Mn(OAc)$_3$	3-4		0	
None	3-4		0	

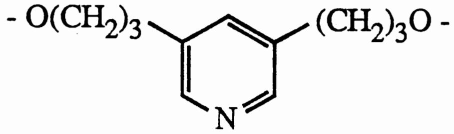
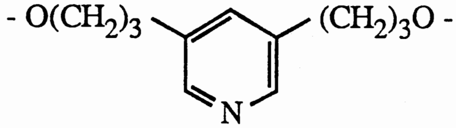
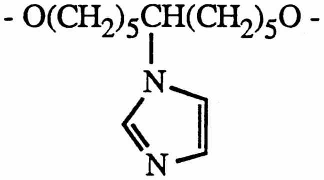
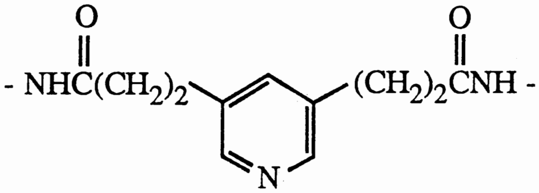
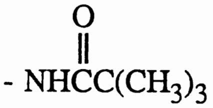
[a] Reactions were carried out under air at room temperature. [b] Conversion and yield were determined after a reaction time of 3 h (numbers in parenthesis are after a reaction time of 1 h). [c] Reaction under inert atmosphere gave 76% conversion and 40% yield after 3 h. [d] Salpr: *N,N'*-(4-azaheptylene)bis(salicylidiniminato). [e] Salphen: *N,N'*-(*o*-phenylene)bis(salicylidiniminato) metal(III). [f] Acac: Acetylacetonate.

Oxidation of cyclohexene by NaOCl and 5,10,15,20-tetraphenylporhinatomanganese(III) acetate (**15**) was studied in water-dichloromethane system using benzyltriethylammonium chloride as a phase transfer catalyst.[90,91] At pH 13, the main product of the reaction was 1,2-epoxycyclohexane (yield >80%). At pH <9 the epoxide was partly converted to *trans*-1,2-cyclohexanediol. In the presence of excess oxidant the reaction was zero order in cyclohexene, and the reaction order in Mn(III) decreased from 1 to 0 with increasing concentration of the catalyst. Pyridine and substituted pyridines enhanced the reaction rate. The oxo-manganese(V) complex was proposed as the key intermediate reacting further to give epoxide or a μ-oxo manganese(IV) dimer.

Banfi reported[69,82,83] epoxidations of olefins under two-phase conditions in the presence of Mn tetraarylporphyrins. Reactions were carried out at 0 °C in CH_2Cl_2-H_2O with 0.35 M aqueous NaOCl solution at pH 9.5, *N*-hexylimidazole as an axial ligand and, generally, a phase-transfer catalyst (Aliquat® 336). The oxidations of cyclooctene and 1-dodecene were chosen as model reactions. The oxidation rates were about 2-2.5 times lower in the absence of the phase-transfer catalyst. The epoxidation of cyclooctene catalyzed by porphyrins **15**, **50**, **52**, **53** was complete in 3-15 min at 0 °C, whereas porphyrin **47** required 60 min under the same conditions.[69] Porphyrins **15**, **50**, **52**, **53** were degraded during the olefin oxidation, while **47**, **48**, and **49** were unaffected. 5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphinatomanganese(III) acetate (**47**) was an efficient catalyst for epoxidation of 1-dodecene, cyclohexene, *α*-pinene, camphene, isoprene, 3-phenylpropene, 3,3-dimethyl-1-butene, and 2,4,4-trimethyl-1-pentene.

5,10,15,20-Tetraphenylporphinatomanganese(III) chloride (**15**) having pyridine or imidazole ligands attached as side chains was used to investigate the proximal effect of the nitrogen ligands in the catalytic epoxidation of olefins by NaOCl[92-94] (Figure 7). Covalently attached imidazole enhanced the catalytic activity of manganese porphyrins more than covalently attached pyridine. However when these nitrogen donors were added as free ligands to the reaction mixture, other factors modulated their influence on the catalyst.



C(1) ∿∿∿∿∿∿ C(2)	C(3) ∿∿∿∿∿∿ C(4) or C(3) = C(4) ∿∿∿∿∿	Ref
	$-O(CH_2)_{12}-$	92, 93
	$-O(CH_2)_4C_6H_4(CH_2)_4O-$	92, 93
	$-O(CH_2)_{12}O-$	92, 93
	 $-NH\overset{O}{\overset{\|}{C}}C(CH_3)_3$	92, 93

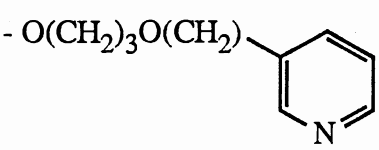
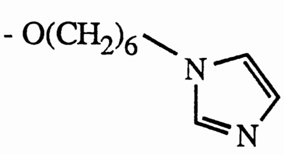
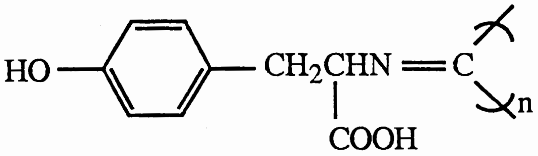
C(1) ∿∿∿∿∿∿		
		94

Figure 7. Nitrogen ligands attached to 5,10,15,20-tetraphenylporphinatomanganese-(III) chloride.

Polymer-Bound Metallotetraarylporphyrin Catalysts. Attempts have been made to immobilize metallotetraarylporphyrins on polymers[89,90,95] and in microheterogeneous media[96-98] to improve the catalytic activity by preventing the formation of inactive porphyrin μ-oxo dimers.[90,92] Manganese(III) and cobalt(III) complexes of 5,10,15,20-tetrakis(sulfonatophenyl)porphyrins (**54** and **55**) loaded on Amberlite® IRA 900 (24-42 mesh) ion exchange resin were used to catalyze conversion of hydrogen peroxide to water and oxygen in aqueous solution.[95] Porphyrin **54** and porphyrin **55** loaded on the resin retained their activities even after ten cycles of repeated use, whereas the low-molecular weight porphyrin **54** and porphyrin **55** were deactivated by hydrogen peroxide in aqueous solution in 30 min.

5,10,15,20-Tetraphenylporphinatomanganese(III) acetate (**15**) was anchored onto either a commercial poly(4-vinylpyridine-*co*-styrene) having a flexible backbone or a polymer of an isocyanide (**56**) having a rigid helical main chain with 4 repeating units per helical turn[90,91] and used in the epoxidations of cyclohexene in a two-phase water-dichloromethane system in the presence of benzyltriethylammonium chloride. The major products were 1,2-epoxycyclohexane (yield >80%), 2-cyclohexen-1-one, 2-cyclohexen-1-ol, and *trans*-2-chlorocyclohexanol. Anchoring of 5,10,15,20-tetraphenylporphinato-manganese(III) acetate (**15**) to uncrosslinked poly(isocyanide) (**56**) led to an activity increase by a factor of 3-6 in the epoxidation, whereas the crosslinked anchored catalyst showed a lower activity than even the non-anchored ones for the same reaction.



56

So far, few studies have been reported of metallotetraaryporphyrin-catalyzed oxidations in aqueous solutions. A synthetic model of cytochrome P-450 was prepared with 5,10,15,20-tetrakis[4-(hexadecyloxy)phenyl]porphrinatomanganese(III) acetate (**57**) and colloidal Pt (obtained from reduction of Pt(II) ions by molecular hydrogen via the electron carrier methylene blue) incorporated into vesicles of polymerized isocyano surfactant[97] (Figure 8). Dynamic light-scattering experiments and electron micrographs revealed that polymerized vesicles with and without Pt had 1000-3000 Å diameters. The vesicles were used to catalyze the epoxidation of water-soluble 2,5-dihydrofuran and water-insoluble styrene by dioxygen. For 2,5-dihydrofuran, the reaction products were 3,4-epoxytetrahydrofuran and *trans*-3,4-dihydroxytetrahydrofuran (molar ratio 1:2.5) (eq. 2). For styrene, only the ring-opened product 1,2-dihydroxy-1-phenylethane was detected (eq. 3). Turnover frequencies [mol of oxygenated product/(mol of Mn(III) x h)] for 2,5-dihydrofuran and styrene were 8 and 1.3 respectively. The cycles of this multiple catalyst system are given in Figure 9.

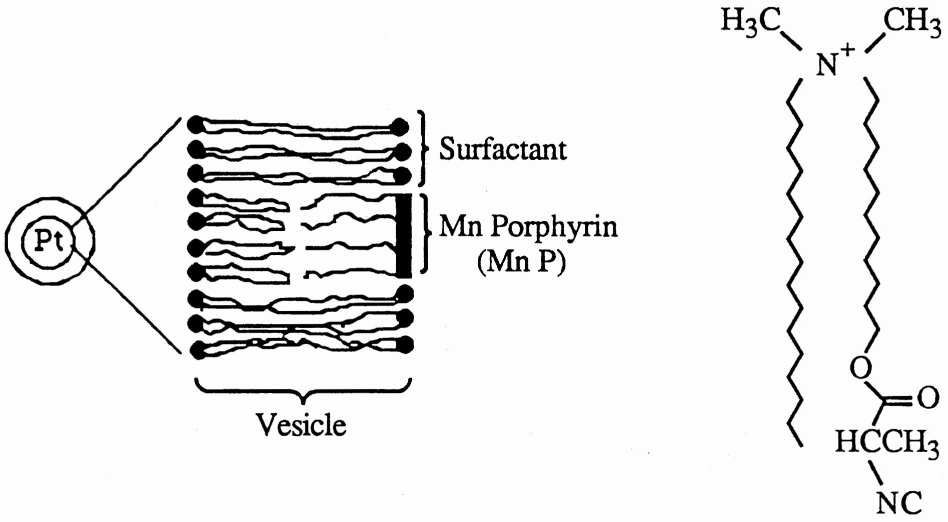
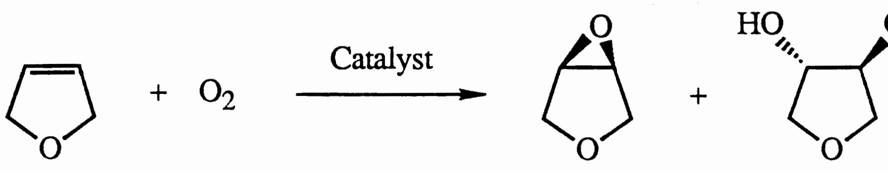


Figure 8. Polymerized isocyano surfactant vesicle containing porphyrin **57** and colloidal Pt and structure of the isocyano surfactant.[97]



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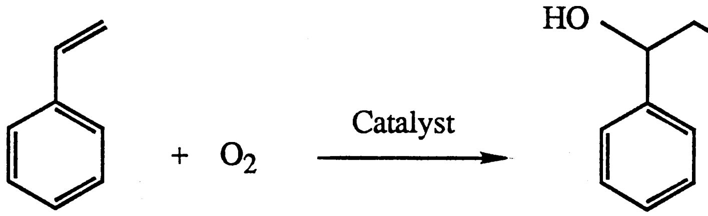

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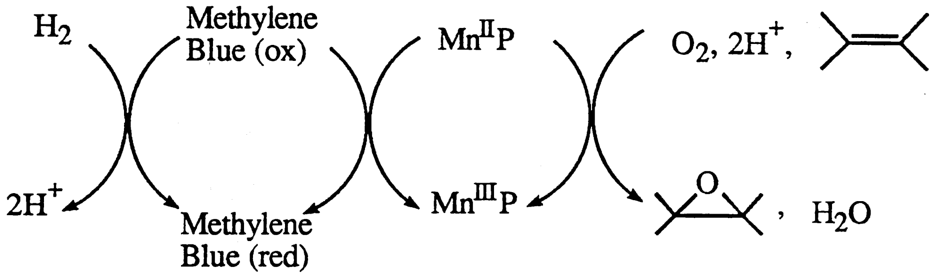
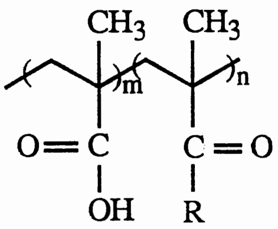


Figure 9. Molecular oxygen activation for epoxidation of alkenes by membrane-bound Mn porphyrin (MnP: porphyrin **57**).[97]

Mn, Fe, and Cr complexes of 5,10,15,20-tetrakis(4-aminophenyl)porphyrins (**58**, **59**, **60**) bound covalently to water-soluble negatively charged polymers [poly(methacrylic acid)] (**61**), positively charged polymers [poly(chloromethylstyrene) (**62**) containing triethylbenzylammonium sites], and uncharged polymers [poly(1-vinylpyrrolidone-*co*-methyl methacrylate)] (**63**) (R is one of the porphyrins) catalyze the autoxidation of water-soluble 2,5-dihydrofuran by OCl^-.[96] The low molecular-weight, negatively charged tetrasodium salt of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphinatomanganese(III) (**54**) and positively charged porphyrin tetrachloride 5,10,15,20-tetrakis[4-(N-methyl-pyridinium)]porphinatomanganese(III) (**64**) were used as references to estimate the effect of the polymer matrix. More than 90% conversion of 2,5-dihydrofuran to 3,4-epoxytetrahydrofuran and 3,4-dihydroxytetrahydrofuran was achieved. This simple system requires neither an organic solvent nor a phase transfer catalyst. The results of the epoxidation of 2,5-dihydrofuran with water-soluble porphyrins in aqueous solution showed dependence neither on polymer binding of the porphyrins nor on the charge of the polymer (Table VII).



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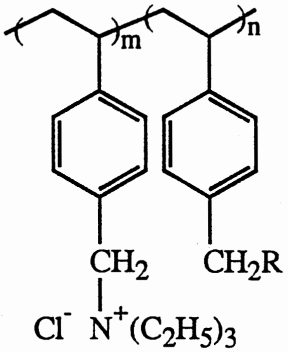

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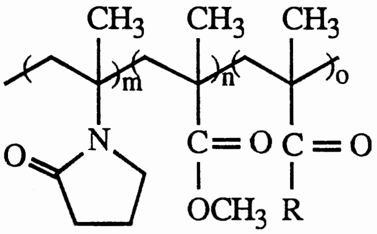


63

Selective C-25 hydroxylation of cholesterol was achieved in aqueous solution with a membrane-spanning Mn(III) porphyrin *α,β, α,β-meso*-tetrakis[*o*-(3*β*-hydroxy-5-cholenamido)phenyl]porphinatomanganese(III) chloride, positioned in a synthetic bilayer vesicle by appended steroidal substituents.[98] Hydroxylation was carried out under aerobic conditions with ascorbic acid as the reducing agent and with sodium periodate as the primary oxidant.

The mechanism of epoxidation of alkenes catalyzed by Mn(III) tetraarylporphyrin has been investigated by identifying the oxo-manganese complexes, measuring their ability to transfer oxygen to an alkene, and comparing their properties to those of cytochrome P-450.[99-101] Oxo-5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphinatomanganese(IV) and the corresponding Mn(V) porphyrin complex catalyze epoxidation of *cis*- and *trans-β*-methylstyrene in the absence of an auxillary oxidant. The oxo-manganese(IV) species transfers oxygen to *cis-β*-methylstyrene in nonstereospecific fashion whereas the oxo-manganese(V) complex transfers oxygen to the olefin with predominant retention of configuration.

Table VII. Epoxidation of 2,5-Dihydrofuran with Metallotetraarylporphyrins in Water Using NaOCl[a]

catalyst[b]	conversion of 2,5-dihydrofuran in %	yield of 3,4-epoxytetrahydrofuran in %
none	32	23
61-MnTAPP	99	2
61-FeTAPP	95	67
61-CrTAPP	86	37
62-MnTAPP	95	53
62-FeTAPP	91	62
62-CrTAPP	93	67
63-MnTAPP	78	49
63-FeTAPP	68	41
63-CrTAPP[c]	32	22
Mn(III)TSPP (**54**)	97	60
Mn(III)TMPP (**64**)	93	70

[a] Reaction temperature: 20 °C, reaction time: 4 h. [b] Catalyst: Water-soluble polymer-metallotetraarylporphyrin. Metal = Mn, Fe, Cr. [c] Reaction time: 2 h

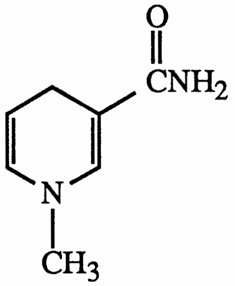
In conclusion, metallotetraarylporphyrins, especially Mn tetraarylporphyrins, are more efficient catalysts for epoxidation of alkenes than other macrocycle-transition metal catalysts. The presence of a nitrogen ligand such as imidazole or pyridine and a phase transfer catalyst promote epoxidations in two-phase mixtures. When metallotetraarylporphyrins are immobilized on polymers, their deactivation rate appears slow. In contrast to these few investigations of homogeneous and polymer bound metallotetraarylporphyrins in water to oxidize water soluble alkenes, no attempt has been made to use colloidal ion exchange resins containing metallotetraarylporphyrins to oxidize water insoluble alkenes by aqueous hypochlorite.

In this investigation 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)-porphinatomanganese(III) chloride (**65**) was used to catalyze epoxidations of water-insoluble alkenes in aqueous dispersions. It combines several features of previous metalloporphyrin oxidation catalysts, such as bulky substituents at ortho positions of the phenyl groups to protect the porphyrin from oxidative degradation, sulfonate groups to provide water solubility, and ionic attachment sites to quaternary ammonium groups containing colloidal ion exchange resins.

Metallotetraarylporphyrin Catalyzed Oxidations of Alkanes and Alkenes by Dioxygen

Synthetic models of cytochrome P-450 were prepared and used for hydroxylation of alkanes and epoxidation of alkenes by dioxygen in the presence of a reducing agent. In living organisms, after the metal center of the protoporphyrin IX of cytochrome P-450 is reduced to iron(II), it binds and cleaves molecular oxygen, whereupon water and a high-valent iron-oxo complex are formed (Figure 3). The latter transfers oxygen to a substrate molecule. NADPH provides the electrons for reduction of the iron back to Fe(II)[59] (Figure 3).

An artificial oxygen activation system was reported by Tabushi.[102] MeNAH (**66**), a NADH analogue, activates dioygen in the presence of flavin mononucleotide and 5,10,15,20-tetrakis(sulfonatophenyl)porphinatomanganese(III) (**54**) to give epoxides from olefins. The artificial system showed both large turnover frequencies of 3.6 and 9.0 [mol of product/mol of porphyrin **54** x min)] and turnover numbers of 60 and 260 [mol of product/mol of porphyrin **54**] for epoxidation of cyclohexene and nerol respectively. An Fe center instead of a Mn center displayed much lower turnover frequency of 0.80 min^{-1}.



66

5,10,15,20-Tetraphenylporphinatoiron(III) chloride (**28**) catalyzed autoxidation of alkenes such as cyclohexene and 2,3-dimethylbut-2-ene, and some alkyl aromatic compounds such as tetralin, by shaking under dioxygen at 25 °C for 8-16 h.[103] The process is described as a free-radical autoxidation and no presence of a reducing agent was mentioned. In a typical experiment; cyclohexene (74 mmol) and catalyst (0.006 mmol) consumed 14.7 mmol oxygen in 12 h at 25 °C. The major product was cyclohex-2-enone.

5,10,15,20-Tetraphenylporphinatomanganese(III) chloride (**15**) in the presence of imidazole was reductively activated by Zn to catalyze autoxidation of certain alkanes and alkenes.[104] Turnover numbers were 75 and 13 per 0.5 h (mol of product/mol of catalyst employed) for epoxidation of cyclooctene and for hydroxylation of adamantane to adamantan-1-ol.

5,10,15,20-Tetra(*p*-tolyl)porphinatocobalt(II) catalyzed the autoxidations of certain alkanes and alkenes.[105] 5,10,15,20-Tetrakis(sulfonatophenyl)porphinatomanganese(III) (**54**) or porphyrin **15** in the presence of $NaBH_4$, $(n\text{-}C_4H_9)_4NBH_4$, or sodium ascorbate also activated dioxygen. In the oxidation of cyclohexene, porphyrin **54** with reducing agent $NaBH_4$ was the most effective for producing cyclohexanol as the main product, and its activity was higher than that of porphyrin **15**.[106] It was suggested that cyclohexanone was an intermediate reduced by $NaBH_4$ to the corresponding alcohol. However another possible intermediate, cyclohexene oxide was not reduced to cyclohexanol in control experiments. In the absence of reductant, no oxidation was observed. So $NaBH_4$ serves two purposes: it facilitates the transfer of oxygen and reduces cyclohexanone to cyclohexanol.

Fuhrhop reported[107] that Co(II) and Fe(III) tetraarylporphyrins (**19**, **28**) were catalysts for oxidation of cyclohexene by dioxygen to allylic hydroperoxides, which then decomposed to give 2-cyclohexenone as the main product. When the metallotetraaryl-porphyrin-catalyzed reaction was carried out in the presence of molybdenum or vanadium complexes, the reaction was stopped, and addition of an activator such as 3-cholesteryl acetate, chrysene, lanosterol, deazaflavin, or 3-desoxy-3-oxo lithocholic acid methyl ester to the deactivated metalloporphyrin led to reactivation of the iron and cobalt catalysts.

Oxidations in Microheterogeneous Media

Microheterogeneous systems composed of micelles, microemulsions, vesicles, colloids, and ion exchange membranes provide models for processes in biological membranes. In general, the oxidation rates increase in microheterogenous environment such as latex, surfactant, vesicle, and soluble polymer. Hydrolyses of carboxylic esters, ortho esters, sulfate esters, phosphate esters, and Schiff bases have been extensively studied. The hydrolysis of esters may occur via general and specific acid-catalyzed, pH-independent, and general and specific base-catalyzed mechanisms.[11-14] A few oxidation reactions catalyzed in microhetergeneous media are reported in the literature. Oxidations of 2,5-dihydrofuran and styrene by a vesicle bound Mn(III) tetraarylporphyrin by van Esch,[97] of cholesterol by membrane-spanning Mn(III) tetraarylporphyrin by Groves[98], of 1-decanethiol by latex-bound cobalt(II) phthalocyaninetetrasulfonate by Hassanein,[57,58] of 2-mercaptoethanol by latex-bound cobalt(II) phthalocyaninetetrasulfonate by van Herk[56] are described previously.

The autoxidation of tetralin to tetrol and tetralone was carried out in aqueous suspension with dioxygen catalyzed by cobalt acrylate and methacrylate latexes in the presence of pyridine at pH 8.5 and at 50 °C.[108] The reaction in microheterogeneous medium was 3.3 times faster than the one catalyzed by Co(II) and pyridine in aqueous solution.

A latex-bound catalyst was applied to the oxidation of ascorbic acid.[109] The 250 nm latex prepared from emulsion polymerization of styrene, acrylic acid and divinylbenzene was modified by covalent attachment of histamine, which complexed Cu(II). The latex catalyst showed Michaelis-Menten type kinetic behavior as well as high catalytic activity and stability.

A rate increase was observed when Ru(III)-EDTA catalyzed oxidation of cyclohexane to cyclohexanol and cyclohexanone by dioxygen was carried out in the presence of hexadecyltrimethylammonium bromide (CTAB) micelles in a 1:1 water-dioxane mixture. The reaction was first order with respect to catalyst and substrate, and one-half order with respect to dioxygen concentrations. The activation energy of the oxidation was lowered about 13 kcal/mol by CTAB micelles.[110]

Preparations and Properties of Water-Soluble Cobalt(II) Phthalocyanine and Manganese(III) Tetraaarylporphyrin Catalysts

Cobalt(II) Phthalocyaninetetra(sodium sulfonate) (38)

The metallophthalocyanines have long been used as blue and green pigments and dyes, and now find applications in many other fields such as electrocatalysis, catalysis, photovoltaics, molecular metals, liquid crystals, chemical sensors, photoconductors, batteries, medical staining agents and medical probes.[111] The first metallophthalocyanine was discovered during the preparation of phthalimide from phthalic anhydride. Currently about 4900 different phthalocyanines are known.

Easy preparation and purification of Co(II), Fe(III), Ni(II), and Mn(II) tetrasulfophthalocyanines have been reported by Weber.[112] The sulfonate groups on phthalocyanines provide water solubility as well as binding sites to polycations such as ionenes.

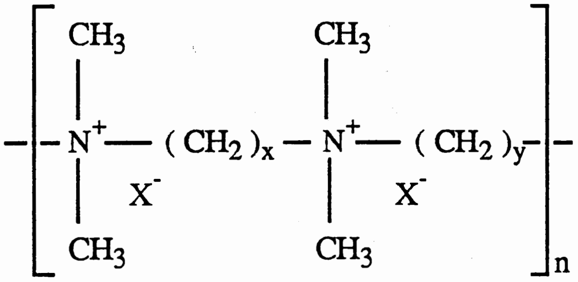
Extraplanar ligands such as pyridine, nitrite, histidine, and benzylimidazole do not influence much the value of the magnetic moment of the cobalt(II) phthalocyaninetetra-(sodium sulfonate) (**38**) in solution.[113] However the ligands cyanide and imidazole promote the oxidation of the phthalocyanine **38** by the oxygen of air.

The formation of a mononuclear adduct of dioxygen with phthalocyanine **38** was detected by ESR spectroscopy.[114] Solutions of phthalocyanine **38** in deoxygenated methanol at -84 °C showed an ESR signal which was converted to a new ESR signal after oxygenation. The spectrum obtained was analogous to those of other Co(II) complexes with 1:1 oxygen adducts. The adduct formation was achieved in the presence and absence of ammonia and was reversible.

The reversible addition of dioxygen to phthalocyanine **38** in aqueous solution was also confirmed by UV/visible spectroscopy. The phthalocyanine **38** could be in the monomeric, dimeric (or higher aggregates) and oxygen adduct forms. The absorption spectra[115,116] and energetics of the dimerization[117,118] of phthalocyanine **38** were studied. Gruen[115] assigned the absorption maxima at 663 nm and 626 nm to monomeric and dimeric phthalocyanine **38** respectively. The oxygen adduct of phthalocyanine **38** was observed at 670 nm only when oxygen was bubbled into an aqueous alkaline solution (0.1 M NaOH), but the type of oxygen adduct was not identified. A stoichiometry Co:O_2 = 2:1 was proposed by Wagnerova.[116] However the absorption bands there observed in oxygenated solutions of phthalocyanine **38** were attributed wrongly to the oxygen-free species (626 nm) and the oxygenated adduct (670 nm).[116]

The monomer-dimer equilibrium of phthalocyanine **38** was studied in aqueous solution at neutral pH[117,118] and in aqueous alcoholic solution.[118] Since the oxygen adduct of phthalocyanine **38** does not form at neutral pH, the results obtained were for purely a monomer-dimer equilibrium. The dimerization constant (K_D) depended only slightly on temperature in the range from 25 to 75 °C.[118] For example, the K_D values were $7.4 \times 10^6\ M^{-1}$ and $9.3 \times 10^6\ M^{-1}$ for 0.879×10^{-7} M and 5.23×10^{-7} M concentrations of phthalocyanine **38** in aqueous solution at 25 °C. The K_D decreased as the temperature increased. The addition of simple salts, such as KCl, to the solution of phthalocyanine **38** increased the formation of dimers and higher aggregates as a result of the shielding effect of the salts on the repulsive electrostatic forces between the sulfonate ions.[115]

Additions of ionenes **67** ($x = 2$; $y = 4, 6, 10$) to the solution of phthalocyanine **38** showed the same effects as simple salts and enhanced the aggregation of phthalocyanine.[119] In a quantitative study with 2,4-ionene (**67**) where $x = 2$ and $y = 4$, no cobalt site isolation occurred at N^+/Co ratios up to $N^+/Co = 10^5$, and ionenes appeared to suppress the formation of the oxygen adduct at pH 12.5.[119]



$$\left[-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^+}}}}-(CH_2)_x-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^+}}}}-(CH_2)_y- \right]_n \quad X^- \quad X^-$$

X = Br, OH
$x = 2;\ y = 4$
$x = 2;\ y = 6$
$x = 2;\ y = 10$

67

Copper, manganese, iron, and vanadyl phthalocyaninetetra(sodium sulfonates) showed behavior similar to that of phthalocyanine **38** in the presence of 2,4-ionene. It can be concluded that ionenes promote phthalocyanine aggregation independent of central metal ion.[120] Congo red, a dye known to associate strongly in aqueous solution, also showed aggregation in the presence of 2,4-ionene.

Further investigation of ionene-phthalocyanine **38** interaction showed that ionenes having $x = 2$ and $y = 10, 12$ in **67** can promote formation of monomer rather than aggregates.[121] Monomer occurred at high N^+/Co ratios $>10^3$ when 2,10- and 2,12-

ionenes were present. In fact, at $N^+/Co = 10^5$ the monomer concentration was higher than it was at the same concentration of homogeneous phthalocyanine **38**. This site isolation effect of 2,10- and 2,12-ionenes was attributed to the hydrophobic character of the C_{10}- and C_{12}- chain segments causing the formation of micelle-like stuructures which induce the monomerization of the phthalocyanine.

The aggregation state of latex bound Co(II) phthalocyaninetetrasulfonate has not been investigated.

5,10,15,20-Tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) Chloride (65)

Tetraphenylporphyrin was first synthesized in 1936 by Rothemund by reacting benzaldehyde and pyrrole in a sealed tube at 150 °C for 24 h.[122,123] Adler modified the Rothemund reaction by allowing benzaldehyde and pyrrole to react for 30 min in refluxing propionic acid open to air,[124] and crystalline tetraphenylporphyrin was obtained in 20 ± 3% yield. Although 70 different aldehydes gave porphyrins under similar conditions, the ones that do not crystallize or precipitate at the end of the reaction were troublesome to isolate. A two-step strategy (Figure 10) developed for the preparation of porphyrins from substituted benzaldehydes by Lindsey and coworkers[125,126] required pyrrole and benzaldehyde to react reversibly at room temperature with trace acid catalysis to form the cyclic tetraphenylporphyrinogen at equilibrium. An oxidant was then added to irreversibly convert the porphyrinogen to the porphyrin.

Lindsey's procedure allowed the preparation of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**47**) without difficult purification problems. Banfi[69,83] reported 7% yield of the porphyrin with this procedure,[125] and <<1% with Longo's procedure.[127] A similar procedure with some modifications was used in the preparation of tetrakis(2,4,6-trimethylphenyl)porphyrin in 20% yield.[128]

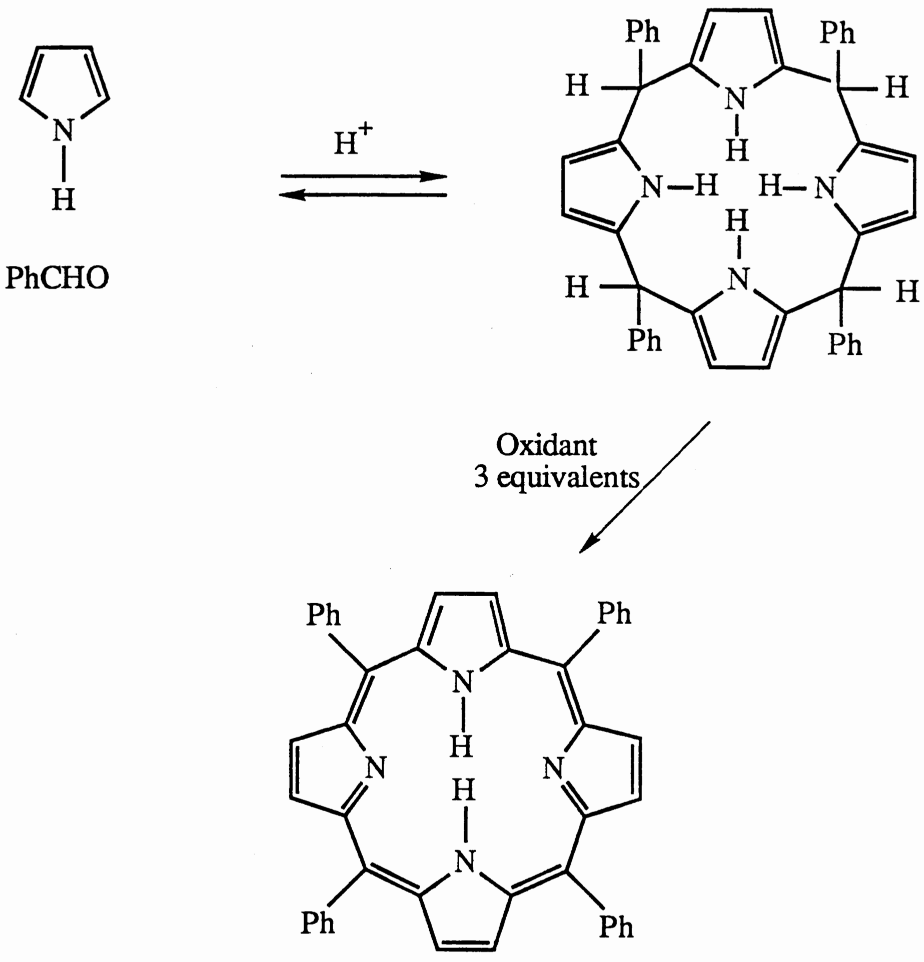
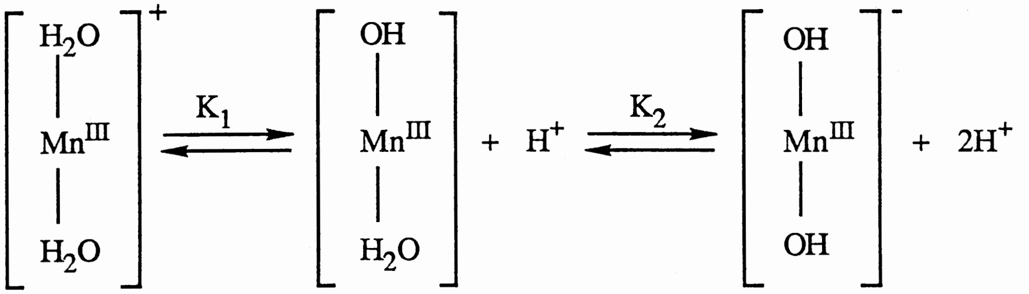


Figure 10. Synthetic route to 5,10,15,20-tetraphenylporphyrin.[125]

The success of the iron(III) and manganese(III) tetraarylporphyrins as epoxidation catalysts is due to the formation of highly reactive oxo-metal species. The available redox states of central manganese ions in tetraarylporphyrins have been identified spectroscopically as Mn(II), Mn(III), Mn(IV), and Mn(V).[81,129-131] The most stable oxidation state of the central manganese ion in a tetraarylporphyrin ligand is +3. The water-soluble manganese(III) porphyrins having 4-carboxyphenyl, 4-sulfonatophenyl, 4-pyridyl, and *N*-methyl-4-pyridyl groups have similar absorption spectra and after oxidation by several oxidants, identical absorption spectral changes were obtained.[81] As the pH was lowered, oxidations of Mn(III) porphyrins became more difficult and at pH <9, increasing instability of the oxo-Mn(IV) product resulted extensive loss of the porphyrin. However, with an excess of a strong oxidant (H_2O_2, peroxodisulphate, hypochlorite, Cl_2, or Br_2), Mn(III) (4-carboxyphenyl)porphyrin can be oxidized at pH as low as 7.0. In alkaline aqueous solution, oxidation of the Mn(III) porphyrin by H_2O_2, BrO_3^-, $KMnO_4$, and stoichiometric OCl^- gave a Mn(IV) porphyrin which appeared to exist in solution as μ-oxo dimers rather than Mn(III) porphyrin π-radical cation. A second oxidation step was proposed to be the reaction of 1 equivalent of μ-oxo Mn(IV) dimer with 1 equivalent of excess OCl^-, to give as the final product an oxo-Mn(V) porphyrin. The Mn(IV) had no ESR signal at room temperature and an anomalously low magnetic moment, which is inconsistent with a formal d^3 configuration. Also the oxo-Mn(V) porphyrin was ESR silent. The λ_{max} of the bands of Mn(IV) and Mn(V) tetrakis(4-carboxyphenyl)porphyrins were 420 and 418 nm respectively. The absorption spectrum of any Mn(III) porphyrin shows pH dependence in the alkaline region, because the central manganese ion has two water molecules coordinated at the axial positions which can be deprotonated in basic solution (eq. 4). The pK_1 and pK_2 values for 5,10,15,20-tetrakis(4-sulfonatophenyl)porphinatomanganese(III) (**54**) were 8.6 and 11.6 respectively. These transitions are indeed associated with the manganese ion. Under identical conditions, there were no changes in the absorption spectrum of metal free porphyrin.[130]



$$\left[\begin{array}{c} H_2O \\ | \\ Mn^{III} \\ | \\ H_2O \end{array}\right]^+ \overset{K_1}{\rightleftharpoons} \left[\begin{array}{c} OH \\ | \\ Mn^{III} \\ | \\ H_2O \end{array}\right] + H^+ \overset{K_2}{\rightleftharpoons} \left[\begin{array}{c} OH \\ | \\ Mn^{III} \\ | \\ OH \end{array}\right]^- + 2H^+ \qquad (4)$$

The study of oxidation of water-soluble Mn(III) porphyrins in a micellar environment revealed by absorption spectroscopy that formation of Mn(IV) and Mn(V) is less efficient in positively charged micelles and formation of Mn(V) porphyrin is prohibited totally by negatively charged micelles.[131] Oxidation states II, III, IV, V, and

III-π radical are available for Mn and the structural characteristics of these tetraarylporphyrins vary from state to state.

Preparation of Colloidal Ion Exchange Resins

Emulsion polymerization was first employed for the production of synthetic styrene-butadiene rubber. Today it is used industrially to produce rubber, coatings, finishes, paints, and floor polishes. It involves the polymerization of emulsified monomers, and the final product of the polymerization, referred to as a latex, is often used directly as an emulsion.[132] Particles from emulsion polymerization are stabilized by amphiphilic surfactant molecules. Diameters of particles in most practical emulsion latexes are between 50 and 2500 nm.[133]

The physical forces between particles, or particles and surfaces, are electrostatic and van der Waals in nature.[134] Once the colloidal particles are charged, the electrostatic repulsive force determines how close two particles can approach each other, and keeps them apart and prevents aggregation. This is called charge stabilization of the particles. The ion-dipole interaction between ionic sites on the colloidal particle surface and water orient the water molecules around the ionic sites on the surface of the particles. Eventually it affects the local dielectric constant of water and a hydration force occurs between charged particle and water. Colloidal particles can also be stabilized by adsorbed hydrophilic polymer (steric stabilization) to prevent aggregation.[135]

Electrostatic particle stabilization can be achieved by preparing the latex in the presence of an amphiphilic surfactant, by preparing the latex in charged form from covalently bound surfactant or ionizable monomer, or by converting the colloidal polymer into ionic, hydrophobic particles with a post-polymerization reaction. The ionic groups can serve as sites to bind ligands, macrocycles, and even transition metal ions by ion-exchange. The ligands and macrocycles can be complexes of transition metals. Benzyltri-*n*-butylphosphonium and benzyltrimethylammonium ions bound to polystyrene latexes have been formed by reacting divinylbenzene crosslinked poly[styrene-*co*-(chloromethyl)-styrenes)] or poly(chloromethylstyrenes) latexes with either tri-*n*-butylphosphine or trimethylamine directly.[136-138] The cationic sites created were used for phase-transfer catalysis of reactions of aqueous sodium cyanide with 1-bromooctane and with benzylbromide[136] and can be used to bind anionic transition-metal complexes.

Ion exchange and conductimetric titration methods were used to characterize the surfaces of latex particles. Dialysis, ion-exchange and *serum replacement* are the common technique to purify latex particles.[139-141] Titration of liberated Cl^- ions, by the Volhard method,[142] is used to determine the amounts of quaternary phosphonium[136] and ammonium sites.

In the literature, there are few investigations of latex-bound catalyst. In this research cobalt(II) phthalocyaninetetrasulfonate (**38**) and 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) chloride (**65**) were prepared, bound to 0.1 μm polymer colloids, and used as catalysts in the autoxidations of water-insoluble organic compounds. Colloidal catalysts <0.1 μm in diameter are expected to overcome most of the diffusional and mass transfer limitations to the activities of heterogeneous catalysts because of short diffusion path length and availibility of large number of catalyst loaded particles dispersed throughout the reaction medium. Conventional heterogeneous catalysts are 0.1-5 mm in diameter, and their activities are limited in part by mass transfer of the reactants to the surface of the solid catalyst particle and sometimes by intraparticle diffusion. Decreasing the spherical particle diameter from 0.1-5 mm to <0.1 μm shortens the diffusion path length from the surface to an internal active site and increases the surface area per unit weight of catalyst inversely proportional to particle diameter.[2]

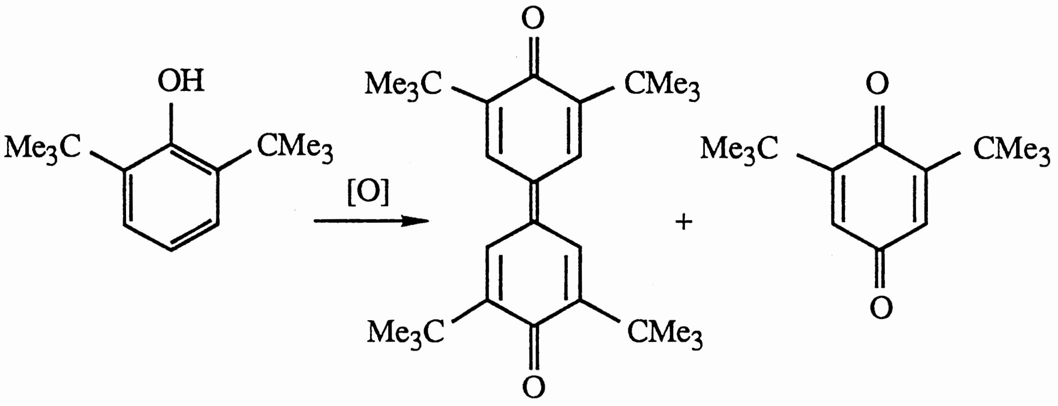
In addition, the affinity of reactants for the colloidal catalyst support helps minimize mass transfer limitation, especially for the reactions of water insoluble organic compounds catalyzed by organic polymer supported catalysts in water. This creates an environment where higher concentration of reactants and more catalyst-substrate interactions are expected. So this type catalyst system may show higher catalytic activity than the homogeneous analogue.

CHAPTER II

AUTOXIDATION OF PHENOLS IN WATER CATALYZED BY COBALT(II) PHTHALOCYANINETETRASULFONATE ON POLYMER COLLOIDS

Introduction

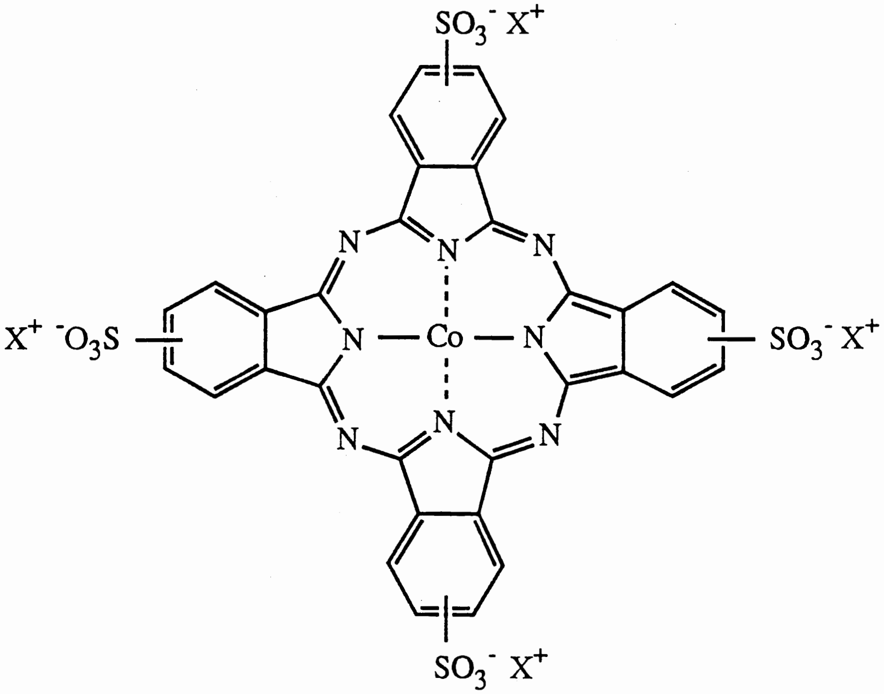
Autoxidation of 2,6-di-*tert*-butylphenol (**7**, DBP) with homogeneous and heterogeneous catalysts has been studied extensively during the last several years.[22-24,26,27,29,33-35,43,45-48,143-149] The oxidation mechanism is believed to follow a free radical process in which one electron is transferred from phenol to catalyst. After formation of resonance-stabilized phenoxy radicals, a complex series of reactions takes place.[22] The products of oxidation of phenol **7** shown in eq. 5 are 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenoquinone (**2a**) and 2,6-di-*tert*-butylbenzoquinone (**1a**). The selectivity for a particular product depends upon the substrate concentration, catalyst and solvent.



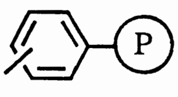
(5)

7 **2a** **1a**

Metallophthalocyanines have been used as commercial dyes, optical and electrical materials, catalysts, and models for naturally occuring macrocycles.[22,150,151] Co(II) phthalocyanine derivatives have been bound to several types of polymers for catalysis.[152-157] In this work, cobalt(II) phthalocyaninetetra(sodium sulfonate) [**38**, Co(II)PcTsNa$_4$], which is soluble in water and can be bound to colloids, was employed to oxidize substituted phenols. It promised to provide rapid electron transfer reactions,[150,151] and it is more stable to oxidative degradation than the porphyrins and tetraarylporphyrins which have been more commonly used as oxidation catalysts.[18-20,158]



38 X$^+$: Na$^+$

39a X$^+$: $(CH_3)_3N^+CH_2$ 

In the literature, there are a few investigations of latex-bound catalysts. Usually latex-bound catalysts showed higher catalytic activities in the autoxidation of organic compounds than either homogeneous or water soluble polymer-bound analogues. Autoxidation of water-soluble 2-mercaptoethanol[52-56] and water-insoluble 1-decanethiol[57,58] with dioxygen catalyzed by cationic latex-bound cobalt(II) phthalocyaninetetrasulfonate systems in aqueous phase gave higher rates than when catalyzed by poly(4-vinylpyridinium-co-styrene) surfactant-bound cobalt(II) phthalocyaninetetrasulfonate and soluble phthalocyanine **38** respectively. Anionic latex-bound Co(II)-pyridine was a better catalyst for autoxidation of tetralin than the homogeneous analogue.[50,108] Similarly a rate increase in the oxidation of ascorbic acid was observed when a histamine-containing latex Cu(II) complex was used as catalyst instead of water soluble poly(L-histidine) Cu(II) complex.[109]

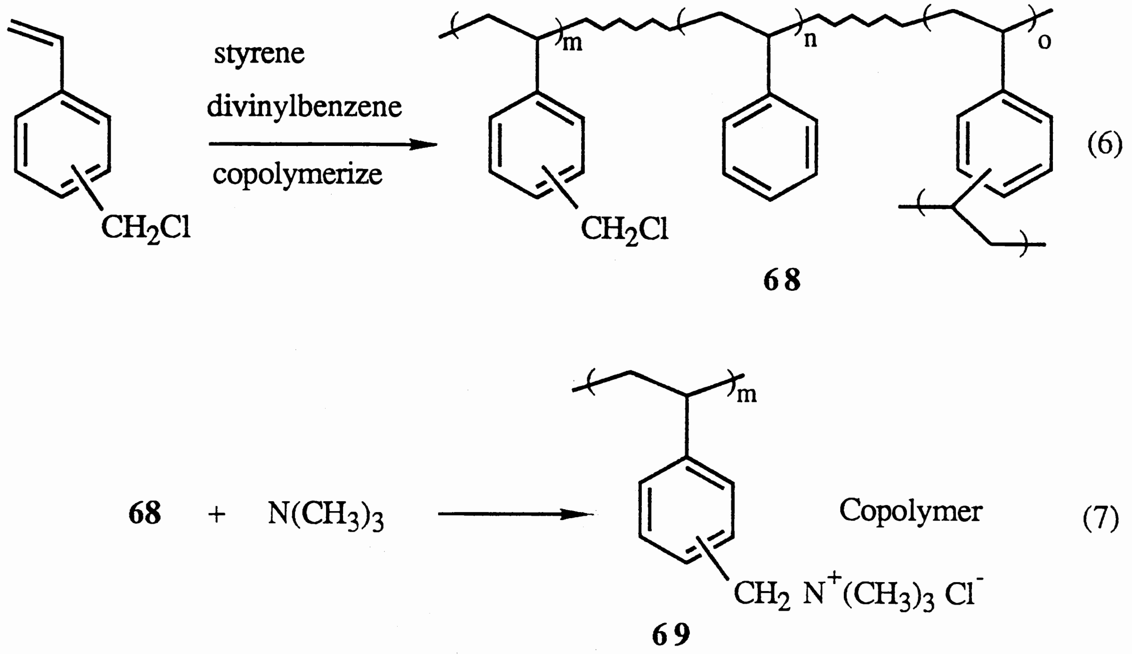
Results

Preparation of Colloidal Anion Exchange Resins. The colloidal anion exchange resins are discrete, spherical polymer particles less than 100 nm in diameter, with quaternary ammonium sites. They were prepared via two-stage process. In the first stage, emulsion polymerization of mixtures of chloromethylstyrenes, styrene and divinylbenzene in various proportions, initiated by potassium persulfate and sodium bisulfite, gave latexes containing chlorobenzyl moieties in polymer chains crosslinked with divinylbenzene (**68**) (Scheme I; eq. 6). The hydrophobic colloidal polymers were charge-stabilized by either anionic sodium dodecylsulfate (SDS) or cationic hexadecyltrimethyl-ammonium bromide (CTAB) surfactant. In the second stage, trimethylamine treatment converted most of the chloromethyl groups into quaternary ammonium chloride latexes (**69**) (Scheme I; eq. 7), which were highly hydrophilic.

The moles of quaternary ammonium cationic sites created by eq. 7 always exceeded the moles of surfactant used in the polymerization (Table VIII). Anionic sodium dodecylsulfate (SDS) and cationic hexadecyltrimethylammonium bromide (CTAB) surfactants used in the polymerization were less than 3% of vinylbenzyl chloride, except in L-9 where CTAB was 14.4% of vinylbenzyl chloride because of low vinylbenzyl chloride content, and the number of anionic $-SO_4^-$ end groups of polymer chains from the initiator was much less than the number moles of surfactant in latexes, so the latexes were always stabilized by net positive charge. The hydrophilic particles do not dissolve or lose their spherical shape due to crosslinking, but they are swollen by water and other polar solvents. Although the swelling ratios (swollen particle diameter/dry copolymer diameter) of colloidal anion exchange resins were not measured, 1% and 5% crosslinked 16-400 mesh anion exchange resins have 1.9 and 1.3 swelling ratios in water respectively.[159] Divinylbenzene contents of 1% and 5% gave different latexes capable of different swelling ratios in good solvents for the polymers. Quaternary ammonium sites created from chloromethylstyrene moieties in **68** of 19% and 91-98% gave greatly different charge densities of the ion exchange latexes **69**. The number of quaternary ammonium sites, as percent of polymer repeat units, of every stable latex was determined by analysis of the chloride ion content with the Volhard method and by determination of the solid content of every latex. The percent ring substitution was 61-87%, except L-9 which had only 21% quaternary sites due to low vinylbenzyl chloride content (Table VIII). Initially latex particles were precipitated for storage purposes. However, the 19% quaternary ammonium chloride dried copolymers could not be redispersed in water. From then on, all polymers were kept as aqueous latexes. The polymers in Table VIII are stable colloids and their ion exchange capacities, solid contents, and average particle sizes were determined. Average particle sizes between 54 and 81 nm were determined from transmission electron micrographs. Figure 11 shows (a) latex 1, (b) Co(II) phthalocyaninetetrasulfonate bound latex 1. Latexes which were not stable even after trimethylamine treatment were discarded.

Preparation of Cobalt(II) Phthalocyaninetetra(sodium sulfonate) (38). The preparations of a mixture of isomers of phthalocyanine **38** and some other metallophthalocyaninetetra(sodium sulfonates) were reported by Weber.[112]

Scheme I. Preparation of Colloidal Cation Exchange Resins



Preparation of Latex-Bound Cobalt(II) Phthalocyaninetetrasulfonate [39a, Co(II)PcTs(NR_4)$_4$] Catalyst. Each ion exchange latex **69** was exposed to various amounts of soluble phthalocyanine **38**. Ultrafiltration of the latex through a 0.1-μm cellulose acetate/nitrate membrane gave colorless filtrate and retained blue latex from each sample as long as no more than one phthalocyanine **38** was added per four ammonium ion sites in the latex. The absence of detectable phthalocyanine **38** in the external water proves that cobalt(II) phthalocyaninetetrasulfonate was completely bound to the latexes. When 0.22-μm cellulose acetate/nitrate membrane was used, some of the latex particles passed through the membrane. In addition, the minimum ratio of trimethylbenzylammonium to phthalocyanine **38** that gave complete binding of blue phthalocyanine to the latexes was determined quantitatively by using a UV/visible spectrophotometer.

Table VIII. Ion Exchange Latexes and Co(II) Phthalocyanine(tetrasodium sulfonate) (**38**) Catalysts

	latex composition[a]							% solids	$R_4N^+Cl^-$,[b]	loading,[c]	diam.[d]
latex	DVB,	EVB,	S,	VBC,[e]	$R_4N^+Cl^-$	surfactant[f]		in water,	meq/g	N^+/CoPcTs	nm
	mol%	mol%	mol%	mol%		type	mol %	w/w			
L-1	4.9	3.9	-	30 (91.2)	61	SDS	2.48	solid	3.3	3.30	54
L-3	1.0	0.8	-	11 (98.2)	87	SDS	2.46	4.6	4.3	2.79	74
L-6	4.8	3.9	-	10 (91.3)	81	CTAB	2.50	9.4	4.1	3.59	55
L-8	1.0	0.8	-	13 (98.2)	85	CTAB	2.71	4.8	4.2	2.77	59
L-9	1.0	0.8	79.4	0 (18.8)	21[g]	CTAB	2.57	8.4	1.7	2.71	60
L-10	1.0	0.8	-	22 (98.2)	76	SDS	2.34	4.0	3.8	-	67
L-12	1.0	0.8	-	23 (98.2)	75	CTAB	2.04	3.8	3.8	-	81[h]

[a] DVB: divinylbenzenes (55% technical grade), EVB: ethylvinylbenzenes, S: styrene, and VBC: chloromethylstyrenes (70/30 m/p) in the latex assuming complete polymerization. Initiator was $K_2S_2O_8$-$NaHSO_3$. [b] Milliequivalent of $R_4N^+Cl^-$ per g of polymer. [$R = Cl^-(CH_3)_3N^+$-$CH_2(C_6H_4)$-]. [c] Minimum ratio of trimethylbenzylammonium to Co(II)PcTs achieved in latex was determined spectrophotometrically. [d] Diameters of 50 particles were measured from transmission electron micrographs to calculate the number average particle diameter. [e] The numbers in parentheses are the mol% of VBC before trimethylamine treatment. [f] SDS: sodium dodecylsulfate, CTAB: hexadecyltrimethylammonium bromide; mol% is relative to the total number of moles of monomers. [g] Complete conversion to ammonium ions within error of measurement. [h] Diameters of 10 particles were used to determine particle size.

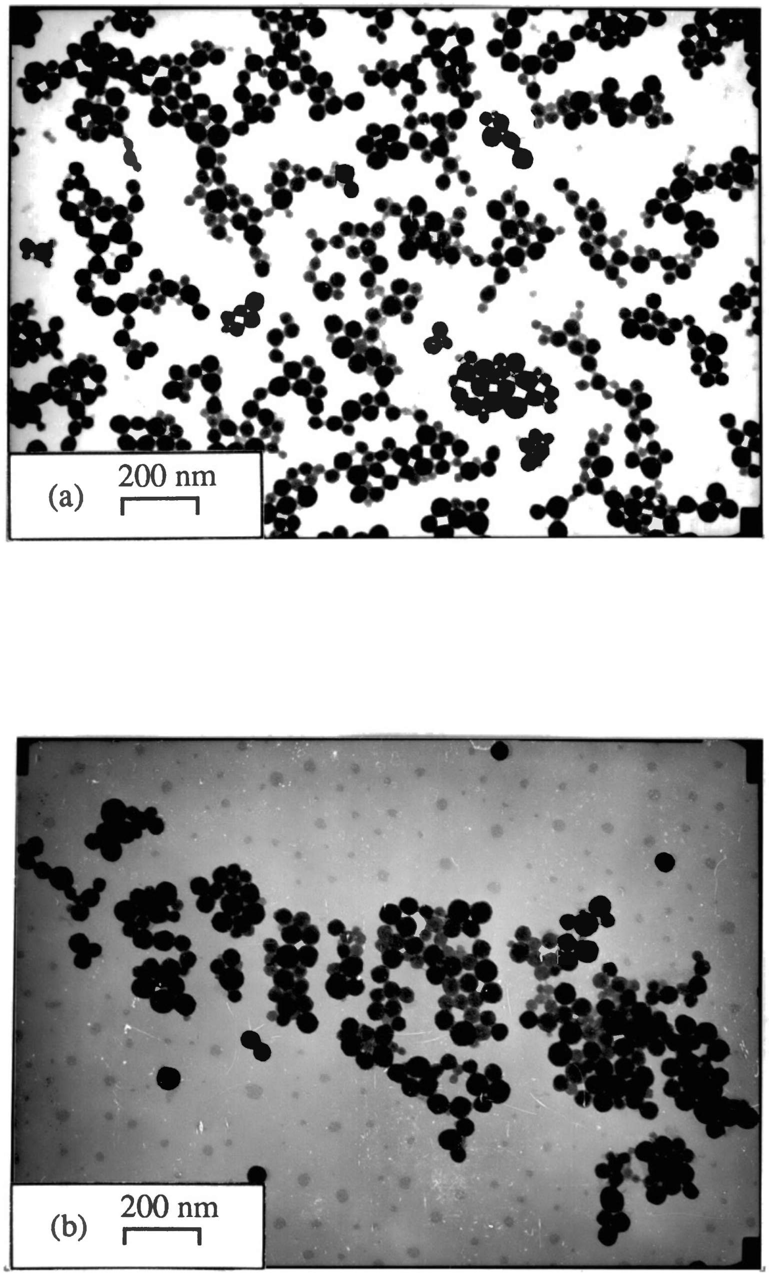


Figure 11. Transmission electron micrographs of (a), latex **1** and (b), cobalt(II) phthalocyanine bound latex **1**.

Autoxidation of 2,6-Di-*tert*-Butylphenol (7). The activities of soluble phthalocyanine **38** and latex-bound phthalocyanine **39a** in water were tested for the autoxidations of 2,6-di-*tert*-butylphenol (**7**) and 2,6-dimethylphenol (**12**). In some cases, a small amount methanol was used to introduce the substrate into the reaction mixture. Autoxidations of phenol **7** were performed under about 0.9 atm pressure of dioxygen. With all latex-bound phthalocyanine **39a** catalysts except L-9, the only product was 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenoquinone (**2a**). With soluble phthalocyanine **38** as catalyst, small amounts of 2,6-di-*tert*-butyl-1,4-benzoquinone (**1a**) were formed also. In the initial experiments the autoxidation reactions were carried out for a certain time, stopped, and worked up. The extents of the reaction and product distributions were determined quantitatively by GLC. The reaction rate depended on temperature, pH, oxygen pressure, method of mixing, and method of introduction of the phenol **7** to the mixture.

Results in Table IX show that the phthalocyanine bound to colloidal quaternary ammonium exchange resins (**39a**) gave faster oxidation rates than the soluble phthalocyanine **38** analogue with magnetic stirring (expts 6 and 7) and with shaking (expts 1 and 10). A platform shaker having an amplitude of 2.5 cm and a frequency of about 1 s^{-1} was used to shake some of the reaction mixtures. Others were stirred rapidly with a magnetic bar. The shaking mixes more vigorously and efficiently than the stirring. The presence of 0.1 volume fraction methanol enhanced the rate of oxidation, assuming zero-order kinetics, by factors of two (expts 1 and 3) to eight (expts 7 and 8) with soluble catalyst and by a factor of two with latex-bound catalyst (expts 6 and 9). Shaking gave faster rates than stirring with colloidal catalyst (expts 6 and 10) but not with soluble catalyst (expts 8 and 23).

Table IX. Autoxidation of 2,6-Di-*tert*-butylphenol (**7**) with Cobalt(II) Phthalocyaninetetrasulfonate Catalysts[a,b]

expt.	catalyst	CH_3OH vol. fr.	mixing method	time, h	% conv.[c]
1[d,e]	soluble	0.0	shaking	24	35[d]
3[e]	soluble	0.1	shaking	24	66[d]
6[d]	C-1	0.0	stirring	6	60
7	soluble	0.0	stirring	6	6
8	soluble	0.1	stirring	6	45
23	soluble	0.1	shaking	6	30
9	C-1	0.1	stirring	6	100
10	C-1	0.0	shaking	6	100

[a] All experiments, unless otherwise given in Table and footnotes, were carried out at 69.0 ± 0.2 °C with 1.20 ± 0.01 mmol of phenol **7**, $6.04 \pm 0.02 \times 10^{-2}$ mmol (5 mol %) of phthalocyanine **38** at pH 9.0 buffered with 4.4 mmol of AMPSO. The reaction mixtures had a volume of 150 mL and were carried out at 700 ± 20 mmHg pressure of dioxygen. The latex bound catalyst (C-1) was prepared by sonication of phthalocyanine **38** with a dispersion of 123 mg of L-1 in Table VIII. [b] Phenol **7** was mixed with the catalyst mixture at room temperature. Reaction temperature was recorded at the time the substrate-catalyst mixture was immersed in the oil bath. [c] Percent of phenol **7** consumed according to GLC analysis. Diphenoquinone **2a** was the only product unless otherwise stated. Estimated error is ± 5%. [d] pH was 9.1. [e] 3-4% yield of quinone **1a** was found in addition to diphenoquinone **2a**.

Data in Table X show the pH (expts. 11, 14, 16, 18, and 20) and temperature (expts. 11,13,14, and 15) dependence of the autoxidation of phenol **7** with colloidal catalyst C-1. The oxidation rates increased with increasing pH in the 7-10 range. The activities of catalysts prepared from five different latexes were similar, showing 77-92% oxidation of **7** under identical conditions (expts. 14, 21, 22, 24, and 25).

Table X. pH and Temperature Dependences of Autoxidation of 2,6-Di-*tert*-Butylphenol (**7**) Using Colloidal Catalysts (**39a**)[a]

expt.	catalyst[b]	pH	temp.,[c] °C	time, min.	% conv.
11	C-1	9.0	69.0	120	100
13	C-1	9.0	24 0	120	16
14	C-1	9.0	69.0	80	79
15	C-1	9.0	49.3	120	50
16	C-1	7.0[d]	69.0	80	17
17[e]	C-1	9.0	69.0	120	55
18	C-1	8.0[f]	69.0	120	31
20	C-1	10.0[g]	69.0	80	100
21	C-3	9.0	69.0	80	83
22	C-6	9.0	69.0	80	77
24	C-8	9.0	69.0	80	92
25	C-9	9.0	69.0	80	87

[a] For conditions see Table IX, footnotes *a-c*. [b] C-1, C-3, C-6, C-8, and C-9 catalysts were prepared by sonication of phthalocyanine **38** with dispersions of L-1 (123 mg polymer), L-3 (143 mg polymer), L-6 (131 mg polymer), L-8 (134 mg polymer), and L-9 (243 mg polymer) latexes in Table VIII respectively. [c] ± 0.2 °C. [d] Buffer was ACES (4.4 mmol). [e] Reaction was run under air with a partial pressure of dioxygen of 150 mmHg. [f] Buffer was TAPS (4.4 mmol). [g] Buffer was CAPS (4.4 mmol).

There was a decrease in the activity of latex-bound phthalocyanine **39a** catalyst when the phthalocyanine concentration was lowered from 5 mol % to 1 mol % of phenol **7** keeping the latex concentration constant (expts. 14 and 26, Table XI). When the latex concentration was lowered relative to that of phthalocyanine, further decrease in the activity was observed (expt. 27). When the phthalocyanine substrate ratio was kept at 0.05 as in expt. 14, and the latex concentration was increased 5 times, there was not much change in the conversion of phenol **7** (expt. 35).

Table XI. The Effect of Latex and Cobalt(II) Phthalocyaninetetrasulfonate Concentrations on Autoxidation of 2,6-Di-*tert*-Butylphenol (**7**)[a]

expt.	latex, mg	[Co(II)PcTs] x 10^4, M	time, min	% conv.
14	123	4.03	80	79
26	123	0.81	80	41
27	25	0.80	80	33
35[b]	616	4.02	60	73

[a] For conditions see Table IX, footnotes *a-c*. [b] Phenol **7** was injected into the catalyst mixture at 69.0 ± 0.2 °C and reaction time was recorded from the injection of phenol **7**.

Also high concentrations of phenol **7** in the reaction mixtures gave lower conversions than lower concentrations (Table XII). This may be due to a smaller amount of dioxygen relative to phenol **7** in the reaction mixtures, or to slow mass transfer of dioxygen from the gas phase to the reaction mixtures.

Addition of H_2O_2 to the reaction mixture had little effect on the rate of oxidation of phenol **7**. Under nitrogen atmosphere in the presence of H_2O_2 very little phenol **7** was oxidized (expt. 42, Table XIII).

Table XII. The Effect of Latex, Catalyst, and Substrate Concentrations on Autoxidation of 2,6-Di-*tert*-Butylphenol (7)[a]

expt.	[latex] mg/L	[Co(II)PcTs] $\times 10^4$, M	[DBP] $\times 10^3$, M	[buffer] $\times 10^2$, M	volume of react. mixt., mL	mixing method	% conv.	turnover mol product/ mol catalyst
28	821	4.03	8.07	2.93	150	stirring	70	14
30[b]	3400	16.69	33.43	12.15	36	stirring	47	9
31[b]	3400	16.69	33.43	12.15	36	shaking	53	11
32	820	4.03	8.07	2.93	150	shaking	76	15
33[b]	1230	6.04	12.10	4.40	100	shaking	76	15
35[b]	4109	4.02	8.07	2.93	150	shaking	73	15
36[b]	3408	16.66	33.43	2.93	36	shaking	49	10

[a] For conditions see Table IX, footnotes *a-c*. [b] For condition see Table XI, footnote *b*.

Table XIII. The Effect of H_2O_2 on the Catalytic Activity of Latex-Bound Cobalt(II) Phthalocyaninetetrasulfonate (**39a**) Catalyst for Autoxidation of 2,6-Di-*tert*-Butylphenol (7)[a]

expt.	$[H_2O_2]$,[b] mM	$[H_2O_2]$/[DBP]	% conv.
32	-	-	76
33[c,d]	-	-	76
40[c]	4.03	0.5	74
42[c,e]	4.03	0.5	9

[a] For conditions see Table IX, footnotes *a-c*. Reaction times were 60 min. [b] H_2O_2 solution was injected into the catalyst mixture at 69.0 ± 0.2 °C before phenol 7 was injected. [c] For condition see Table XI, footnote *b*. [d] The volume was 100 mL. [e] Reaction was run under nitrogen atmosphere.

Addition of a good ligand for Co(II) phthalocyaninetetrasulfonate to the reaction mixture did not alter the catalytic activity. When 2 moles of pyridine or imidazole per mole of phthalocyanine were used, a slight decrease in the conversion was observed (Table XIV).

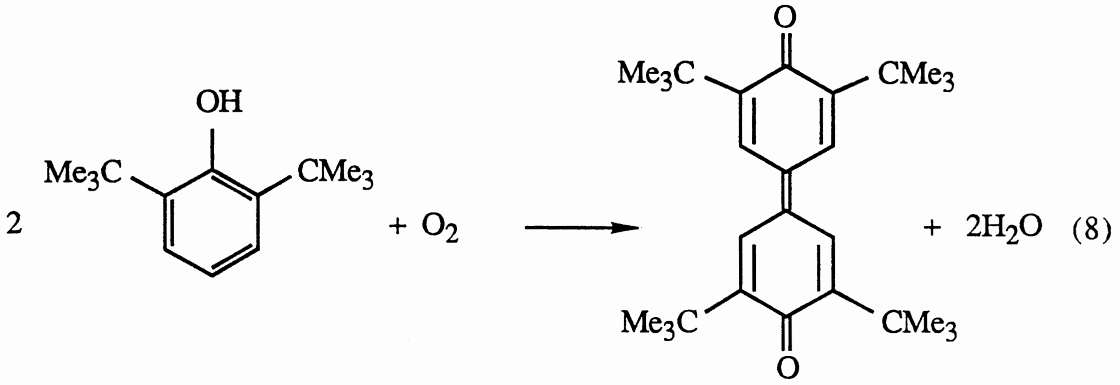
Table XIV. The Ligand Effect on the Catalytic Activity of Cobalt(II) Phthalocyaninetetrasulfonate-Bound Latex Catalyst for Autoxidation of 2,6-Di-*tert*-Butylphenol (**7**)[a]

expt.	ligand	[ligand] x 10^4, M	[ligand]/ [Co(II)PcTs]	% conv.
32	-	-	-	76
33[b,c]	-	-	-	76
37[b]	pyridine	4.01	1: 1	78
39[b,d]	pyridine	8.00	2: 1	64
41[b,e]	imidazole	8.00	2: 1	63

[a] For conditions see Table IX, footnotes *a-c*. Reaction times were 60 min. [b] For condition see Table XI, footnote *b*. [c] The volume was 100 mL. [d] Phthalocyanine **38** and pyridine were stirred for 18 h before addition of the latex. [e] Phthalocyanine **38** and imidazole were stirred for 10 h before addition of the latex.

The latex 8 (L-8) in Table VIII was ultrafiltered through a 0.1 μm cellulose acetate/nitrate membrane to remove water-soluble surfactant and salts in latex until the conductivity of the latex dropped from 1360 x 10^{-6} ohm^{-1} cm^{-1} to 220 x 10^{-6} ohm^{-1} cm^{-1}. The purified latex was used to bind phthalocyanine **38**, and the catalyst obtained was used in the autoxidation of phenol **7**. The reaction gave 88% conversion in 80 min. When unpurified latex-bound Co(II) phthalocyaninetetrasulfonate was used, the conversion was 100% in 80 min under similar reaction conditions.

Kinetics of Autoxidation of 2,6-Di-*tert*-Butylphenol (7). Gas buret measurements of dioxygen consumption were used to follow kinetics of autoxidation of phenol **7** catalyzed by Co(II) phthalocyaninetetra(sodium sulfonate) (**38**) and latex-bound Co(II) phthalocyaninetetrasulfonate (**39a**). The oxygen uptake profiles showed an induction period, and then the rate of dioxygen consumption was linear with time to about 70% conversion of the phenol **7** to diphenoquinone **2a**. The slopes of the profiles of duplicate and triplicate experiments were reproduced within ± 20%. Therefore the rate law has a zero-order dependence on substrate concentration. The rate of the autoxidation of the phenol **7** depended on temperature, pH, oxygen pressure, and catalyst concentration. From oxygen uptake measurements and formation of only one product, the stoichiometry of the autoxidation of phenol **7** was established: one half mole of dioxygen is required per mole of phenol **7** (eq. 8).



Effect of the Concentration of Latex-Bound Phthalocyanine 39a: The factors such as catalyst and latex concentrations that affect the rate of the autoxidation of phenol **7** were investigated to find what extent they limit the reaction. First the concentration of phthalocyanine was varied systematically while the amounts of latex (L-3 in Table VIII) and phenol **7** were kept constant. As shown in Figure 12; 5 mol % homogeneous catalyst phthalocyanine **38** based on phenol **7** gave a slower rate than all latex-bound phthalocyanine **39a** catalysts (0.5-6.4 mol %). The most active latex contained 5 mol % phthalocyanine based on phenol **7**, which corresponds with 47% of the quaternary ammonium sites of the latex used to bind phthalocyanine. Higher and lower catalyst loadings gave slower rates. In experiments not shown in Figure 12, 0.1 mol % latex-bound phthalocyanine **39a** based on phenol **7** in 193 min gave only 14% of the diphenoquinone **2a** (0.085 mmol dioxygen), and 8 mol % catalyst loading (use of about 75% of quaternary ammonium sites of the latex) caused coagulation of the latex as the reaction progressed and a slower autoxidation rate than 3, 5, and 6.4 mol % catalyst loadings.

Effect of Temperature on the Autoxidation of 2,6-Di-*tert*-butylphenol (7): Autoxidation proceeded at a reasonable rate at 69.0 °C. As the temperature was lowered, the reaction became slower (Figure 13). The Arrhenius plot (Figure 14) obtained from the zero-order rate constants was linear, and the activation energy (E_a) of the reaction was 64.9 kJ/mol.

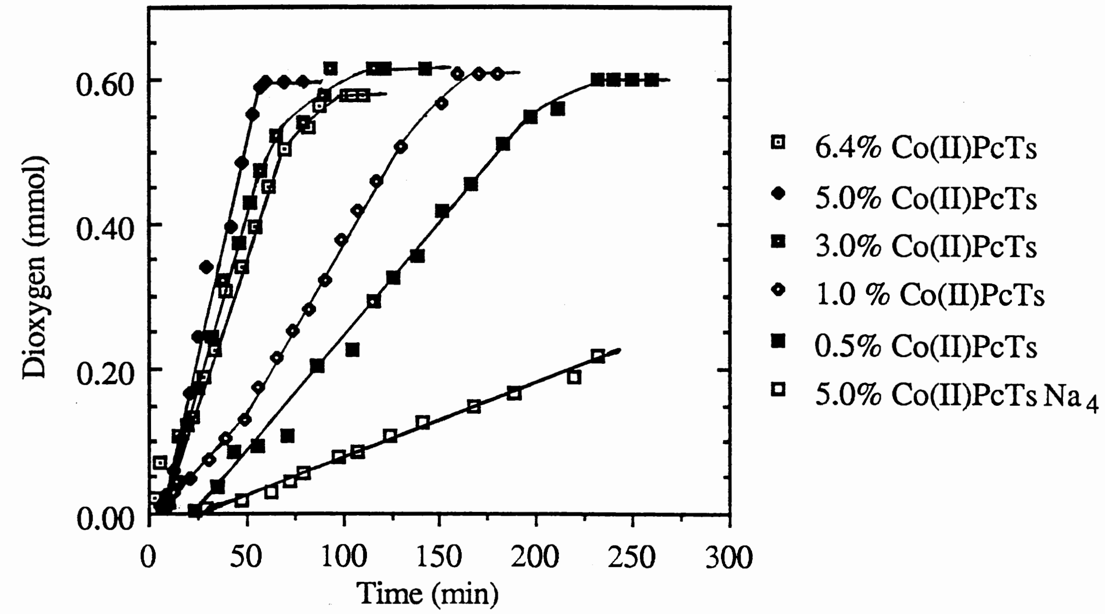


Figure 12. Dioxygen consumption with time during autoxidation of 2,6-di-*tert*-butylphenol (**7**) catalyzed by latex-bound phthalocyanine **39a** and by soluble phthalocyanine **38**. The catalyst percentages shown on the right side of the plot are mol % based on the amount of substrate. All kinetic experiments, unless otherwise stated, were carried out in water at 69.0 ± 0.2 °C with 1.20 ± 0.01 mmol of phenol **7**, 6.04 ± 0.02 x 10^{-2} mmol of phthalocyanine **38** at pH 9.0 buffered with 3.0 x 10^{-2} M sodium borate. The reaction mixtures had a volume of 100 mL including 1 mL methanol solution of phenol **7** and were carried out with mechanical shaking under 700 ± 10 mmHg pressure of dioxygen. Phenol **7** was injected into the catalyst mixture at 69.0 ± 0.2 °C, and reaction times were recorded from the time of injection of phenol **7**. The latex-bound catalysts were prepared by sonication of phthalocyanine **38** with a dispersion of 120 mg of polymer in Table VIII. The latex used was L-3 in Table VIII.

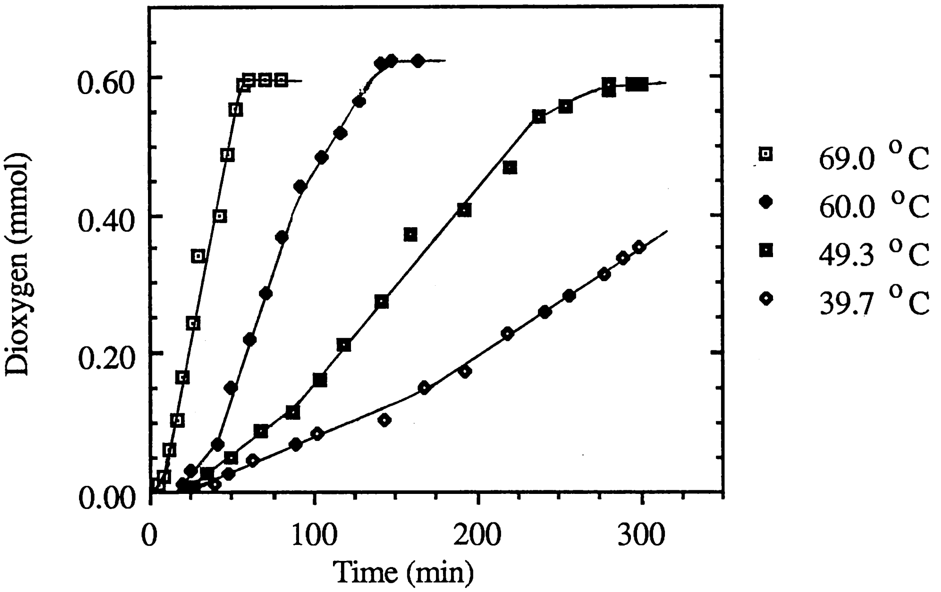


Figure 13. Dependence of autoxidation of 2,6-di-*tert*-butylphenol (7) on temperature. For conditions, see the legend of Figure 12.

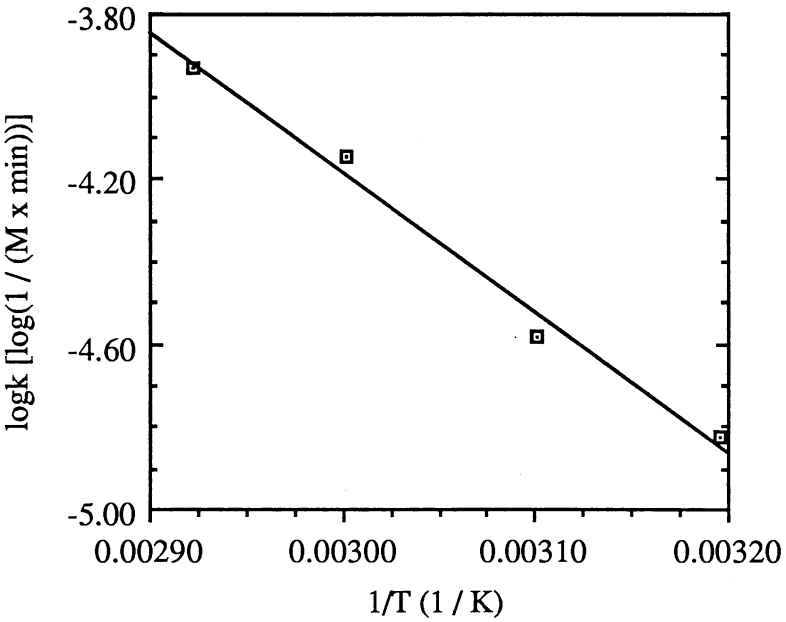


Figure 14. The Arrhenius plot of rate data at 39.7-69.0 °C under the conditions given in Figure 13.

Effect of pH on the autoxidation of 2,6-di-*tert*-butylphenol (7) (Figure 15): The plot of zero-order rate constants of several autoxidations with different latexes, catalyst loadings, and under varied dioxygen pressure vs. pH showed an increase on the rate constants between pH 7.0 and 10.0 (Figure 16).

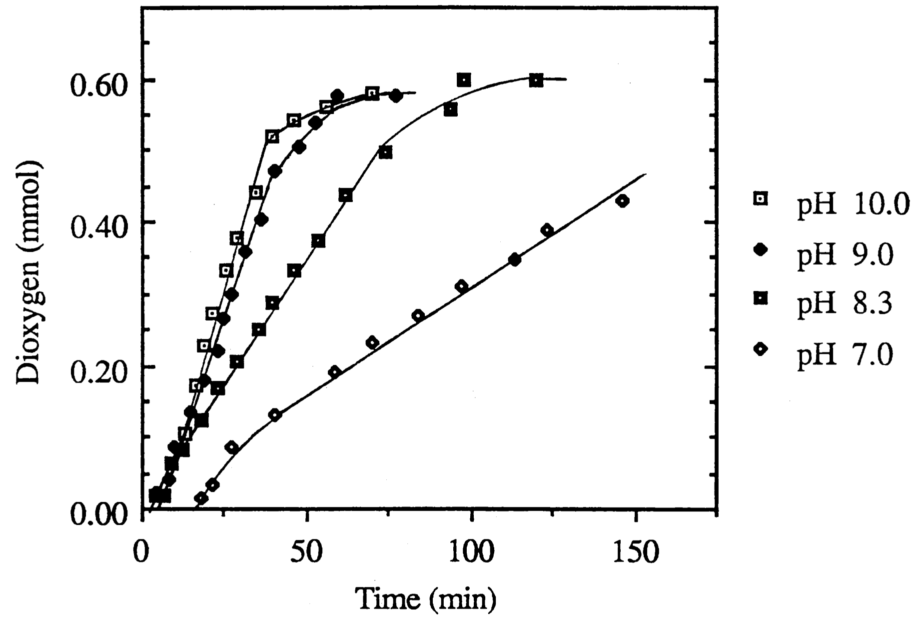


Figure 15. Dependence of autoxidation of 2,6-di-*tert*-butylphenol (7) on pH. For conditions, see the legend of Figure 12. Latex used was L-8 in Table VIII. The pH 7.0 reaction was buffered with 3.0 x 10^{-2} M potassium dihydrogen phosphate.

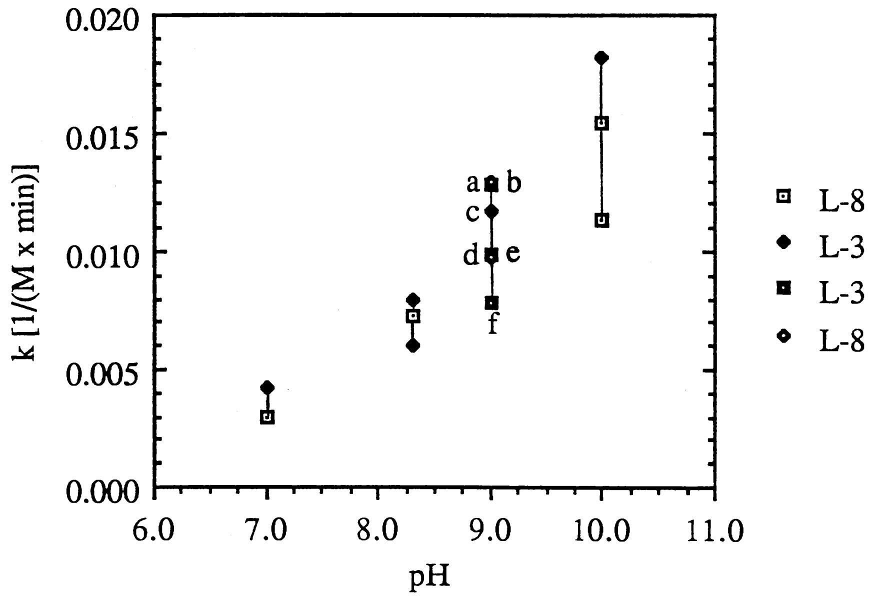


Figure 16. Rate constants of the autoxidation of 2,6-di-*tert*-butylphenol (7) vs. pH (as shown on the right side of the plot, the data points are from the pH experiments carried out with latex 3 (L-3) and latex 8 (L-8). pH 9.0 experiments: (a), L-8, 5% catalyst and 690 mmHg dioxygen; (b), L-8, 5% catalyst and 508 mmHg dioxygen; (c), L-3, 5% catalyst and 704 mmHg dioxygen; (d), L-8, 5% catalyst and 342 mmHg dioxygen; (e), L-3, 3% catalyst and 702 mmHg dioxygen; (f), L-3, 6.4% catalyst asnd 696 mmHg dioxygen).

Reactions under 342-690 mmHg partial pressure of dioxygen under 690 ± 5 mmHg of dinitrogen-dioxygen did not depend on oxygen content, but the rate at 145 mmHg of dioxygen was slower (Figure 17).

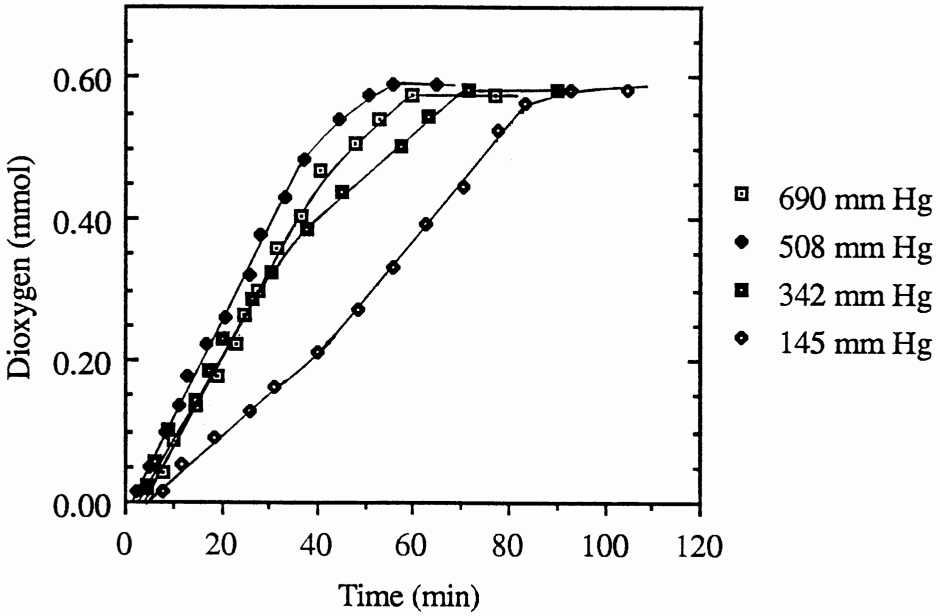


Figure 17. Dependence of autoxidation of 2,6-di-*tert*-butylphenol (**7**) on partial pressure of dioxygen. For conditions, see the legend of Figure 12. The latex used was L-8 in Table VIII.

The latex bound catalyst loses its activity gradually after additions of fresh batches of the phenol **7** to the reaction mixture (Figure 18).

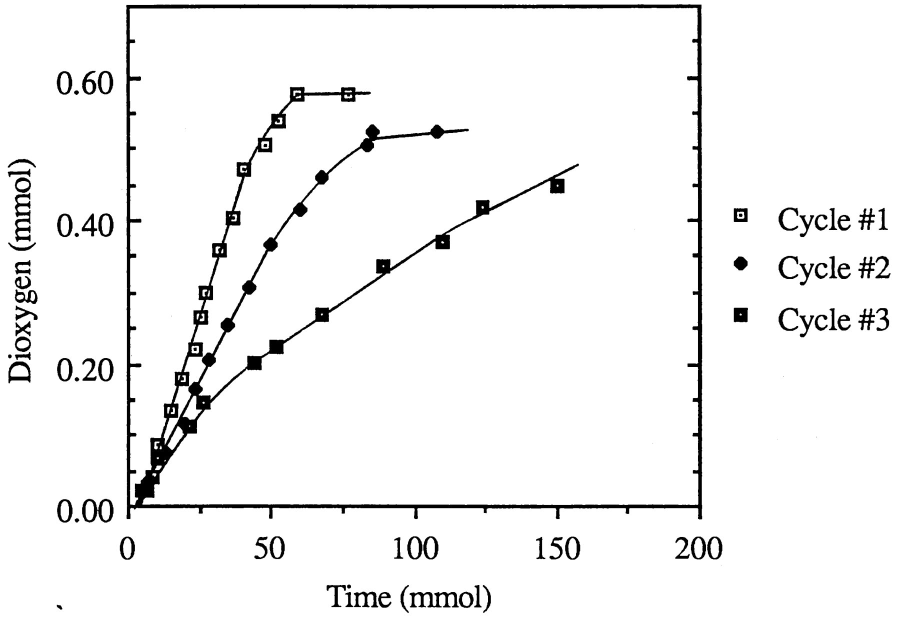


Figure 18. Recycle of latex-bound Co(II) phthalocyaninetetrasulfonate (**39a**): For conditions, see the legend of Figure 12. The volume was 100-102 mL. Latex used was L-8 in Table VIII. Dioxygen pressure was 690 ± 5 mmHg. Cycle #1: 1.20 mmol phenol **7** in 1 mL solution of methanol was added via a syringe. Cycle #2: 1.20 mmol phenol **7** in 1 mL solution of methanol was added 90 min after the first addtion of phenol **7**. Cycle #3: 1.20 mmol phenol **7** in 1 mL solution of methanol was added 20 h after the second addition of phenol **7**. [Note: After the data of Cycle #2 was collected, the reaction mixture was cooled to room temperature and reheated to 69.0 ± 0.2 °C before addition of the 3rd batch of phenol **7**.

Visible Spectrophotometry of Aqueous Co(II) Phthalocyaninetetra-(sodium sulfonate) (38) and Latex-Bound Co(II) Phthalocyaninetetra-sulfonate (39a). Absorption spectra of the aqueous phthalocyanine **38** and latex-bound phthalocyanine **39a** were obtained in the presence and absence of dioxygen and substrate with varying temperature. The absorption bands of the monomeric and dimeric phthalocyanine **38** occur at λ_{max} 663 nm and 626 nm respectively.[115] The dimerization equilibrium of phthalocyanine **38** in water (eq. 9) is affected by the ionic strength and pH (Figure 19).

$$2\ Co(II)PcTs^{-4} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(II)PcTs^{-4}]_2 \qquad (9)$$

In pure water, the monomeric form of 9.98 x 10^{-6} M phthalocyanine **38** at λ_{max} 666 nm dominates the spectrum without any added salt (elemental analysis shows about 0.1 mol residual Cl per mol of phthalocyanine **38**). At pH 11.1, there was increase in the amount of dimer. However the presence of 3.0 x 10^{-2} M NaCl in phthalocyanine **38** solution enhanced the formation of dimer at pH 7.0 and caused total domination of dimer at pH 11.1. The spectrum of phthalocyanine **38** solution at pH 9.0 buffered with 3.0 x 10^{-2} M sodium borate (the conditions of most catalysis experiments) was identical to the one obtained at pH 11.1 in the presence of 3.0 x 10^{-2} M NaCl (Figure 19).

Under dioxygen free (argon saturated) conditions, spectra of phthalocyanine **38** at pH 9.0 buffered with 3.0 x 10^{-2} M sodium borate in the absence and presence of various amount of benzyltrimethylammonium chloride latexes were obtained at 30 °C (Figure 20). The solution of phthalocyanine **38** was mostly in dimeric form (λ_{max} 626 nm), and addition of a latex containing benzyltrimethylammonium chloride groups converted some of phthalocyanine **38** to the monomeric form (λ_{max} 670 nm). As the amount of latex increased, meaning that the N^+/Co(II)PcTs-ratio increased, more monomeric and less dimeric phthalocyanine **38** were present (Figure 20).

Absorption spectra of a dioxygen free latex-bound phthalocyanine **39a** sample were taken at pH 9.0 buffered with sodium borate at 30-70 °C (Figure 21). As the temperature increased, the λ_{max} of the monomer shifted toward lower wavelength and the shoulder of the dimer almost disappeared at 70 °C. The same type of experiment with homogeneous phthalocyanine **38** also showed a decrease in the fraction of dimeric Co complex with increasing temperature.

Dioxygen saturated solutions of homogeneous phthalocyanine **38** and latex-bound phthalocyanine **39a** buffered with sodium borate at 30-70 °C had almost the same spectra (not shown) as the argon saturated solutions. However there was slight change on the shoulder or peak of dimeric phthalocyanine as the temperature increased. As in the dioxygen free case, more monomeric phthalocyanine formed when the temperature went up. However there was no evidence of spectral changes due to oxygen.

These oxygen saturated homogeneous phthalocyanine **38** and latex-bound phthalocyanine **39a** solutions at 70 °C were cooled to room temperature and their absorption spectra were taken after 18 h. The spectrum of homogeneous phthalocyanine **38** was similar to the one taken at 30 °C previously. But the latex-bound phthalocyanine **39a** gave a spectrum similar (with a very slight appearance of the dimer shoulder) to the one taken at 70 °C and did not return to the starting spectrum at 30 °C.

The absorption spectra of latex-bound phthalocyanine **39a** samples taken from the reaction flask during the autoxidation of phenol **7** were similar to that of latex-bound phthalocyanine **39a** taken in the absence of phenol **7** under both inert and dioxygen atmospheres (Figure 22). However the sample taken during the first minute of the autoxidation of phenol **7** catalyzed by latex-bound phthalocyanine **39a** showed the presence of the diphenoquinone **2a** at 360-470 nm (Figure 22). A methanol solution of diphenoquinone **2a** gives a λ_{max} at 411 nm.

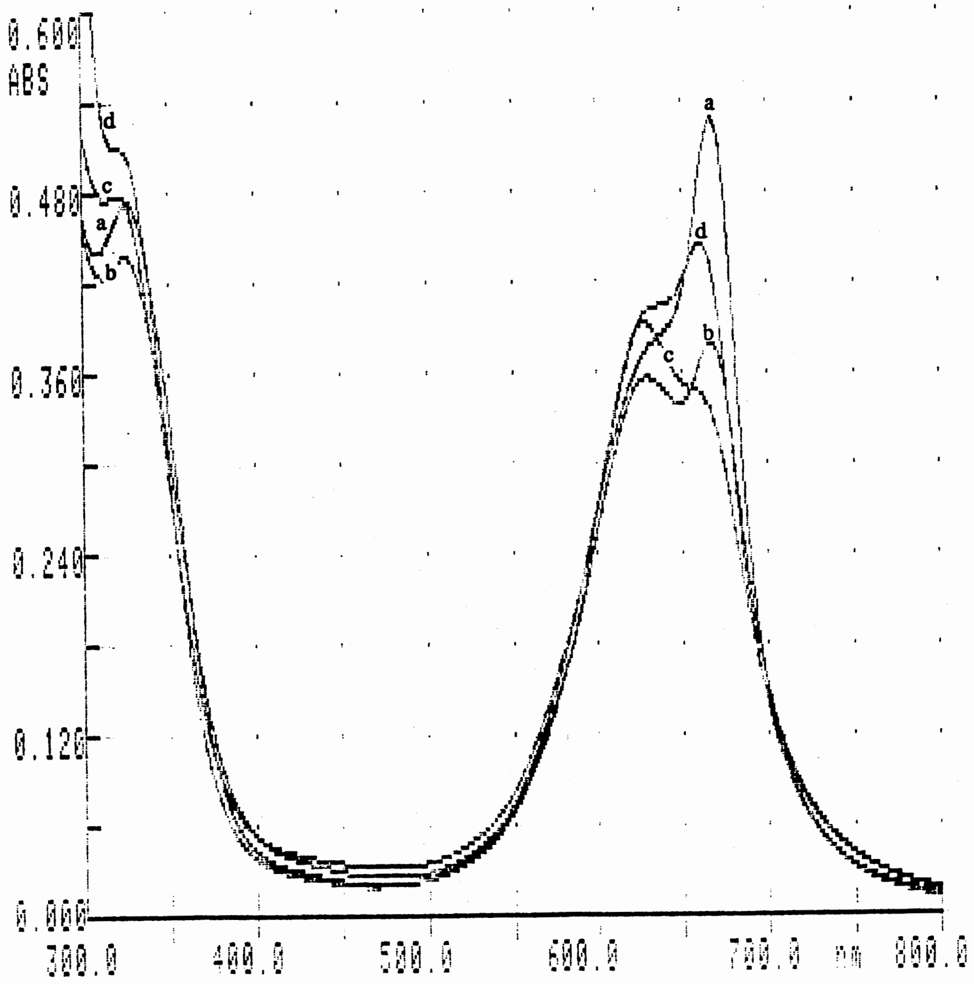


Figure 19. Absorption spectra of 9.98 x 10^{-6} M phthalocyanine **38**. (a), in pure water (λ_{max} 666 nm, ε 5.28 x 10^4 M^{-1} cm^{-1}); (b), in 3.0 x 10^{-2} M NaCl at pH 7.0 (λ_{max} 665 nm, ε 3.79 x 10^4 M^{-1} cm^{-1}; λ_{max} 628 nm, ε 3.56 x 10^4 M^{-1} cm^{-1}); (c), in 3.0 x 10^{-2} M NaCl at pH 11.1 (λ_{max} 627 nm, ε 3.93 x 10^4 M^{-1} cm^{-1}); (d), at pH 11.1 (λ_{max} 659 nm, ε 4.45 x 10^4 M^{-1} cm^{-1}).

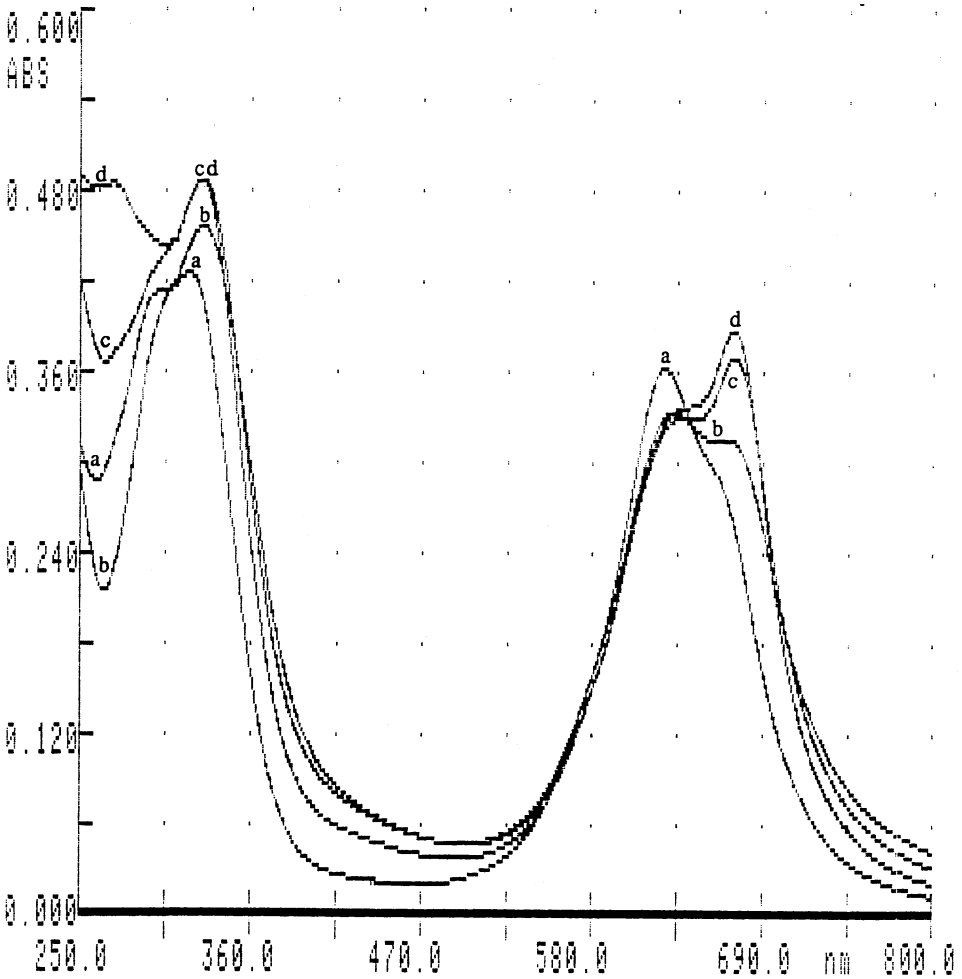


Figure 20. Absorption spectra of 9.98 x 10^{-6} M phthalocyanine **38** in the presence of various amount of latex (L-8, Table VIII) at 30.0 ± 0.1 °C and pH of 9.0 buffered with 3.0 x 10^{-2} M sodium borate. (a), Homogeneous (no latex) (λ_{max} 626 nm, ε 3.63 x 10^4 M^{-1} cm^{-1}); (b), 0.009 mg latex per mL (λ_{max} 630 nm, ε 3.33 x 10^4 M^{-1} cm^{-1}); (c), 0.020 mg latex per mL (λ_{max} 670 nm, ε 3.69 x 10^4 M^{-1} cm^{-1}); (d), 0.056 mg latex per mL (λ_{max} 669 nm, ε 3.88 x 10^4 M^{-1} cm^{-1}).

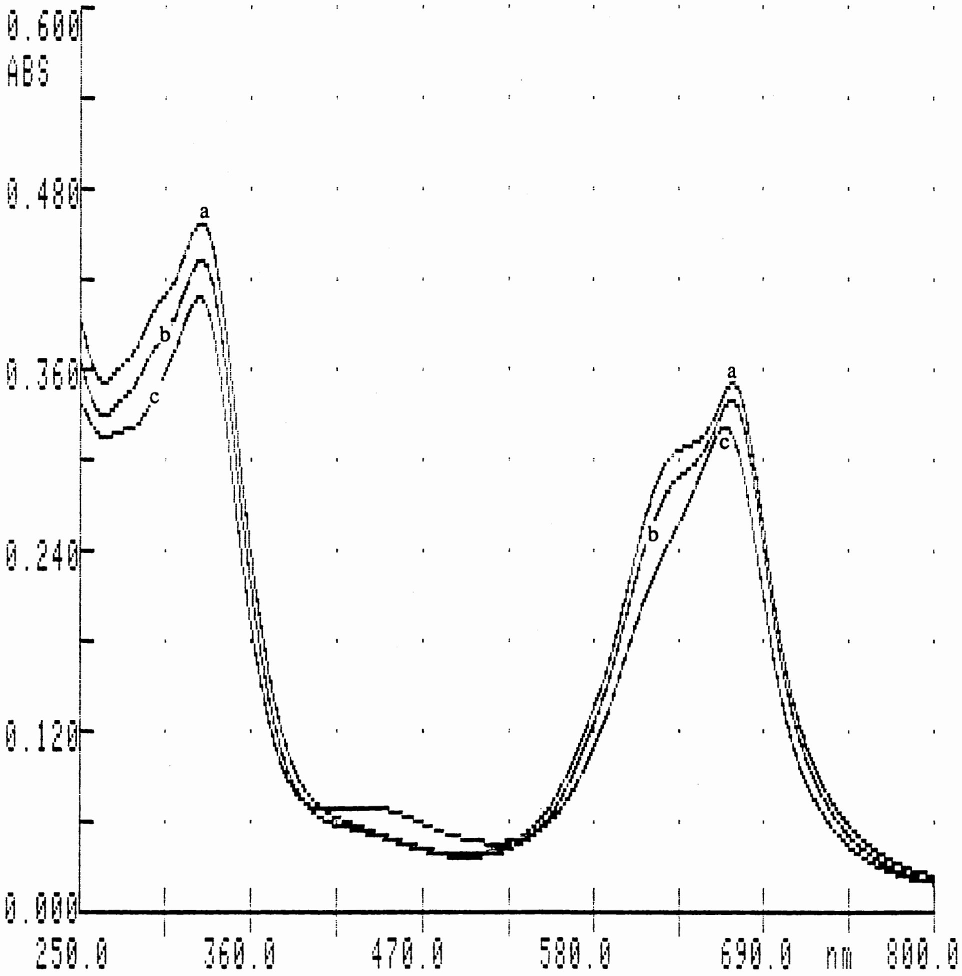


Figure 21. Absorption spectra of latex (0.020 mg mL^{-1}) bound phthalocyanine **39a** (9.98×10^{-6} M) at various temperatures under inert atmosphere. The solutions had a pH of 9.0 and were buffered with 3.0×10^{-2} M sodium borate. (a), 30.0 ± 0.1 °C (λ_{max} 669 nm, ε 3.50×10^4 M^{-1} cm^{-1}); (b), 48.0 ± 0.1 °C (λ_{max} 668 nm, ε 3.39×10^4 M^{-1} cm^{-1}); (c), 70.0 ± 0.1 °C (λ_{max} 664 nm, ε 3.21×10^4 M^{-1} cm^{-1}).

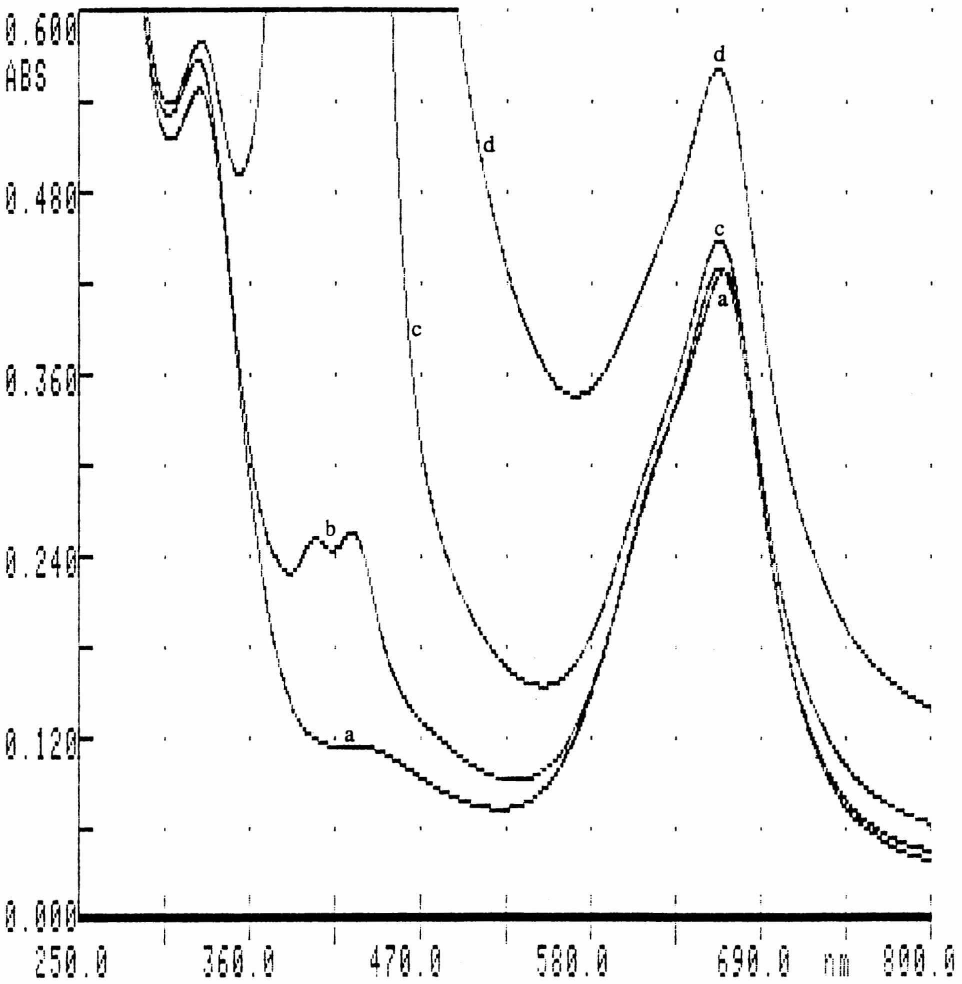


Figure 22. Absorption spectra of latex-bound phthalocyanine **39a** during autoxidation of 2,6-di-*tert* -butylphenol (**7**, DBP). The spectrophotometer samples had 1.17 x 10^{-5} M phthalocyanine **38** and 0.024 mg mL^{-1} latex (L-8), and 3.0 x 10^{-2} M sodium borate at pH 9.0. The spectra were run at 71.5 ± 0.1 °C. (a), Before DBP addition (λ_{max} 664 nm, ε 3.65 x 10^4 M^{-1} cm^{-1}); (b), 1 min after DBP addition (λ_{max} 662 nm, ε 3.67 x 10^4 M^{-1} cm^{-1}); (c), 15 min after DBP addtion (λ_{max} 662 nm, ε 3.82 x 10^4 M^{-1} cm^{-1}); (d), 38 min after DBP addition (λ_{max} 661 nm, ε 4.79 x 10^4 M^{-1} cm^{-1}). 60 min after DBP addition (trace not shown) (λ_{max} 662 nm, ε 5.34 x 10^4 M^{-1} cm^{-1}). The bands emerging around 415 nm are due to diphenoquinone **2a**. The traces shifted toward higher absorption because of the increase of the turbidity of the reaction mixture with time.

Autoxidation of 2,6-Dimethylphenol (12): 2,6-Dimethylphenol (**12**) was tried before 2,6-di-*tert*-butylphenol (**7**) to test the activity of the latex-bound phthalocyanine **39a** catalysts. Preliminary oxidations of phenol **12** at pH 8-10 and 69-80 ^{o}C took place, but no mass balance of these reactions could be established at the end. Small amounts of 3,5,3',5'-tetramethyl-4,4'-diphenoquinone (**2b**) (<5%) and phenol **12**, and almost no 2,6-dimethylbenzoquinone (**1b**) were recovered from the reaction mixtures. The formation of poly(2,6-dimethyl-1,4-phenylene oxide) (**3**) from oxidation of phenol **12** could not be detected. The oxidation rate of phenol **12** catalyzed by latex-bound Co(II) phthalocyaninetetrasulfonate was slower than that of phenol **7** and further oxidations of phenol **12** and/or its products took place (Figure 23). One possible explanation of the problem with mass balance might be that 2,6-dimethylbenzoquinone (**1b**) is unstable at pH 9.0-9.4 under inert atmosphere as well as under dioxygen. Addition of OH^- ions to the quinone **1b** may have formed highly hydrophilic compounds that were not extracted from the aqueous phase. In control experiments; after 18 h stirring, only 56-71% of **1b** was recovered from buffered pH 9.0 aqueous solutions. Usually the color of the mixture turned from light yellow to brown. If the mixture was not buffered, the pH of quinone **1b** mixture decreased to 5.0 from 9.9 after 24 h stirring.

Oxidation of 2,6-dimethyphenol (**12**) by dioxygen catalyzed with Cu(II) bound to an acrylic acid-styrene-divinylbenzene copolymer latex (ref.108, Table II, latexes LC-3 and LC-5) in the presence of pyridine was investigated (Table XV). The latexes contained 19.6 mol % acrylic acid, 78.6 mol % styrene, 1.0 mol % divinylbenzene, and 0.8 mol % ethylvinylbenzene. $CuCl_2$, Cu-pyridine, and Cu-pyridine derivative complexes are known to polymerize phenol **12** to poly(2,6-dimethyl-1,4-phenylene oxide) (**3**).[38-42,44] The reaction mixtures containing pyridine and Cu in ratios of 2 and 20 respectively gave small amounts of 3,5,3',5'-tetramethyl-4,4'-diphenoquinone (**2b**) along with unidentified product(s) at pH 7.5-9.2 and 69 ^{o}C. Two of the reactions were carried out in the presence of about 1% 1,2-dichlorobenzene, because 1,2-dichlorobenzene-methanol (13/2 v/v) was used before with success as the solvent in the autoxidation of phenol **12** with $CuCl_2$.[39-41]

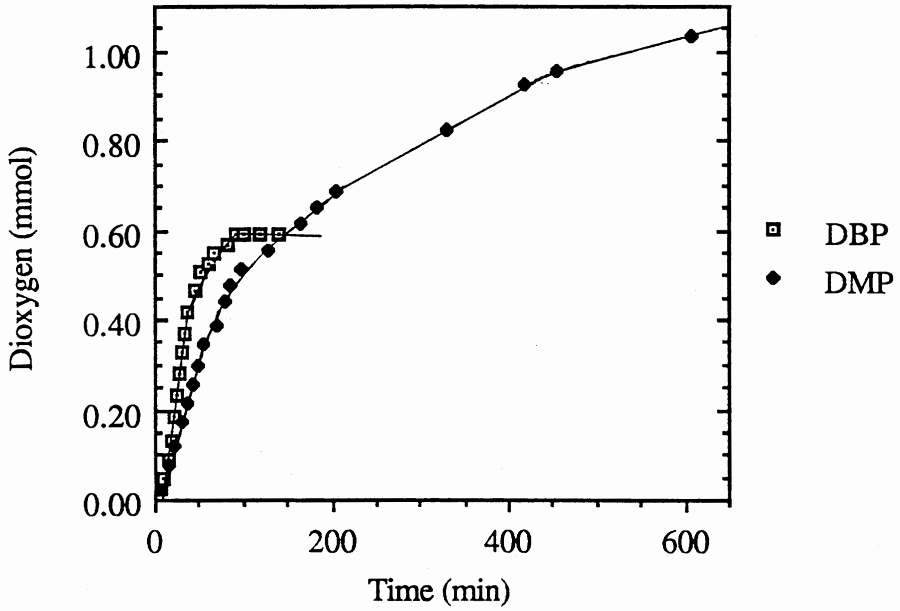


Figure 23. Autoxidation of 2,6-di-*tert*-butylphenol (**7**, DBP) and 2,6-dimethylphenol (**12**, DMP). Experiments were carried out with 1.20 mmol of substrate, 6.0×10^{-2} mmol of phthalocyanine **38** and 120 mg latex at pH 9.0 buffered with 4.8×10^{-2} M sodium borate under 700 ± 5 mmHg dioxygen pressure at 69.0 ± 0.2 °C. L-8 in Table VIII was the latex.

Table XV. Autoxidation of 2,6-Dimethylphenol (**12**) Catalyzed by Latex-Bound Copper-Pyridine Complex[a]

expt.	DMP[b], mmol	pyridine, mmol	pH	time, h	observation
1	1.20	0.12	9.2	5	0.15 mmol TMDPQ was obtained.
2	1.20	0.12	9.0	2.2	0.07 mmol TMDPQ was obtained.
3	0.83	1.20	9.0	40	0.37 mmol TMDPQ was obtained.
4[c]	1.20	0.12	9.0	2.2	Trace amount TMDPQ was observed.
5[d]	1.20	0.24	7.5	2	Trace amount TMDPQ was observed.
6[e]	1.20	0.24	9.0	2	Trace amount TMDPQ was observed.
7[e,f,g]	9.90	0.24	9.0	1	1.33 mmol O_2 was consumed and complex product mixture was obtained.
8[e,g]	4.55	0.24	9.0	3	1.80 mmol O_2 was consumed and brown product mixture was obtained (264 mg)

[a] All experiments were carried out with 6.0 x 10^{-2} mmol of $CuCl_2$ catalyst and 150 mg of poly(acrylic acid-co-styrene) latex under 700 ± 15 mm Hg pressure at 69.0 ± 0.2 °C. The reaction mixture volume was 100 mL. The reaction mixtures were buffered with 2.0 mmol of sodium borate unless otherwise stated. [b] 1.0 mL of a methanol solution of DMP (**12**) was injected to the flask at 69.0 ± 0.2 °C unless otherwise stated. [c] No latex was present. [d] No buffer was present. [e] 1 mL of o-dichlorobenzene was added to the reaction mixtures. [f] Volume was 110 mL. [g] DMP (**12**) was added to the flask at room temperature, and then the temperature of the flask contents was brought to 69.0 ± 0.2 °C.

Autoxidations of Other Phenols and Styrene. Autoxidations of 2,6-dichlorophenol, *o*-cresol, phenol, and styrene by dioxygen catalyzed by latex-bound Co(II) phthalocyaninetetrasulfonate (**39a**) were attempted, but all failed to react. In the attempted autoxidation of phenol, varying the pH from 4.2 to 10.4, the temperature from 40 to 70 °C, and the buffer did not help the reaction proceed.

It is reported that phenol reacts with primary and secondary amines but not with tertiary amines in the presence of copper salts.[160-164] A possible Cu(II)-tertiary amine catalyst was investigated to activate dioxygen and transfer it to phenol. Cu(acetate)$_2$ in the presence of excess pyridine [6-158 moles per mol of Cu(II)] in water at pH 7.0-8.3 and at 50-70 °C catalyzed the oxidation of phenol, but the products were not characterized. At higher pH (9.0-9.3), copper(II) complexed with OH^- and precipitated.

Cu(II) with imidazole as a ligand was inactive. When 2,2'-bipyridine (N/Cu = 2 and 10) was used with Cu(acetate)$_2$, no phenol oxidation took place. Presumably strong coordination of the ligand to copper inhibited its activity. Trimethylamine, tri-*n*-butylamine, morpholine, and quinuclidine ligands gave precipitates with Cu(acetate)$_2$.

Discussion

The autoxidations of 2,6-di-*tert*-butylphenol (**7**) and 2,6-dimethylphenol (**12**) in water catalyzed by latex-bound Co(II) phthalocyaninetetrasulfonate (**39a**) and soluble Co(II) phthalocyaninetetra(sodium sulfonate) (**38**) are heterogeneous reactions. So mass transport phenomena as well as intrinsic activity of the catalyst may be important in the reaction kinetics.[165] In the latex-bound phthalocyanine (**39a**) case, the phenol must be transported from the bulk phase through the aqueous phase to the catalyst particle surface and then diffuse from the particle surface to the active sites within the particle. After chemical reaction occurs, the product must diffuse out of particle and away from the particle surface. In principle any of these mass transport steps could be rate-limiting. On the other hand in the soluble catalyst case, the only mass transfer step is the transport of the phenol from the bulk phase to the catalyst in the aqueous phase.

In polymer supported catalysts, the transport phenomena, mass transfer and intraparticle diffusion, are affected by agitation of the reaction mixture, catalyst particle size, and polymer crosslinking. Also some of the intrinsic activity parameters may affect intraparticle diffusion. The intrinsic activity parameters that affect the rate are catalyst loading, polymer structure, substrate structures, and electrolyte strength.[165] In the autoxidation of 2,6-di-*tert*-butylphenol (**7**), the rate depended on Co, phenol **7**, O_2, and pH but the kinetic orders obtained did not fit any integral order such as first, or second.

In the literature, there is a disagreement over the nature and role of dioxygen cobalt complexes in the oxidation of substituted phenols, but all authors agree that the phenoxy radical is the first intermediate in the mechanism of formation of the oxidized coupled product.[22,23,26,29,30,33,45,47,48]

The mononuclear oxo complexes of Co-Schiff bases,[22,23,26,29,30,33] Co-tetraarylporphyrins,[26,45] Co-phthalocyanine[22] were proposed as the species which generate the phenoxy radicals from phenol. Nishinaga[23,166] detected the 2,6-di-*tert*-butyl-4-alkylphenoxy radicals by ESR formed by H abstraction from the phenol by Co-O_2 and simultaneously observed disappearance of Co-O_2 ESR signal. Yamamoto[167] employed ESR to demonstrate reversible binding of molecular oxygen to Co(II) tetraphenylporphyrin at 77 ^{o}K. Also hydrogen bonding of trifluoroethanol to the cobalt-dioxygen adduct of a Schiff base was reported by Zombeck.[29]

Zombeck[29] proposed Scheme II as the possible mechanism for oxidation of 2,6-dimethylphenol by O_2 catalyzed by Co(II) bis(3-salicylideneamino)propyl)methylamine. The reaction is first order in [O_2], [phenol **12**], and [Co] when [phenol **12**] <0.09 M and [phenol **12**]/[Co] <20. The product of step 10 is believed the active catalytic species. Step 11, which is supported by the observed hydrogen bonding of trifluoroethanol to the terminal Co-O_2 adduct,[29] and step 12, which is supported by the ESR detection of 2,4,6-

tri-*tert*-butylphenoxy radical,[23] are not the rate determining steps. The slow step in this reaction was proposed to be the decomposition of $HO_2^{\cdot}$ to hydrogen peroxide and dioxygen (eq. 13). The phenoxy radical formed reacts faster itself in the presence of O_2 to form diphenohydroquinone (eq. 14) and subsequently diphenoquinone (eq. 15).[168]

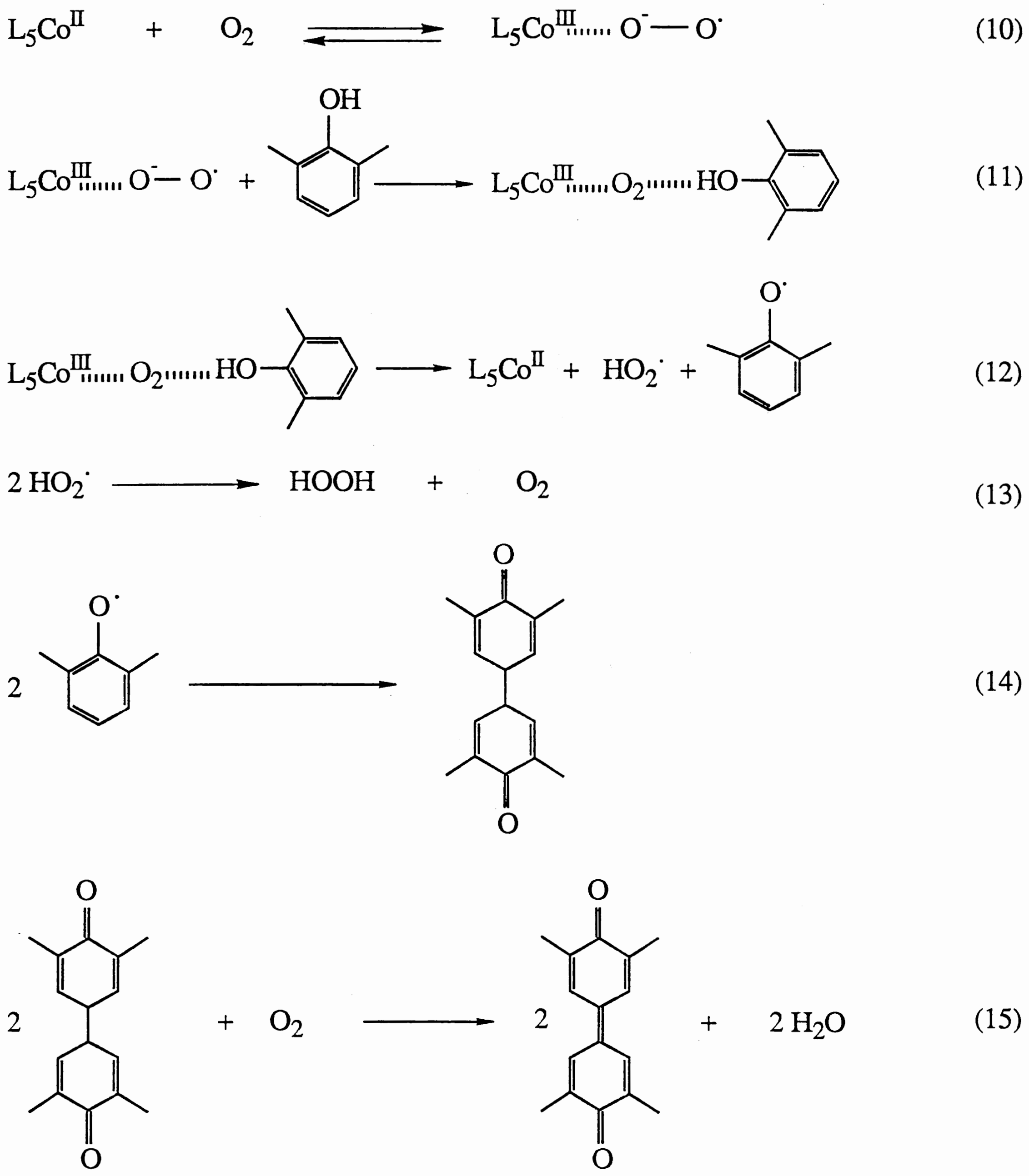
The Scheme II does not include the steps shown in the reference to form the corresponding benzoquinone from the phenoxy radical. When the amount of Co-Schiff base catalyst increases, the generated radical has a high probability of encountering another Co-O_2 center which leads to formation of benzoquinone.

Another mechanism proposed by Bedell[47,48] for oxidation of substituted phenols by dioxygen suggests that a mononuclear dioxygen adduct and a binuclear dioxygen adduct both abstract hydrogen from the phenol (Scheme III). The mononuclear superoxo cobalt(III) complex formed by equilibrium-controlled dissociation of the binuclear adduct, tetrakis(bipyridyl)(μ-peroxo)(μ-hydroxo) dicobalt(III), is indicated as the reactive intermediate. Ligands with greater binding constants than that of bipyridyl gave binuclear dioxygen complexes of very high stability, which left little mononuclear dioxygen complex in the reaction mixture, and gave lower catalytic activity than bipyridyl.

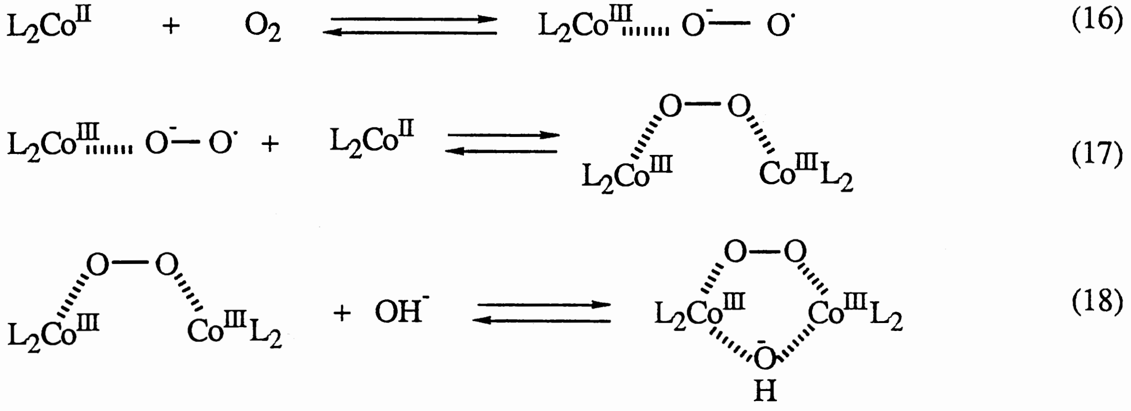
Abel[114] reported ESR spectra that support the reversible formation of a 1:1 molecular oxygen adduct with phthalocyanine **38** at -175 °C in a frozen solution and at -100 °C in a fluid solution in 90-95 % methanol. Tovrog[169] estimated from the results of EPR spectroscopy that after coordination of dioxygen to Co-Schiff base and Co porphyrin complexes, 0.1 to 0.8 e^- is transferred from cobalt to oxygen.

The mechanism of autoxidation of 2,6-di-*tert*-butylphenol catalyzed by phthalocyanine **38** and latex-bound phthalocyanine **39a** should be similar to the mechanisms proposed by Zombeck[29] and Bedell[47] (Schemes II and III). Both mechanisms were based on reactions carried out in organic media. However neither mechanism includes a phenoxide ion as the precursor of the coupled product. So in the aqueous phase autoxidation of 2,6-di-*tert*-butylphenol, the pH presumably affects the stability of the Co-O_2 species rather than the ionization of phenol **7**. In fact the rate depends only weakly on the pH of the aqueous phase. The proposed mechanism is in Scheme IV.

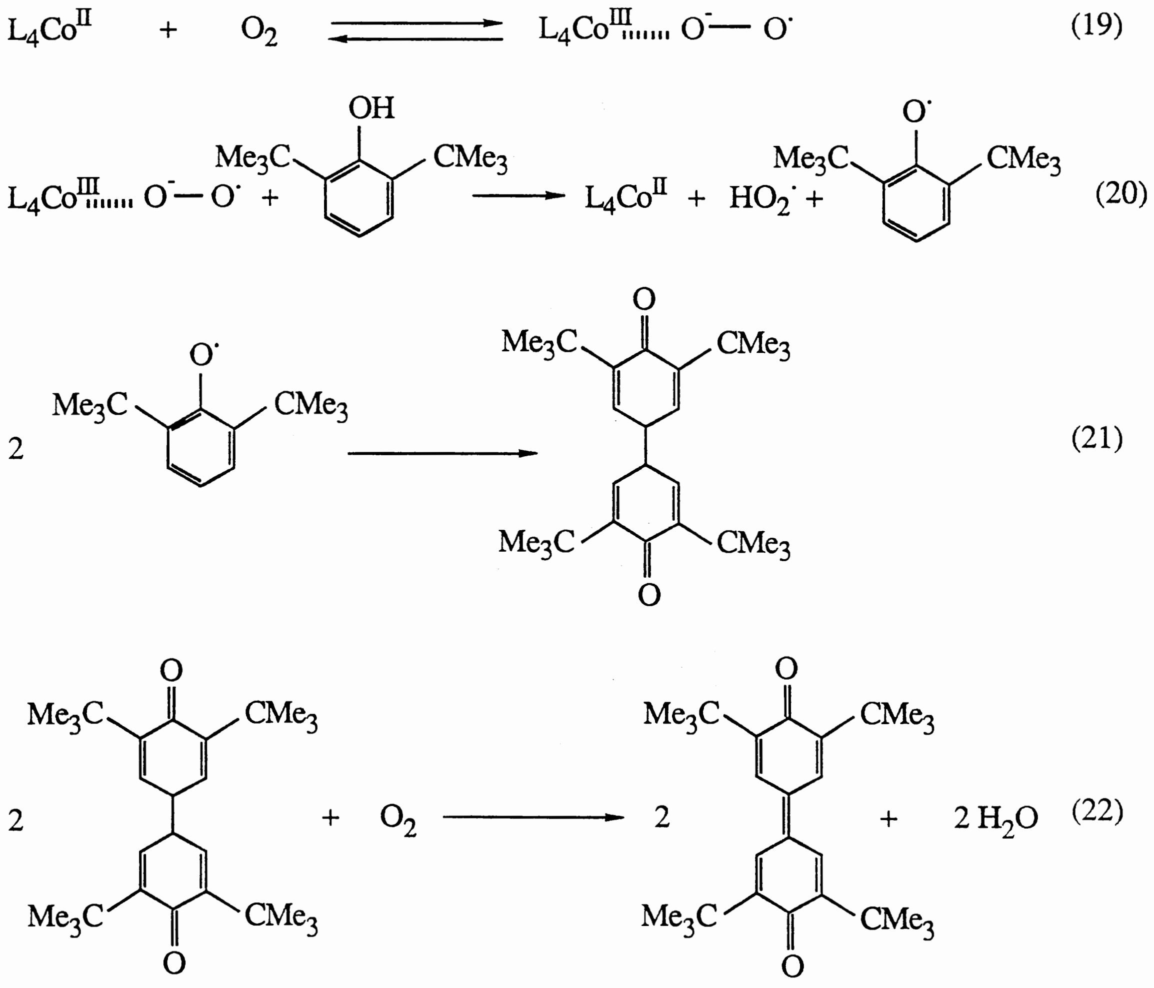
Scheme II. Mechanism of 2,6-Dimethylphenol Oxidation by Co(II) Bis(3-(Salicylideneamino)propyl)methylamine (L_5Co^{II}) in the Presence of O_2[29]



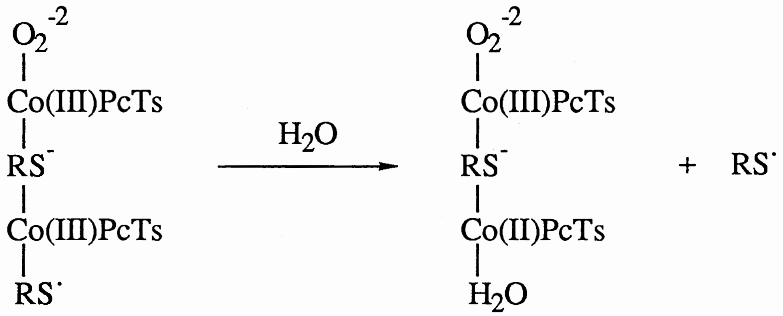
Scheme III. Mechanism of Formation of Tetrakis(bipyridyl)(μ-hydroxo) Dicobalt(III) in the Presence of O_2. (L = bipyridyl)[47]



Scheme IV. Proposed Mechanism for Oxidation of 2,6-Di-*tert*-Butylphenol by O_2 with Either Phthalocyanine **38** [$L_4Co(II)$] or Latex-Bound Phthalocyanine **39a** [$L_4Co(II)$]



In the autoxidation of thiol compounds by Co(II) phthalocyaninetetra(sodium sulfonate) (**38**), different mechanisms from that of phenol oxidation by Co complexes were proposed. The ionene induced dimers of Co(I) phthalocyaninetetrasulfonate and Co(II) phthalocyaninetetrasulfonate were observed spectrophotometrically in the autoxidation of 2-mercaptoethanol.[121] The mechanism includes Co(III) phthalocyanine-tetrasulfonate as well. Leung[170] observed a dimer spectrophotometrically in the autoxidation of 2-aminoethanethiol and proposed the structure as a dimer linked with 2-aminoethanethiolate (eq. 23 and 24). Since no spectral changes in the formation of dimer in the phenol autoxidation was observed after addition of phenol **7**, the mechanism of autoxidation of phenol **7** with Co(II) phthalocyaninetetrasulfonate must be different from the mechanisms of 2-mercaptoethanol and 2-aminoethanethiol.



$$\begin{array}{c} \mathrm{O_2}^{-2} \\ | \\ \mathrm{Co(III)PcTs} \\ | \\ \mathrm{RS}^- \\ | \\ \mathrm{Co(III)PcTs} \\ | \\ \mathrm{RS}^{\cdot} \end{array} \xrightarrow{\mathrm{H_2O}} \begin{array}{c} \mathrm{O_2}^{-2} \\ | \\ \mathrm{Co(III)PcTs} \\ | \\ \mathrm{RS}^- \\ | \\ \mathrm{Co(II)PcTs} \\ | \\ \mathrm{H_2O} \end{array} + \mathrm{RS}^{\cdot} \qquad (23)$$

$$\mathrm{RS}^{\cdot} + \mathrm{RS}^{\cdot} \longrightarrow \mathrm{RSSR} \qquad (24)$$

The differences in the extents of the autoxidation of phenol **7** with mechanical shaking vs. magnetic stirring (Table IX) are likely the result of slower mass transport of the substrate from insoluble droplets or of dioxygen from the gas phase to the active sites in the latex particles. Since mechanical shaking mixes faster than magnetic stirring, it gives higher conversion of phenol **7** to diphenoquinone **2a** under identical conditions. The transport of dioxygen from the gas phase to the solution may depend on the agitation as well. Mechanical shaking creates larger exposed liquid surface to the gas phase which eases the transport of dioxygen from the gas phase to the aqueous phase. The conversion of phenol **7** was enhanced by 0.10-0.01 volume fraction methanol (Table IX).

Presumably methanol promotes the solubility of phenol **7** in the aqueous phase and increases the rate of mass transfer of substrate to the active sites. The surfaces of colloidal cation exchange resin supports (Table VIII) are covered with hydrophilic benzyltrimethylammonium chloride groups. Although the number of these quaternary sites on the surface relative to inside of the particles is not known, most of the Co(II) phthalocyaninetetrasulfonate anions at low loadings should bind the quaternary sites on the surface or near surface. This catalyst gradient eliminates most of intraparticle diffusion limitation and the possible effect of crosslinking, since the reaction occurs on or near the surface of particle. That is why five latexes with different crosslinking, different charge density, and with different surfactant used in preparations gave similar conversions of phenol **7** (Table X). This indicates that the rate is not limited by intraparticle diffusion and only limited by the transport of the phenols from the bulk phase to the surface of latex particles where the Co(II) phthalocyaninetetrasulfonate is bound. However 1% crosslinked latexes gave slightly higher yield than 5% crosslinked ones (4-15% more).

The intrinsic activity of latex-bound phthalocyanine **39a** catalyst in the autoxidation of phenol **7** must depend on several factors such as polymer structure, active site structure, catalyst loading, solvent, and solvent strength.[165] The phthalocyanine bound to latexes was determined by visible spectroscopy to be in monomeric form, so the latex promoted the site isolation of phthalocyanine **39a**. Monomeric phthalocyanine **38** is known to form 1:1 and 2:1 adducts with molecular oxygen. The 1:1 adduct is believed to be the active species to oxidize substrates, and its formation is believed to be the rate determining step.[116] The 1:1 oxygen adduct of phthalocyanine **38** can react rapidly with another complex of phthalocyanine **38** to form μ-peroxo complex of phthalocyanine **38** [(Co(II)PcTsNa_4-O_2-Co(II)PcTsNa_4] (2:1 adduct)[116] which is believed to be inactive in autoxidations.[171] However the 2,4-ionene-bound dimeric Co(II) phthalocyaninetetra-sulfonate (eq. 9) that can not form μ-peroxo Co(II) phthalocyaninetetrasulfonate adduct with dioxygen was proposed being the active species in the autoxidation of

2-mercaptoethanol.[121] In conclusion, the colloidal quaternary ammonium cation exchange resins prevent the formation of dimeric Co(II) phthalocyaninetetrasulfonate and possibly also the μ-peroxo Co(II) phthalocyaninetetrasulfonate complex, and promote the formation of a 1:1 adduct of Co(II) phthalocyaninetetrasulfonate with molecular oxygen as a reactive intermediate in autoxidation of phenols.

All of the latex catalysts were more active in the autoxidation of phenol **7** than homogeneous phthalocyanine **38** catalyst (Tables IX and X, and Figure 12). The higher activity of latex-bound phthalocyanine **39a** could have several causes such as higher local concentration of phenol **7** in the catalyst phase, and site isolation of the catalyst. The cationic latexes bind phenoxide anions as well as Co(II) phthalocyaninetetrasulfonate. The polymer matrix swollen with water and substrate provides a common phase for water insoluble substrate phenol **7** and water soluble catalyst Co(II) phthalocyaninetetrasulfonate. Since all catalyst molecules are bound to quaternary sites of latex particles irreversibly, the reaction is confined to a volume of no more than 0.6 mL, while in solution the catalyst is in 100-150 mL of water. Overall the reaction takes place in a phase where the catalyst concentration and phenol **7** concentration, increased due to the affinity between polymer and substrate, are high. However, a small part of the 248 mg of phenol **7** in a standard reaction mixture is in 120 mg of latex particles. So bulk of the phenol **7** is present as dispersed insoluble droplets.

The rate of the autoxidation increases with increasing amount of Co(II) phthalocyaninetetrasulfonate bound to a constant amount of latex (120 mg, DF = 4.3 meq/g) up to 5% Co(II) phthalocyaninetetrasulfonate based on 1.20 mmol of phenol **7** in the reaction mixture (Figure 12). This particular loading used up 47% of trimethylbenzylammonium sites in the latex. However decreased rates were observed when 6.4 and 8 mol % Co(II) phthalocyaninetetrasulfonate were used, and the amount of latex was kept constant. There are several possible causes for the decrease of the rate when the Co(II) phthalocyaninetetrasulfonate concentration is higher than 5 mol %: decrease of the number of available quaternary ammonium sites on the polymer for phenoxide binding, less swelling of the polymer with high Co(II) phthalocyaninetetrasulfonate loading, and increase in the aggregation of Co(II) phthalocyaninetetrasulfonate. In fact, 8 mol % catalyst which used 74 mol % of the quaternary ammonium sites, decreased the net charge on the particles so much that it caused gradual coagulation of the latex during the autoxidation.

The conversion of autoxidation of phenol **7** was not as sensitive to the amount of latex in the dispersion as it was to the concentration of Co(II) phthalocyaninetetrasulfonate (Table XI). An intriguing catalyst effect is the dependence of the % conversion on the volume of reaction mixture (Table XII). As the reaction volume decreased from 150 mL to 36 mL, always there was a decrease in the conversion of phenol **7**. The major factor that affects the conversion is believed to be the mass transport of molecular oxygen from gas phase to reaction mixture. When dioxygen is depleted rapidly from the smaller volume of mixture, the stationary concentration of dioxygen will be lower than it is in a larger volume.

The pH dependence of the oxidation rate may indicate that a change of the redox potential of the Co(III)PcTs/Co(II)PcTs or of the polymer environment affects the activity. The pH has a direct effect on the concentration of 2,6-di-*tert*-butylphenoxide ion, which should bind to the cationic latex. The cyclic voltammetry curves for CoPcTs complexes in 0.05 M Na_2SO_4 on OPG (ordinary pyrolytic graphite disk) showed pH dependence of peak potentials.[172] It was found that the Co(III)PcTs/Co(II)PcTs couple is very sensitive to the presence or absence of axial ligands. In the absence of a strong donor ligand or in the presence of only a weak ligand such as water, Co(III) phthalocyaninetetrasulfonate was very unstable, but in alkaline medium, the hydroxide ion acted as a good axial ligand for Co(III) phthalocyaninetetrasulfonate (eq. 25). The plot of peak potential (V vs. SCE) vs. pH gave a -95 mV/unit pH slope. This effect must be the major reason that is responsible with activity increase with pH (Table X, and Figure 15). In highly alkaline medium (0.1 N NaOH), the Co phthalocyaninetetra(sodium sulfonate)-dioxygen adduct can be observed spectrophotometrically.[115,116]

$$[(HO)Co(III)PcTs]^{-2} + e^{-} \rightleftharpoons [Co(II)PcTs]^{-2} + OH^{-} \qquad (25)$$

The rate of autoxidation of phenol **7** was accelerated by increasing the reaction temperature (Table X and Figure 13). The linear Arrhenius plot (Figure 14) indicates that there is no change of the reaction mechanism with change in temperature.

The autoxidation of phenol **7** catalyzed by latex-bound phthalocyanine **39a** was not affected by the presence of 0.6 mmol of hydrogen peroxide (50 mol % relative to phenol **7**). In the absence of dioxygen, hydrogen peroxide gave very low conversion (Table XIII). Therefore hydrogen peroxide is not an intermediate in the oxidation of phenol **7**. The catalytic decomposition of H_2O_2 to water and molecular oxygen in aqueous solution by phthalocyanine **38** at pH 3.8 to 10[151,173] and by Fe phthalocyaninetetra-(sodium sulfonate) at pH 5.5 to 10[151,174] is known, however no attempt was made to detect if H_2O_2 formed after autoxidations.

The presence of an added ligand such as pyridine or imidazole did not alter the conversion of phenol **7** substantially, although these ligands affect the strength and irreversibility of the Co-oxygen bond on the reverse side of the phthalocyanine ring and facilitate the oxidation of Co(II) to Co(III) (Table XIV).[151]

Recycling of latex catalyst showed reduced activity during second and third runs (Figure 16). Deactivation may be attributed to accumulation of diphenoquinone **2a** on the surface of the polymer particles as well as changes in colloidal structure. Some change in colloidal structure was evidenced by increase in the turbidity of the reaction mixtures as the reactions progressed and by higher baseline absorption on the spectrophotometer experiments of polymer particles due to increase in scattering.

Based on spectroscopic observations, monomeric Co(II) phthalocyaninetetra-(sodium sulfonate)-dioxygen adduct is the active species in the phenol oxidation, rather than the dimeric Co(II) phthalocyaninetetra(sodium sulfonate)-dioxygen adduct proposed as the active species in thiol oxidations.[121,170] Phthalocyanine **38** in neutral aqueous solution exhibits two absorption maxima due to monomeric phthalocyanine **38** and dimeric or higher aggregate phthalocyanine **38**. The dimeric complex shows a maximum at 626 nm whereas the monomer appears at 663 nm.[115] The kinetics of dimerization were studied extensively and found to depend upon concentration, ionic strength, and temperature.[117,118] The dioxygen adduct of phthalocyanine **38**, a third species, was observed at 670 nm in 0.1 N NaOH solution.[115]

Increase of concentration of phthalocyanine **38** or of ionic strength favors the dimeric species (or polynuclear aggregates), whereas increase in temperature promotes the monomeric phthalocyanine **38**. Indeed, the effect of ionic strength on dimerization was observed in the presence of sodium borate, sodium chloride, and sodium hydroxide and always the maximum of dimer at 626 nm was incresed as the ionic strength increased.

van Welzen[119-121] investigated the structure of phthalocyanine **38** in the presence of ionenes, which are poly(quaternary ammonium) salts. Upon addition of 2,4-, 2,6-, 2,8-, 6,4-, or 6,6-ionene to a solution of phthalocyanine **38**, the amount of aggregates gradually increased and no monomeric Co(II)PcTs was observed even at a ratio of $N^+/Co = 10^5$. On the other hand 2,10- and 2,12-ionenes favored monomeric Co(II) phthalocyaninetetrasulfonate at $N^+/Co > 10^3$.

In contrast to the ionene induced aggregation of phthalocyanine **38**, colloidal quaternary ammonium cation exchange resins promoted the site isolation of Co(II) phthalocyaninetetrasulfonate even when there were 2.7 N^+ sites per phthalocyanine **38**. As the number of N^+ sites increased, the aggregation of Co(II)PcTs was supressed more. That is what was expected in a colloidal system to occur in order to prevent the formation of inactive dimers.

The amount of monomeric Co(II) phthalocyaninetetrasulfonate increased as the temperature increased, which is consistent with the dimerization kinetic results.[117,118]

The absorption spectrum of latex bound Co(II) phthalocyaninetetrasulfonate in the presence of phenol **7** with time was the same during the reaction as in the absence of phenol **7**. This shows that monomeric Co(II) phthalocyaninetetrasulfonate is the dominant species and presumably the concentration of mononuclear oxo-cobalt complex, which is believed the active species, is too low to detect. Possibly this complex reacts with phenol **7** whenever it forms. The formation step of mononuclear cobalt-dioxygen complex is the rate determining step, which may be caused by deficiency of molecular oxygen in the reaction mixture and slow transfer from gas phase to the aqueous phase.

The research described here has created a new kind of catalysis, called colloidal catalysis, and investigated the fundamental science on which it is based. It could proceed further in several directions. One of the directions is to understand chemistry of the colloid surface better. It can be investigated by varying charge density and charged sites on colloids, and varying particle size of colloids. In order to understand why colloidal catalysis are more active than soluble analogs, the interactions between organic substrate and polymer need to be explored. The interaction between colloid and Co(II) phthalocyaninetetra(sodium sulfonate) and the effect of this interaction on the aggregation of the catalyst may be investigated. For possible large scale applications, the activity of the colloidal catalyst and colloid stability need to be improved.

Experimental Part

Materials and Reagents. Styrene (Aldrich), divinylbenzene (meta/para mixture, 55% technical grade, containing 45% ethylvinylbenzene, Polysciences), and chloromethylstyrenes (70/30 m/p, Dow Chemical Co.) were washed with 0.1 N NaOH and distilled under vacuum (3-5 mmHg) before use. 2,6-Di-*tert*-butylphenol (**7**) (Aldrich) was vacuum distilled (0.9-1.7 mmHg, 86-89 ^{o}C). 2,6-Dimethylphenol (99.8+%) (**12**) was obtained from Aldrich and used as received. Sodium dodecylsulfate (98%), sodium bisulfite, potassium persulfate, aqueous trimethylamine (24%), trisodium salt of 4-

sulfophthalic acid, urea (Gold label), cobalt(II) sulfate-7-hydrate, ammonium molybdate, and hexadecane were used as received from Aldrich. Hexadecyltrimethylammonium bromide (Fisher), ammonium chloride (Fisher), sodium borate (Fisher), AMPSO (2-hydroxy-3-[(2-hydroxy-1,1-dimethylethyl)amino]-1-propanesulfonic acid) (Sigma), TAPS (3-[(2-hydroxy-1,1-bis(hydroxymethyl)ethyl)amino]-1-propanesulfonic acid) (Sigma), CAPS (3-(cyclohexylamino)-1-propanesulfonic acid) (Sigma), ACES (2-[(2-amino-2-oxoethyl)amino]-ethanesulfonic acid) (Sigma) were used as received. Dowex® 50W X8 ion exchange resin and cellulose acetate/nitrate membranes were obtained from J. T. Baker and Millipore respectively. Poly(acrylic acid-co-styrene) latex[108] was provided by Dr. Rama S. Chandran. Dioxygen pressures lower than 0.9 atm were obtained from the gas cylinders containing 75, 50, and 21% dioxygen (rest is nitrogen). Water was distilled after passing through columns of active carbon and a mixed bed ion exchange resin. The conductivity of the distilled water was always <1 μmho cm^{-1} (usually 0.5-0.6 μmho cm^{-1}), and it was stored under CO_2-free air.

Equipment. Gas chromatographic analyses of 2,6-di-*tert*-butylphenol (**7**) reaction mixtures were performed on a Hewlett-Packard 5840A GC equipped with a 6-ft 10% silicon gum W98 packed column on 80/100 mesh GAS-CHROM® Q column support, and a TCD detector and interfaced with a Hewlett-Packard 5840A terminal. The silicon gum W98 column does not separate 2,6-dimethylphenol (**12**) and 2,6-dimethylbenzoquinone (**1b**), so a 6-ft 5% Carbowax 20M packed column on 80/100 mesh GAS-CHROM® Q column support was employed to determine the quantities of phenol **12** and benzoquinone **1b** as well. Infrared spectra were taken on a Perkin-Elmer 681 instrument, and the NMR spectra were taken on a Varian XL-300 spectrometer using $(CH_3)_4Si$ as an internal standard. The electron micrographs were taken with a JOEL 100 CXII instrument in the Electron Microscopy Lab. at Oklahoma State University. Visible spectroscopy measurements were performed with a double beam Varian DMS 200 spectrophotometer equipped with thermostated cell holders. Cells of 1.00-cm length were used. When the absorption spectrum of latex-bound phthalocyanine **39a** was taken, a latex of the same concentration was used in the reference path. pH was measured with an Altex Zeromatic IV pH-meter. For ultrafiltration, a 200-mL pressure filtration funnel (Gelman 4280) or all glass ultrafiltration apparatus (Millipore) fitted with 47 mm membranes in diameter was used. The conductivities were measured with a YSI 31 conductivity bridge equipped with 3402 and 3403 cells. The oxygen absorption measurement apparatus was constructed in our lab, and is a modified version of the apparatus described elsewhere.[175] The dioxygen pressure reported in Tables is the pressure at room temperature. When the reaction flask was immersed in a 70.0 ± 0.1 ^{o}C oil bath, the pressure in the apparatus increased about 40 mmHg due to evaporation and temperature increase. This final pressure was within ± 10 mmHg of the atmospheric pressure which varied usually from 730 mmHg to 750 mmHg.

Analysis. Elemental analyses were performed by the Galbraith (Knoxville, TN.), MicAnal. (Tucson, AZ.), and Huffman (Wheat Ridge, Co.) Laboratories. Melting points were measured with a Mel-Temp apparatus and are uncorrected.

General Procedure for Emulsion Polymerization.[138] A 500-mL round-bottomed flask was equipped with an overhead stirrer with a teflon blade, a condenser, a thermometer, a nitrogen inlet, and an addition funnel. The addition funnel was also equipped with an overhead stirrer with a teflon blade and a nitrogen inlet. Solution A: The 500-mL round-bottomed flask was charged with sodium dodecylsulfate (0.40g, 1.4 mmol) and deoxygenated distilled water (120 mL). This dispersion in the flask was stirred under nitrogen and heated to 65 ^{o}C in a thermostated oil bath. Solution B: The addition funnel was charged with sodium dodecylsulfate (1.12 g, 3.9 mmol), deoxygenated distilled water (30 mL), divinylbenzene (2.4 g, 55% active, 0.01 mol.), and chloromethylstyrenes (29.0 g, 0.190 mol). The mixture was stirred continuously to give a milky-white pre-emulsion, and then sodium bisulfite (50 mg, 0.48 mmol) was added to the addition funnel. Sodium bisulfite (11 mg, 0.10 mmol) and potassium persulfate (0.25 g, 0.93 mmol) were added to the solution A before solution B was added dropwise to stirred solution A over 1 h. The flow from the addition funnel to the flask was regulated with a stopcock. After addition was completed, more sodium bisulfite (7 mg, 0.07 mmol) and potassium persulfate (25 mg, 0.09 mmol) were added to the emulsion. The polymerization was continued for 1 h at 65 °C, then the emulsion was cooled to 20 °C. The emulsion was acidic from partial hydrolysis of vinylbenzyl chloride, so it was neutralized to pH 7.0 with 0.5 M NaOH.

Quaternization of Chloromethyl Sites in the Latexes.[138] A solution of 47 g of 24% aqueous trimethylamine diluted with 70 ml of distilled water was added to the stirred latex at once. In some cases, addition of trimethylamine caused the formation of a thick curd or swollen gel, creating handling and stirring problems. Addition of about 50 ml water to the flask transformed the gel to a less viscous latex. The mixture was stirred at 40 °C for 16 h and at 60 °C for 2 h.

All prepared cationic polymer colloids except latex 1 (L-1 in Table VIII) were filtered through qualitative filter papers and stored for further use.

Recovery of Latex 1 (in Table VIII). The colloidal particles in emulsion were precipitated by adding 4 volumes of acetone. The clear liquid was decanted, and the polymer was washed with acetone several times and dried in a vacuum desiccator.

Determination of Solid Content of Cationic Polymer Colloids. Samples (10.00 mL) of latexes (except L-1 kept in solid form) were dried first by using a rotary evaporator and then a vacuum dessicator, and weighed. The determination for each latex was done twice and the variations of the duplicate experiments for latexes in Table

VIII were 0.07-0.36 g per 100 g of aqueous colloid. The average of two measurements is reported in w/w percentages in Table VIII.

Determination of Trimethylbenzylammonium Sites in Latexes. The amount of liberated chloride ions from latexes which are counterions of trimethylbenzylammonium sites was determined by the Volhard titrimetric method.[142] The determination of [-$(C_6H_4)CH_2N^+(CH_3)_3$ Cl^-] ($R_4N^+Cl^-$) sites for each polymer colloid was performed three times, and the results were within ± 2% of the avaraged value of $R_4N^+Cl^-$ given in Table VIII. In a typical titrimetric determination; 5 or 10 mL of colloid (in L-1 case known weight) was taken in an Erlenmeyer flask, and a few drops of HNO_3 (50%) and 25 mL of $AgNO_3$ solution (9.75×10^{-2} M) were added. The AgCl precipitate was either filtered and washed with distilled water or coated with 2-3 mL of toluene. After a few drops of $NH_4Fe(SO_4)_2$ solution were added as indicator, the filtrate or mixture was titrated against NH_4SCN solution (9.94×10^{-2} M). From titration results, the degree of functionalization of the colloid was calculated as follows.

The polymer composition before trimethylamine treatment is assumed the same as monomer composition (L-6, Table VIII): divinylbenzene (4.8 mol%), ethylvinylbenzene (3.9 mol%), and vinylbenzyl chloride (91.3 mol%) give an average formula weight of 150.7 g per repeat unit (polymer-A). From Volhard and solid content analyses, the latex contained 4.063 mmol of quaternary ammonium sites per g of polymer-B, which is the polymer obtained after trimethylamine tratment.

f = Conversion factor of polymer-A to polymer-B

f = (1.0 + 0.059 X) g polymer-B/1.0 g polymer-A

$$\left[\frac{4.063 \text{ mmol N}^+}{1.0 \text{ g polymer-B}}\right] \times f + \frac{[(913/150.7) - X] \text{ mmol VBC}}{1.0 \text{ g polymer-A}} + \frac{(39/150.7) \text{ mmol EVB}}{1.0 \text{ g polymer-A}}$$

$$+ \frac{(48/150.7) \text{ mmol DVB}}{1.0 \text{ g polymer-A}} = \frac{1000 \text{ mmol repeat unit}}{150.7 \text{ g polymer-A}}$$

X = 5.344 mmol of vinylbenzyl chloride reacted with trimethylamine

Number of trimethybenzylamine per repeat unit = [5.344/(1000/150.7)] = 0.805

Ultrafiltration of Latex 8. Latex 8 (L-8, Table VIII) containing 720 mg polymer was filtered by using a 200 mL pressure filtration funnel equipped with 0.1 μm cellulose acetate/nitrate membrane under 60 psi of nitrogen. The conductivity of the initial filtrate was 340 μmho cm^{-1}. After washing the latex several times with distilled water over a period of 4 days. The final conductivities 33 and 220 μmho cm^{-1} for the filtrate and latex were achieved.

Determination of Particle Sizes of Latexes. The TEM micrographs were used to determine the particle sizes of latexes. The samples for TEM were prepared by placing a drop of a latex on a Formvar®-coated Cu grid, removing the excess latex by touching a piece of filter paper to the drop, and drying in air. Subsequently a drop of a 5% or 1% solution of uranyl acetate was placed on the grid, excess solution was removed, the grid was dried in air. If $Co(II)PcTsNa_4$ (**38**) was present in the latex, no staining agent was used. The filament current and accelerating voltage of TEM were 100 μamp and 80 KV respectively. Particles were photographed at 36000-100000 magnification. The diameters of 50 non-aggregated particles from either the TEM negative or a photographic print were measured by using a 1/10-cm scaled ruler or a calibrated stage microscope equipped with a 10-fold magnification lens. When the microscope was used, all measurements were corrected with a factor obtained from the measurement of a standard length. The number averages of the diameters are reported as the particle sizes of latexes.

Synthesis and Characterization of Tetrasodium Salt of Cobalt(II)-4,4',4'',4'''-Phthalocyaninetetrasulfonate-2-hydrate (38). The tetrasodium salt of cobalt(II)-4,4',4'',4'''-phthalocyaninetetrasulfonate-2-hydrate (**38**) was prepared twice by the method of Weber.[112] In the first preparation, the trisodium salt of 4-sulfophthalic acid was converted to 4-sulfophthalic acid by ion-exchange with Dowex® 50W X8 having 2.0 meq/mL (wet) exchange capacity. The resin (ca 350 mL) was charged in a column and washed first with excess 1N H_2SO_4 then with distilled water several times until the washings were neutral. The salt (25 g, 72 mmol) dissolved in about 50 mL of water was passed through the ion-exchange resin. The pH of the eluent was 1.25, and to the eluent NaOH (2.9 g, 72 mmol) was added. After lyophilization, 19.7 g of monosodium salt of 4-sulfophthalic acid was recovered. To determine the extent of conversion, a sample solution was titrated against 0.1 N NaOH solution and 2.1 acidic protons per molecule were found.

The monosodium salt of 4-sulfophthalic acid (19.4 g, 72 mmol) was mixed with urea (22.9 g, 0.38 mol), ammonium chloride (1.9 g, 35.4 mmol), cobalt(II)sulfate-7-hydrate (5.3 g, 19 mmol), and ammonium molybdate (0.29 g, 0.24 mmol), and the mixture was ground until homogeneous. A 250-mL round-bottomed flask equipped with an overhead stirrer with a Pyrex® blade, a condenser, and a thermometer was charged with 60 mL of nitrobenzene, which was stirred and heated to 180 °C. The temperature was controlled with a Therm-o-Watch®. The solid ground mixture was added slowly to the stirred hot nitrobenzene to prevent any rapid decrease in the reaction temperature. The heterogenous mixture was stirred for about 2 h until the solid cake became stiff and was heated for a total of 6 h at 180 °C. The product was ground and washed with excess methanol to remove nitrobenzene. The remaining phthalocyanine **38** with some unreacted starting metarials was added to 1N HCl (ca 500 mL) and saturated with NaCl to remove excess cobalt ions from product. The mixture was heated to boiling, cooled, and filtered through filter paper. The filtered solid was dissolved in 1N NaOH (ca 400 mL), and the mixture was heated to 80 °C and immediately filtered through a filter paper to remove insoluble impurities. The filtrate was heated to 80 °C, saturated with NaCl, and cooled slowly to prepicitate phthalocyanine **38**. The product from initial precipitation was separated by filtration and washed with 80% aqueous ethanol until no chloride was detected qualitatively in the filtrate (by adding $AgNO_3$ solution). Additional precipitations were not done to avoid possible contamination of NaCl and impurities. The remaining product was refluxed for 4 h in 110 mL of absolute ethanol. The product was filtered through a filter paper and dried in a vacuum desiccator for 6 h at 60 °C. Co(II)$PcTsNa_4$ is hygroscopic and was dried before preparing any standard solution. Anal: Calcd for $CoC_{32}H_{12}N_8S_4O_{12}Na_4 \cdot 2H_2O$ (FW 1015.66): C, 37.82; H, 1.59; N, 11.03; S, 12.62; Na, 9.05; Co, 5.80. Found: C, 37.27; H, 1.70; N, 11.27; S, 9.96; Na, 6.45; Co, 5.02. UV (H_2O) λ_{max} 627 nm (ε 46,100 $M^{-1}cm^{-1}$), λ_{max} 666 nm (ε 58,700 $M^{-1}cm^{-1}$) Lit.[118] λ_{max} 625-633 nm (ε_{max} 80,000 $M^{-1}cm^{-1}$), 662 nm (ε_{max} 121,000 $M^{-1}cm^{-1}$).

In the second preparation of phthalocyanine **38**, 4-sulfophthalic acid (50% in water) obtained from Eastman Kodak Co. was used after water was removed instead of monosodium salt of 4-sulfophthalic acid. The phthalocyanine **38** obtained from this preparation showed properties identical to those of the one prepared earlier. Anal: Calcd for $CoC_{32}H_{12.5}N_8 \cdot 3.5(SO_3Na) \cdot 9H_2O \cdot NaCl$ (FW 1148.86): C, 33.42; H, 2.68; N, 9.75; S, 9.77; Na, 9.01; Co, 5.13. Found: C, 33.36; H, 3.14; N, 8.43; S, 9.64; Na, 8.99; Co, 4.38.

Preparation of Latex-Bound Co(II) Phthalocyaninetetrasulfonate (39a). Each latex was exposed to various amounts of cobalt(II) phthalocyaninetetra-(sodium sulfonate) (**38**) with sonication for 0.5 h. Ultrafiltration of the latexes through 0.1 μm cellulose acetate/nitrate membrane revealed no unbound blue phthalocyanine **38** in the filtrate and retained blue latex from each sample as long as no more than approximately one phthalocyanine **38** was added per four ammonium ion sites in the latex. The filtration rate was 5 mL per h.

Determination of Minimum N^+/Co(II) Phthalocyanine Ratios of Latexes. Phthalocyanine **38** (2.0×10^{-2} mmol, binds to four quaternary sites) in excess relative to the number of quaternary sites (3.2×10^{-2} mmol) was added to a latex. The mixture was sonicated for 10-15 min and filtered through a 0.1 μm cellulose acetate/nitrate membrane. The polymer on the membrane was washed extensively until filtrate became colorless. The filtrate was diluted to 200 mL and its visible spectrum was obtained. Since the spectrum of phthalocyanine **38** is pH and ionic strength sensitive, a standard solution of phthalocyanine **38** was prepared as follows. The same amount latex as above was filtered. Phthalocyanine **38** (8.0×10^{-3} mmol) was added to the filtrate, and the filtrate was diluted to 200 mL. From the spectrum of this standard solution, the concentration of phthalocyanine **38** of the original filtrate was determined and the amount of phthalocyanine **38** bound to the latex was calculated.

Autoxidation of 2,6-Di-*tert*-Butylphenol (7). The progress of autoxidation was monitored by dioxygen consumption, and in some experiments the products were determined quantitavely by GLC analysis. In a typical experiment, the latex containing 123 mg solid and a solution of phthalocyanine **38** (0.060 mmol in 10-30 mL) was mixed and sonicated for 0.5 h. The catalyst was not protected from air. Sodium borate (3.0 mmol) or AMPSO (4.4 mmol) buffer was added, and the pH was adjusted to 9.0 in 100 or 150 mL. The catalyst suspension was charged in a 250 or 500 mL single neck round-bottomed flask (with a side arm) equipped with a condenser to which the oxygen absorption measurement apparatus was attached. The phenol **7** was either added to the flask at this stage or injected after the temperature of catalyst suspension reached at desired temperature. Two methods were used for introduction of phenol **7**. Addition of phenol **7** dissolved in methanol gave droplets containing phenol **7** dispersed in 0.1 volume fraction methanol in water. Addition of solid phenol **7** to a mixture of catalyst in water at 70 °C gave fine droplets of melted phenol **7** dispersed in water. Injection of phenol **7** was done with 1 mL of a solution of phenol **7** in methanol. In this case, the volume fraction of methanol was 0.01. After the system (apparatus and flask) was sealed to the gas buret, it was evacuated and filled with dioxygen gas 5 times. The flask having about 0.9 atm dioxygen pressure was placed in a thermostated oil bath. The bath temperature was kept at 70.0 ± 0.1 °C. Some reaction mixtures were stirred rapidly with a magnetic bar. Others were shaken horizontally with a platform shaker having an amplitute of 2.5 cm and a frequency of about 1 s^{-1}. The volume of reacted dioxygen was recorded manually or on a strip chart recorder. When reactions were worked up, the flask was separated from the system quickly, evacuated by using a vacuum pump and pressurized with argon gas.

The reaction mixture was acidified to pH 2-3 with 1N HCl, and organic components were extracted from the aqueous phase using CH_2Cl_2 and diethyl ether. First, the latex was swollen with 10-20 mL of CH_2Cl_2 and then shrunk with 100-150 mL of diethylether, expelling solvents from the latex. The extraction process was repeated at least 3 times. The extracted organic phase was dried with $MgSO_4$ and concentrated by using a rotary evaporator.

The extracted and concentrated residues were analyzed qualitatively with TLC (2% ethyl acetate-petroleum ether). Before quantitative GLC analysis, a known amount hexadecane (100-200 mg) was added to the sample as an internal standard. GLC temperature programming from 150 °C to 275 °C at 15 °C/min was employed and the flow rate of carrier gas helium was 35 mL/min. The initial and final temperatures were kept constant for 6 min. The retention times of **7**, **2a**, **1a** and hexadecane were about 3.1, 15.0, 3.5, and 6.7 min respectively. With all colloidal CoPcTs catalysts except L-9 the only product detected was 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenoquinone (**2a**), which analyzed for between 90% and 102% of the starting 2,6-di-*tert*-butylphenol (**7**).

3,5,3',5'-Tetra-*tert*-butyl-4,4'-diaphenoquinone (**2a**); mp 238.5-240 °C (lit.[43] 239-242 °C); IR (KBr): 2950 (s, C-H stretch), 1620 (s, C=O stretch), 1360 (s, C-H bending), 1090 (s, C-H bending) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.71 (s, 4 H), 1.37 (s, 36H); ^{13}C NMR ($CDCl_3$) δ 186.46 (C-4), 150.43 (C-3 and C-5), 136.13 (C-1), 126.01 (C-2 and C-6), 36.03 (4 x tert C), 29.59 (12 x CH_3).

Visible Spectrophotometry of Co(II) Phthalocyaninetetrasulfonate

Effect of Latex on the Absorption Spectrum of Co(II) Phthalocyaninetetrasulfonate: The spectrophotometer cell temperature was 30.0 ± 0.1 °C and all solutions were dioxygen free. Air and argon saturated solutions of latex-bound phthalocyanine **39a** buffered with 3.0 x10^{-2} M sodium borate at pH 9.0 were prepared. Their absorption spectra at 30.0 °C did not show any significant changes in the presence of dioxygen.

Effect of Dioxygen on the Absorption Spectrum of Co(II) Phthalocyaninetetrasulfonate: The homogeneous and latex (0.020 mg mL^{-1}) bound solutions of Co(II) phthalocyaninetetrasulfonate (9.98 x 10^{-6} M) buffered with sodium borate (3.0 x 10^{-2} M) at pH 9.0 were heated first to 30 °C in an oil bath and stirred for 1h under 2.6 atm pressure of dioxygen. After the absorption spectra were taken, the oil bath temperature was raised to 51 °C and the solutions were stirred at that temperature for 1 h under the same dioxygen pressure. The same procedure was followed at 70 °C.

Visible Spectrophotometry of Autoxidation of 2,6-Di-*tert*-Butylphenol (7) with Dioxygen Catalyzed by Latex-Bound Co(II) Phthalocyaninetetrasulfonate: Oxidation was carried out in a way similar to that used with the gas buret. Before addition of phenol **7**, and 1, 15, 38, and 60 min after the addition of phenol **7**, 1 mL samples were drawn from reaction mixture. Each sample was diluted with 50 mL of dioxygen-saturated water buffered with 3.0 x10^{-2} M sodium borate at pH 9.0 at 70 °C. A small portion was transferred to a cell and its spectrum was taken at 71.5 °C.

Autoxidation of 2,6-Dimethylphenol (12), 2,6-Dichlorophenol, Phenol, *o*-Cresol, and Styrene. The same procedure described for autoxidation of phenol **7** was followed.

Autoxidation of 2,6-Dimethylphenol (12) Catalyzed by Cu-Pyridine. A $CuCl_2$ solution (18 mL, 3.34×10^{-3} M) was added to 150 mg of solid containing poly(acrylic acid-co-styrene) latex (DF_{COO^-} = 1.99 meq. per g of polymer) dropwise while it was sonicated. The Cu(II) to COO^- ratio was 0.2. After addition of 2.0 mmol of sodium borate and pyridine (3.82 mL, 3.14×10^{-2} M), the pH was adjusted to 9.0 in 99 mL. The 500-mL round-bottomed reaction flask with a side arm equipped with a stopcock and septum was attached to the gas buret. The apparatus was set up and the flask was heated in a 70.0 ± 0.1 °C oil bath as described for autoxidation of 2,6-di-*tert*-butylphenol (**7**). Finally 2,6-dimethylphenol (**12**) in methanol (1.0 mL, 1.20 M) was added by syringe to the reaction flask.

Dioxygen Uptake Apparatus. The rate of dioxygen uptake was utilized to determine the rate and extent of the autoxidation of phenol **7** and other substrates. An apparatus was designed using a figure provided by Meinders[175] and constructed with a buret, manifold, and an electrical circuit with a solenoid valve that is triggered by pressure changes.

Operation of the Apparatus: Using a flexible tubing and adapter, valve 2 in Figure 24 is connected to the top of a condenser and reaction vessel. Before evacuating the apparatus through valve 1 and filling with dioxygen through valve 3, valve 4 is left open and valve 10 is closed. After the apparatus is evacuated and filled with dioxygen 4-5 times, valves 1 and 3 are closed and, if needed, the temperature of the reaction mixture is raised. After that, valve 10 is opened, the substrate is injected through the side arm equipped with a septum and stopcock, and the valve 4 is closed. It is preferred to keep the gas pressure in the apparatus close to the atmospheric pressure (± 10 mmHg). If the apparatus pressure is much different from atmospheric pressure, the water flowing into the buret can be pushed back or the buret can be filled more than the needed amount to balance the levels in the U-tube 8. The gas pressure in the apparatus was measured by using the U-type Hg manometer 6 and a barometer.

The solenoid valve 12 which controls the flow of stock solution into buret 9 is controlled by a relay unit 7 that is activated only when the level of salty water in the U-tube 8 rises in the left arm due to drop of the gas pressure, and the water touches the tip of the wire. The gap between the surface of the water in the U-tube and the tip of the wire is usually 1-3 mm. A needle valve 11 is employed to regulate the rate of flow into the buret 9.

When the activated circuit opens valve 12, water from the stock solution flows into buret until the pressures of the reaction vessel side and buffer volume 5 equilibrate. The volume of the gas replaced by water is the volume of dioxygen consumed by the reaction. The scheme of the relay circuit is given in Figure 25.

The level of the water in the buret can be recorded by reading manually from the buret scale or automatically with a X-Y recorder. The automatic recording circuit diagram (shown in Figure 26) and sensor carriage assembly were designed by Dr. Rama S. Chandran and the circuit was assambled by Mr. Bill Barnes in the Department of Chemistry. An infrared sensor to detect the water level was mounted on a carriage which can go up and down along the buret on two rod and one screw rails. The screw rail with 20 turns per inch is connected on one end to a 12 V DC motor and on the other end to a coupled gear system. Once the position of the sensor is lower than the level of the water in the buret, the infrared beam sent from one D1 of the sensor is focused on the Q1 collector, which activates the circuit and drives the motor and the attached screw. This motion makes the carriage on which sensor is mounted move up. Once the sensor reaches the meniscus of the water in the buret, the infrared beam is no longer collected on Q1 due to the change of refractive index and scattering of the glass and meniscus. This causes the circuit to open and stops the motor.

The vertical motion is transferred into rotational motion with a gear system connected to a potentiometer. The gear system converts 30 turn vertical motion on the screw to 1 rotation of the potentiometer shaft. The potentiometer is connected to an X-Y recorder and coupled with an adjustable potentiometer to control the position of recorder pen. A reference voltage (9.5 V) is applied, and changes in the current are recorded.

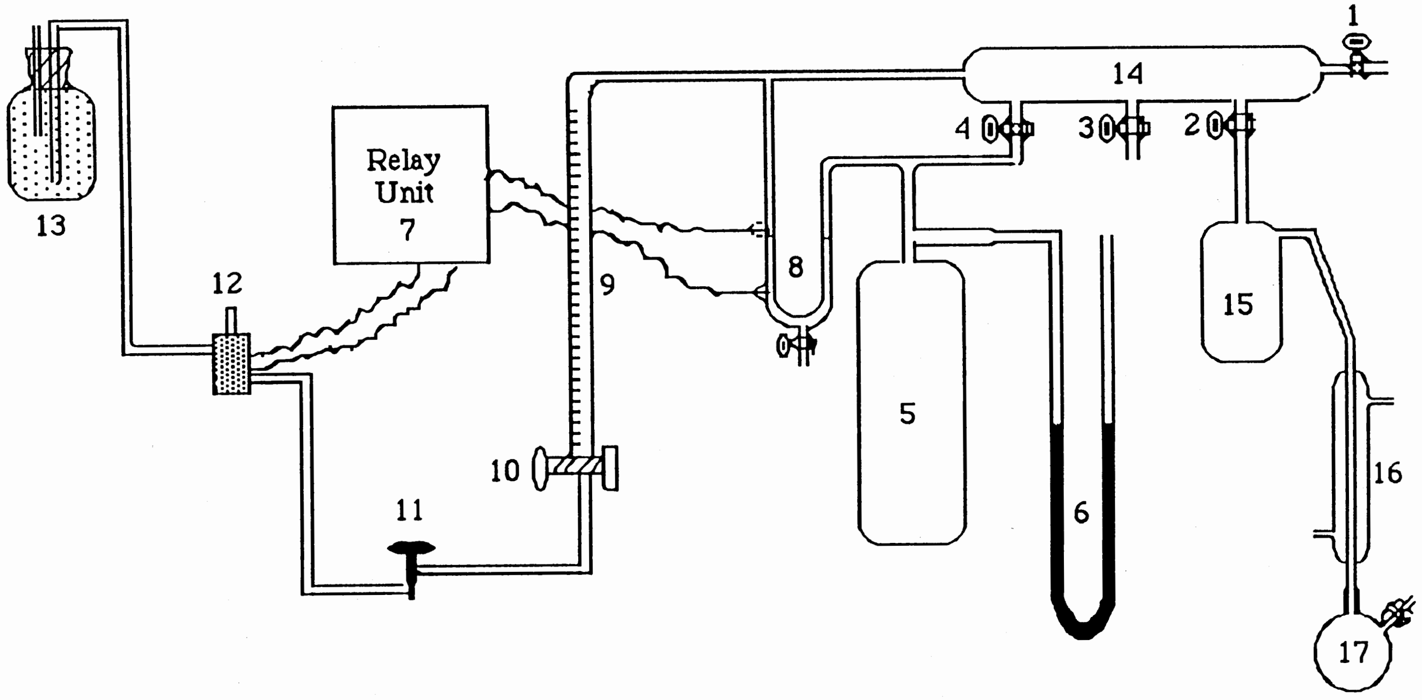


Figure 24. Oxygen uptake apparatus (not drawn to scale). 1, 2, 3, 4, and 10 : Teflon stopcocks. 5 : Buffer flask (1.1 L). 6 : Mercury manometer. 7 : Relay unit. 8 : U-tube (0.8 cm ID glass tubing). 9 : Burette (50 mL). 11 : Needle valve. 12 : Solenoid valve. 13 : Water bottle (4 L). 14 : Manifold (200 mL). 15 : Buffer flask (500 mL). 16 : Condenser. 17 : Reaction flask (500 mL).

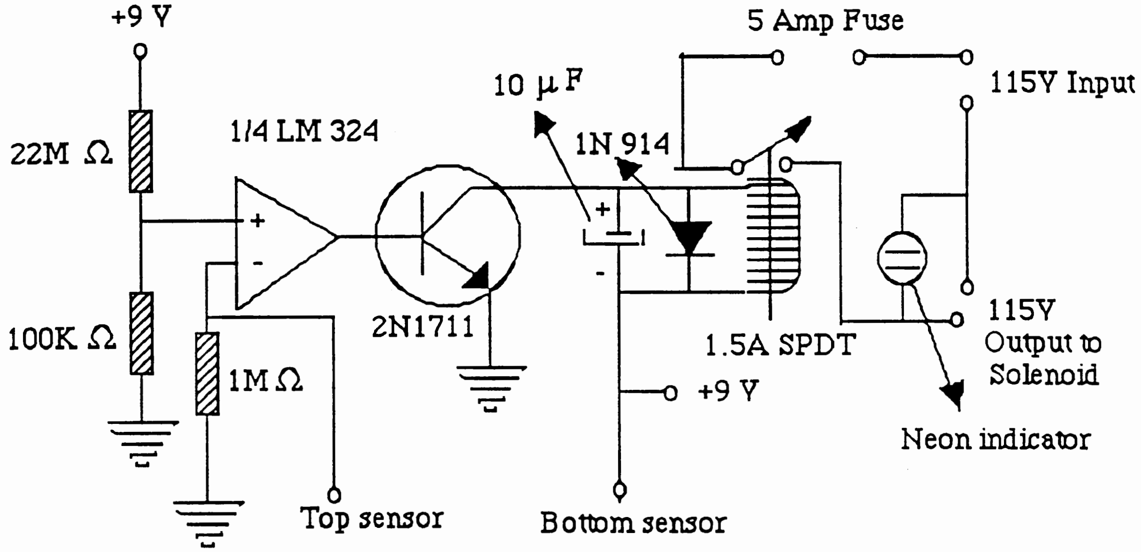


Figure 25. Relay unit for the oxygen uptake apparatus. SPDT relay is a Radio Shack Part # 275-004.

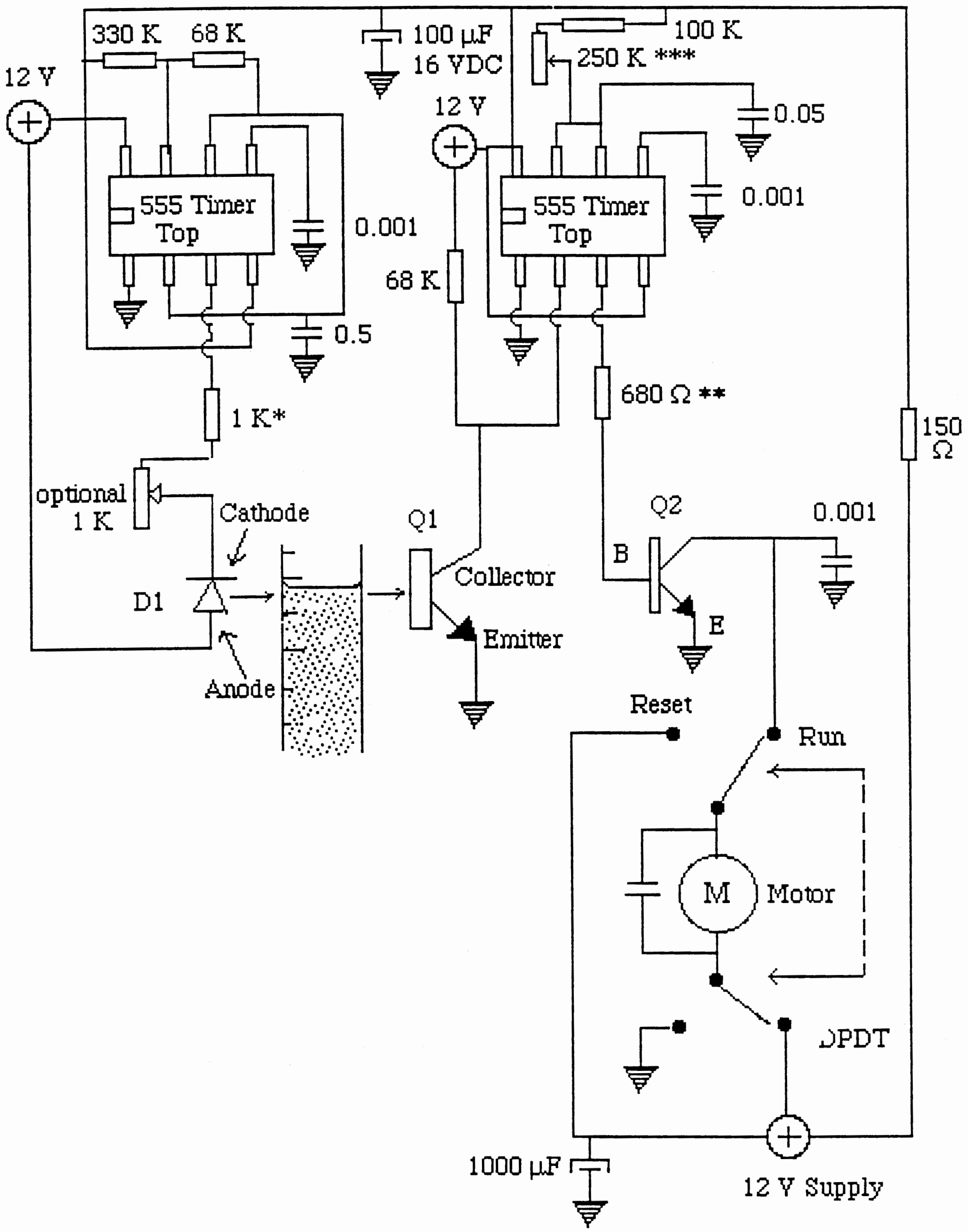


Figure 26. Circuit diagram for automatic level recorder for oxygen uptake apparatus. D1 and Q1 are infrared emitter and collector (Radio Shack Part # 276-142). Resistors are 1/2 watt 5%. *Adjusts D1's output ** Adjusts Q2 Drive. *** Adjusts Pulse width to Q2

CHAPTER III

EPOXIDATION OF ALKENES WITH SODIUM HYPOCHLORITE CATALYZED BY A WATER-SOLUBLE MANGANESE(III) TETRAARYLPORPHYRIN ON POLYMER COLLOIDS

Introduction

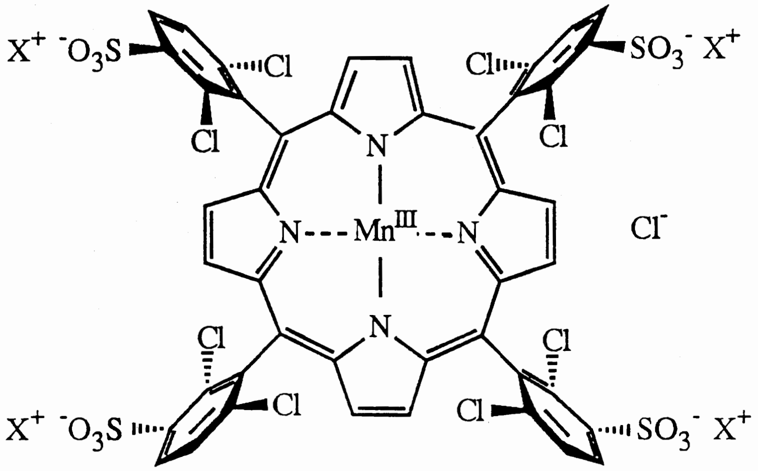
The synthetic metallotetraarylporphyrins have been used extensively to model the natural heme prosthetic group protoporphyrin IX in cytochrome P-450 enzymes.[59] They were found to act as catalysts for the transfer of oxygen to hydrocarbons with formation of epoxides from alkenes and alcohols from alkanes.[18-20,59] As oxygen sources iodosylbenzene, hypochlorite, molecular oxygen in the presence of an electron source, alkyl hydroperoxides, hydrogen peroxide, amine *N*-oxides, and potassium hydrogen persulfate were employed.[19,20,59]

Unfortunately, metallotetraarylporphyrins are easily deactivated by oxidants. The activity losses of the metallotetraarylporphyrins are caused by autocatalytic oxidative destruction and irreversible formation of μ-oxo dimers.[83,85] The stability of a porphyrin depends on the nature of the oxidizing species as well as the substituents on the phenyl and pyrrole moieties of the porphyrin. In order to get a deeper insight into the effects of substituents on the porphyrin stability, a few systematic studies have been conducted.[66,69,82,83,85,93]

The characterization of metallotetraarylporphyrins in different oxidation states is often done by UV/visible spectroscopy,[81,129-131,176] ^{1}H NMR spectroscopy,[177,178] IR spectroscopy,[177] stopped-flow spectrophotometry,[176] ESR spectroscopy,[176,178] and rapid-repitative scan spectrophotometry.[178] Some of these methods were employed to measure the stabilities of metallotetraarylporphyrins as well.

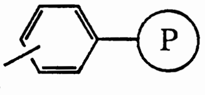
The oxidations of water-insoluble compounds in aqueous dispersions are rarely investigated and reported in the literature.[50,51,57,58,108] Epoxidations are not an exception, even though most of the oxidizing agents used in epoxidations are inorganic and soluble in water. When the primary oxidizing agent is water-soluble, most often biphasic mixtures are used for epoxidations. Organic solvent dissolves the substrate and the metalloporphyrin, and keeps the metalloporphyrin away from the aqueous oxidant. However, some metallotetraarylporphyrin epoxidations have been performed in aqueous media. 5,10,15,20-Tetrakis[4-(hexadecyloxy)phenyl]porphinatomanganese(III) acetate with colloidal Pt in polymerized vesicle dispersions was used in the epoxidations of water-soluble 2,5-dihydrofuran and water-insoluble styrene with dioxygen.[97] Water-soluble polymer-bound Mn-, Cr-, and Fe-5,10,15,20-tetrakis(4-aminophenyl)porphyrins and water-soluble low molecular-weight Mn-5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin and Mn-5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)porphyrin catalyzed epoxidation of water-soluble 2,5-dihydrofuran with hypocholorite in aqueous solution.[96] The transfer of mono-oxygen was efficient and the results of epoxidation of 2,5-dihydrofuran were not affected by polymer and the charges on the porphyrin.

In this research the water-soluble and oxidative self-destruction resistant tetrasodium salt of 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) chloride [**65**, $Mn(III)TSPPCl_8Na_4$ (Cl)] was prepared in three steps and used as a catalyst for the epoxidation of styrene and derivatives. The epoxidations were carried out with 0.25 M sodium hypochlorite (NaOCl) as the oxidant in the absence and presence of colloidal polymers (latexes) containing quaternary ammonium groups which bind the metallotetraarylporphyrin ionically. Both homogeneous and latex containing reactions gave styrene oxide. Colloidal polymers were first prepared by emulsion polymerization of mixtures of chloromethylstyrenes and divinylbenzene, and then treated with trimethylamine to give highly ionic, hydrophilic, crosslinked latexes.



65 X^+ : Na^+

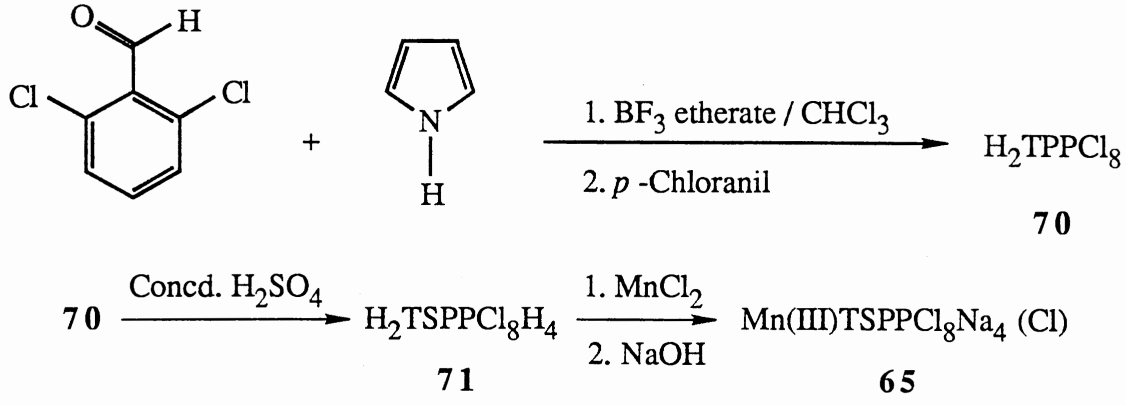
72 X^+ : $(CH_3)_3N^+CH_2$



Results

Porphyrin Synthesis. Soluble porphyrin **65** was prepared in three steps as shown in Scheme V. The first step was formation of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**70**, H_2TPPCl_8) from pyrrole and 2,6-dichlorobenzaldehyde. Second the sulfonation of the phenyl moieties of the porphyrin introduced water solubilizing sulfonic acid groups and gave 5,10,15,20-tetrakis(2,6-dichloro-3-sulfophenyl)porphyrin (**71**, $H_2TSPPCl_8H_4$). The final step was the insertion of manganese to form the high spin d^4 porphyrin.

Scheme V. Synthesis of 5,10,15,20-Tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) Chloride (**65**)



A new method devoloped by Lindsey and coworkers[125,126] allows the synthesis of porphyrins under mild conditions in small quantities from temperature sensitive benzaldehydes and 2,6-disubstituted benzaldehydes without difficult purification problems. This method was adapted to prepare 5,10,15,20-tetrakis(2,6-dichlorophenyl)-porphyrin (**70**) which is the precursor of the tetrasodium salt of 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) chloride (**65**). The yields of 10-16% porphyrin **70** were higher than the 7% yield reported Banfi.[83] In the preparation of porphyrin **70** the progress of the reaction was not monitored spectrophotometrically, but the color of the reaction mixture was evidence that the reaction made little progress in 1 to 2 h. Lindsey[125] found 1 h to be the optimal time for reacting benzaldehyde (10^{-2} M) and pyrrole (10^{-2} M) catalyzed by BF_3 etherate (10^{-3} M), but did not specifically report preparation of porphyrin **70**. My use of $CHCl_3$ instead of CH_2Cl_2, and the use of high concentration of BF_3 etherate are the deviations from the original procedure.[125] Also the procedure employed water scavenger triethyl orthoacetate in some reactions. In fact, the acid concentration significantly changes the rate of the reaction but results in only slightly altered yields.[125] Recently it was reported[179] that in the preparation of 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin, the yield was 31% when the solvent was a commercial $CHCl_3$ which contains 0.75% (v/v) ethanol as a stabilizer. However the yield was 0% when the solvent was absolute CH_2Cl_2 or $CHCl_3$ without ethanol stabilizer. Addition of 0.75% (v/v) ethanol to absolute CH_2Cl_2 resulted in a 25% yield of 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin. Also crude $CHCl_3$ and distilled $CHCl_3$ from K_2CO_3 gave nearly identical yields of 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin showing that distillation was ineffective in removing ethanol from $CHCl_3$.

After the synthesis of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**70**), solvent was rotary evaporated. The porphyrin **70** was separated from some of the impurities by filtration of the methanol solution and purified by column chromatography on silica gel and crystallization from $CHCl_3$/n-heptane.

Table XVI lists the quantities of the starting materials, acid, oxidant used, and durations of condensation and oxidation in the preparation of seven batches of porphyrin **70**.

A modified procedure of the Rothemund reaction[122] described by Adler[124] was tried first to prepare 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**70**) by reacting 2,6-dichlorobenzaldehyde and pyrrole in refluxing propionic acid. The porphyrin **70** failed to crystallize or precipitate at the end of reaction. Column chromatographies on Florisil® and alumina also did not separate the porphyrin fraction. Banfi reported <<1% yield of porphyrin **70** with the Adler procedure.[69]

Table XVI. Syntheses of 5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphyrin (**70**)[a]

	pyrrole, mmol	DCBA,[b] mmol	BF_3 etherate, mmol	reaction time, h	reflux time, h	yield[c] %
1	9.3	9.3	4.0	21	2.5	11
2	10.1	10.1	4.0	21	3	16
3	10.3	10.3	3.9	21	3	11
4	9.4	9.4	3.9	45	2.5	10
5[d]	7.8	7.8	3.1	45	2.5	10
6	10.3	10.3	4.0	23	3	15
7	10.4	10.4	3.8	23	3	13

[a] The volume of $CHCl_3$ was 1 L. [b] DCBA: 2,6-Dichlorobenzaldehyde. [c] Based on % of 2,6-dichlorobenzaldehyde or pyrrole moieties in porphyrin **70**. [d] The volume of $CHCl_3$ was 800 mL.

The procedure for sulfonation of tetraphenylporphyrin described by Fleischer[180] and by Zipplies[181] was used with some modifications to sulfonate porphyrin **70**. More vigorious conditions were needed to sulfonate the electron deficient 2,6-dichlorophenyl groups of porphyrin **70**, and less than one sulfonate group per phenyl ring was achieved. Elemental analysis and ^{1}H NMR analysis showed 3.4-3.5 sulfonate groups per porphyrin, which was enough to provide water solubility as well as binding sites to colloidal quaternary ammonium ion exchange resins (latexes). This partial substitution led an isomeric mixture of the 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrin (**71**) with mostly 3 and 4 sulfonate groups per porphyrin. ^{1}H NMR was used to detemine the extent and the position of the sulfonate substitution by comparing the areas of *m*-Hs at 7.9-8.1 ppm and *p*-Hs at 8.4-8.6 ppm with the area of 16β-H of pyrrole moiety at 8.9-

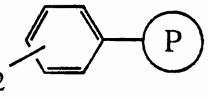
9.1 ppm. Most of the substitutions occurred on the carbon at 3 position due to ortho-para directing ability of Cl groups. However about 25% of the sulfonic acid groups were at the 4-position. Concd. H_2SO_4 was the sulfonation reagent (Scheme V).

The method used to incorporate manganese into porphyrin **6** was adapted from Fleischer,[180] Zipplies,[181] and Harriman.[130] Treatment of porphyrin **71** with $MnCl_2$ resulted in only partial metalation of the porphyrin **71** (in Na^+-form). However it is not clear whether metalation is not complete at the metalation stage or manganese is lost during the ion-exchange process employed for the removal of the excess manganese cations. During the metalation, care was taken to keep the pH of the reaction mixture between 6.0 and 9.5 by addition of NaOH so the reaction of porphyrin **71** (in Na^+-form) with $MnCl_2$ could proceed. At pH <6, the metalation ceases and the metal ion is lost from the metalated porphyrin.[180] Due to high solubilities of porphyrin **65** and impurities in methanol, the further purification after ion exchange was difficult, and attempts to precipitate porphyrin **65** from methanol into acetone failed. This precipitation procedure was used successfully in the further purification of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphinatomanganese(III).[180] The elemental analyses of two batches of porphyrin **65** gave 85 and 65% managanese incorporation and presence of 1 and 11 mols of NaCl per porphyrin.

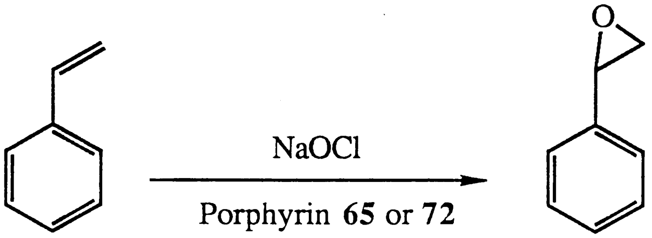
Porphyrin **65** is soluble at $<10^{-2}$ M in water and methanol. The binding of porphyrin **65** to colloidal quaternary ammonium ion exchange resins (latexes) was quantitative (>99.9%) according to UV/visible spectrophotometry. The binding force was the ionic attraction of SO_3^- groups of porphyrin **65** to trimethylbenzylammonium groups of the latex (eq. 26).

$$\mathbf{65} \quad + \quad R_4N^+\,Cl^- \longrightarrow \underset{\mathbf{72}}{Mn(III)TSPPCl_8(NR_4)_4\,(Cl)} + 4NaCl \qquad (26)$$

where R_4N^+ : $(CH_3)_3N^+CH_2$



Epoxidation of Styrene. Styrene (1.20 mmol) was epoxidized by sodium hypochlorite (1.50 mmol) in the presence 2.22 x 10^{-3} mmol of soluble porphyrin **65** and latex-bound porphyrin catalysts (**72**) in 6.0 mL aqueous dispersions at room temperature (eq. 27). The reaction usually was carried in NaOH solution (>0.1 M) to retard oxidative destruction of the Mn porphyrin[66,69,82,83,85,93] and prevent the formation of the powerful oxidizing agent hypochlorous acid (pK_a 7.54).[182]



(27)

In the absence of the catalyst, hypochlorite did not react with styrene. The catalytic reaction is highly selective for epoxide. The only by-product observed was <1% of benzaldehyde. A typical reaction mixture contained 1040:830:1.54:1 relative molar amounts of hypochlorite: styrene: porphyrin **65**: Mn(III).

When latex-bound porphyrin **72** was used as a catalyst, a higher amount of styrene oxide was obtained than when soluble porphyrin **65** was used. As given in Table XVII, the activities of the catalysts bound to different colloidal quaternary ammonium anion exchange resins (latexes) were similar. The type of surfactant used to prepare the latexes and the degree of crosslinking of the latexes did not affect the outcome of the reaction to any great extent. The yield of the reaction 5 in Table XVII was comparable to the yields of other reactions, although reaction 5 was carried out in the presence of pyridine under different conditions.

The time course of the styrene epoxidation catalyzed by latex-bound porphyrin **72** shows 47% conversion to styrene oxide in the first 15 min, and then the reaction slows down (Figure 27).

Table XVII. Epoxidation of Styrene with NaOCl Catalyzed by Soluble Porphyrin **65** and Latex-Bound Porphyrin **72**[a,b]

expt.	latex,[c]	latex, mg	styrene, mmol	styrene oxide,[d] %
1	-	-	1.24	32
2	L-10	40.4	1.20	71
3	L-12	40.8	1.18	78
4	L-6	40.4	1.19	73
5[e]	L-8	48.0	1.20	81

[a] Porphyrin **65** = 2.22 x 10^{-3} mmol [65% of porphyrin rings contain Mn(III)]. [NaOCl] = 0.25 M, [NaOH] = 0.38 M, volume 6.0 mL, reaction time 1 h. [b] The reaction mixtures were stirred. [c] For latexes see Chapter II, Table VIII. [d] Determined by GLC analysis. The estimated error is ± 5%. The remainder is styrene. Benzaldehyde (<1%) was not included in calculations. [e] Porphyrin **65** = 2.59 x 10^{-3} mmol, [NaOCl] = 0.185 M, [NaOH] = 0.57 M, pyridine = 10 μL, volume 6.7 mL.

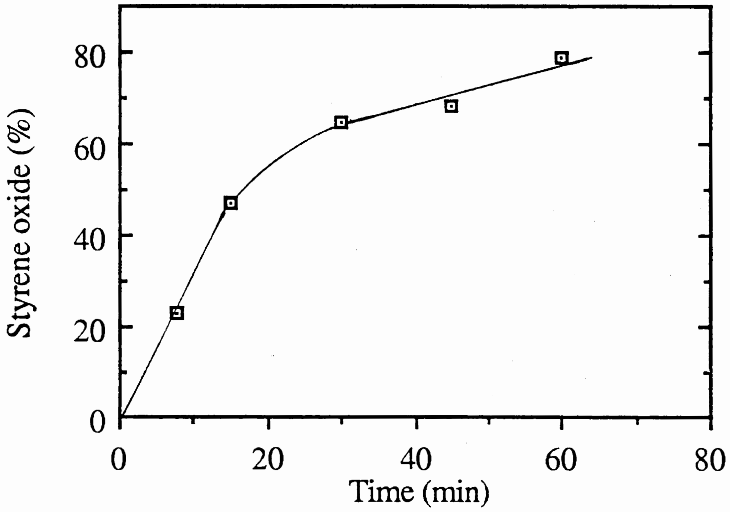


Figure 27. The time course of the styrene epoxidation catalyzed by porphyrin **72** bound to 40.4 mg of latex L-10 (see Chapter II, Table VIII). Conditions were those of footnote *a* of Table XVII. The reaction mixtures were shaken.

At constant amount of porphyrin **72** bound to varied amounts of latex, % conversion to styrene oxide increased with the amount of latex used (Table XVIII).

Table XVIII. Epoxidation of Styrene: Effect of the Latex Concentration[a]

expt.	latex,[b] mg	styrene, mmol	styrene oxide,[c] %
1	40.4	1.20	71
2	20.2	1.20	63
3	10.1	1.26	39
4	-	1.24	32
5[d]	40.4	1.25	0

[a] Conditions were those of footnote *a* and of Table XVII. [b] Latex L-10 (see Chapter II, Table VIII). [c] See footnote *d* of Table XVII, [d] No manganese porphyrin was present.

At constant latex concentration, % conversion decreased when the porphyrin concentration was decreased (Table XIX).

Table XIX. Epoxidation of Styrene: Effect of Concentration of Porphyrin **65** Bound to Latex[a,b,c]

expt.	[Mn(III)] x 10^4 M	styrene, mmol	styrene oxide,[d] %
1	2.41	1.20	71
2	1.32	1.18	55
3	0.60	1.18	26

[a] Conditions were those of footnotes *a* and *b* of Table XVII. [c] 40.4 mg of latex L-10 (see Chapter II, Table VIII). [d] See footnote *d* of Table XVII.

The solubility of styrene is 0.07 g per L of water at room temperature,[183] and is expected to be lesser in a high ionic strength solution. Due to limited solubility of styrene in the aqueous phase where the reaction takes place, the rate of the epoxidation might be limited by mass transfer of styrene from droplets to latex particles rather than by chemical reactivity. Therefore several techniques were used to mix the substrate with the aqueous phase, as shown in Table XX.

Table XX. Epoxidation of Styrene: Effect of the Mixing Method[a]

expt.	porphyrin	mixing method	reaction container	styrene, mmol	styrene oxide,[b] %
1[c]	latex-bound (**72**)	shaking[d]	20 mL test tube	1.20	79
2[c]	latex-bound (**72**)	stirring	25 mL flask	1.20	71
3[c,e]	latex-bound (**72**)	stirring	25 mL flask	1.22	25
4[c]	latex-bound (**72**)	rotating[f]	12 mL conical tube	1.23	61
5[c]	latex-bound (**72**)	sonication	25 mL flask	1.19	6
6	soluble (**65**)	shaking[d]	20 mL test tube	1.21	46
7	soluble (**65**)	stirring	25 mL flask	1.24	32
8[g]	soluble (**65**)	osc. shaking[h]	25 mL flask	1.19	31

[a] Conditions were those of footnote *a* of Table XVII. [b] See footnote *d* of Table XVII. [c] 40.4 mg of latex L-10 (see Chapter II, Table VIII). [d] A wrist action shaker with 5-cm amplitude and a frequency of 160 per min was used. [e] 0.15 volume fraction methanol was present. [f] Test tube was clamped in the middle to a head stirrer which was positioned with a 45° angle relative to the bench and rotated end over end. The stirring speed was about 400 rpm. [g] [NaOCl] = 0.21 M and [NaOH] = 0.63 M. [h] An oscillating shaker was used.

All other methods of mixing gave higher yields than sonication did, and the wrist shaking method gave the highest amount of styrene oxide (reaction 1, Table XX). When 0.15 volume fraction methanol as a co-solvent was added to one of the reaction mixtures, the reaction unexpectedly gave very poor yield (reaction 3, Table XX).

As given in Table XXI, the addition of external ligands such as pyridine and 1-methylimidazole to the reaction mixtures had little effect on the reaction.

Table XXI. Epoxidation of Styrene with Soluble Porphyrin **65** Catalyst[a]

expt.	ligand	porphyrin **65** x 10^3 mmol	[ligand]/ [porphyrin]	styrene, mmol	volume, mL	[NaOH], N	styrene oxide,[b] %
1	1-MeIm[c]	2.59	47	1.15	6.2	0.61	40
2	pyridine	2.59	49	1.25	5.5	0.69	44
3	-	2.22	-	1.39	5.2	0.73	43

[a] 1.24 mmol of NaOCl was used. The reaction time was 3 h, and the reaction mixture was stirred magnetically. [b] See footnote *d* of Table XVII. [c] 1-MeIm: 1-methylimidazole.

Epoxidation showed little dependence on the concentration of manganese porphyrin, or on the concentrations of oxidant and styrene when one of them was used in excess, but substantial rate increases occurred when latex was present in the reaction mixture (Table XXII).

Table XXII. Epoxidation of Styrene: Effects of Concentrations of Porphyrin, Oxidant, and Styrene[a]

expt.	porphyrin	styrene, mmol	NaOCl, mmol	[NaOH], M	mixing method	styrene oxide,[b] %
1[c]	soluble (**65**)	1.20	1.50	0.62	stirring	31
2	soluble (**65**)	1.26	1.24	0.63	stirring	27
3	soluble (**65**)	1.24	1.50	0.38	stirring	32
4	soluble (**65**)	1.19	1.24	0.63	shaking[d]	31
5[e]	latex-bound (**72**)	1.20	1.50	0.38	stirring	71
6[e]	latex-bound (**72**)	2.11	1.50	0.38	stirring	31
7[e]	latex-bound (**72**)	1.22	2.23	0.38	stirring	68

[a] Conditions were those of footnote *a* of Table XVII. [b] See footnote *d* of Table XVII. [c] Volume was 3.7 mL. [d] An oscillating shaker was used. [e] 40.4 mg of latex L-10 (see Chapter II, Table VIII).

The basicity of the reaction mixture had one of the most remarkable effects on epoxidation. The pH effect on the epoxidation was studied at constant 0.63 M ionic strength, maintained by adding NaCl when needed. As hydroxide ion concentration increased, the amount of epoxide formed increased, as shown in Table XXIII. At even higher ionic strength, the yield was slightly lower (expt. 5, Table XXIII).

The experiments in Tables XVII to XXIII used commercial laundry bleach. Styrene epoxidation carried out with NaOCl solution freshly prepared from chlorine and aqueous NaOH gave 63% and 72% styrene oxide. Due to low ClO^- concentration of this solution, the reaction was carried out in 9.2 and 7.9 mL respectively rather than usual 6.0 mL (Table XXIV).

Table XXIII. Epoxidation of Styrene: pH Effect[a]

expt.	styrene, mmol	[OH],[b] M	[NaCl],[c] M	styrene oxide,[d] %
1	1.17	6.5×10^{-4}	0.63	61
2	1.27	0.01	0.62	54
3	1.22	0.06	0.57	74
4	1.20	0.38	0.25	79
5	1.22	0.81	0.25	69
6[e]	1.19	3.2×10^{-5}[f]	0.65[g]	50

[a] Conditions were those of footnote *a* of Table XVII. The reaction mixtures were shaken. 40.4 mg of latex L-10 (see Chapter II, Table VIII). [b] $[OH] = 6.5 \times 10^{-4}$ M contribution from bleach solution (calculated from the pH of the bleach) plus added NaOH. The pH of the bleach solution was 11.3. [c] [NaCl] = 0.25 M from bleach solution plus added NaCl. The NaCl concentaration of the bleach was estimated from the reaction of 2 moles of NaOH with 1 mole of Cl_2 which gives 1 mole of NaOCl, NaCl, and H_2O each. [d] See footnote *d* of Table XVII. [e] Porphyrin **65** = 3.03×10^{-3} mmol [85% of porphyrin rings contain Mn(III)]. [f] pH 9.5. [g] [NaCl] = 0.25 M from bleach solution plus added NaCl (1.35 mmol) and HCl (0.91 mmol).

Table XXIV. Epoxidation of Styrene with Freshly prepared NaOCl[a]

expt.	source of NaOCl	styrene, mmol	NaOCl, mmol	[NaOH], M	solume, mL	styrene oxide,[b] %
1	fresh prep.	1.28	1.50	0.25	9.2	63
2	fresh prep.	1.32	1.49	0.29	7.9	72
3	Clorox®	1.20	1.50	0.38	6.0	79

[a] Conditions were those of footnote *a* of Table XVII. Reaction mixture was shaken. 40.4 mg of latex L-10 (see Chapter II, Table VIII). [b] See footnote *d* of Table XVII.

In order to find if the catalyst retains its activity, epoxidations were carried out for 1 h and for 2 h. The yields of the 1 h and 2 h reactions were the same within experimental error. When a second batch of styrene and hypochlorite was added to the reaction mixture 1 h after the addition of the first batch, and the reaction was run an additional 1 h, the catalyst showed loss activity than during the first hour (reaction 3, Table XXV).

Table XXV. Epoxidation of Styrene: Recycle of Catalyst[a]

expt.	styrene, mmol	volume, mL	reaction time, h	styrene oxide,[b] %
1	1.20	6.0	1	79
2	1.15	6.0	2	76
3	1.17+1.19	6.0-8.2	1+1	63

[a] Conditions were those of footnote *a* of Table XVII. 40.4 mg of latex L-10 (see Chapter II, Table VIII). Reaction mixtures were shaken. [b] See footnote *d* of Table XVII.

In another approach to find if the catalyst retains its activity, the reaction was run with excess styrene (19.2 mmol), and 1.50-1.51 mmol portions of hypochlorite were added at 11 min intervals. Ten min after the addition of each batch of NaOCl, a sample from the reaction mixture was analyzed by GLC (Figure 28). The product analyses showed styrene oxide (>99%) as major product and benzaldehyde (<1%). The rate of epoxidation of styrene was extremely fast during the first 10 min after addition of the first batch of NaOCl. As time progressed, the epoxidation slowed down even though new batches of NaOCl were added. After 5-5.5 h, the color of the reaction mixture was yellow, which indicates the bleaching of the red-brown latex-bound porphyrin **72.** After 30 h, GLC analysis showed no increase in the amount of products, and partial conversion to a mixture of styrene oxide (60%) and benzaldehyde (40%).

When a similar experiment was carried out with fewer additions of NaOCl and with longer reaction time, comparable results to the ones in Figure 28 were obtained (Figure 29).

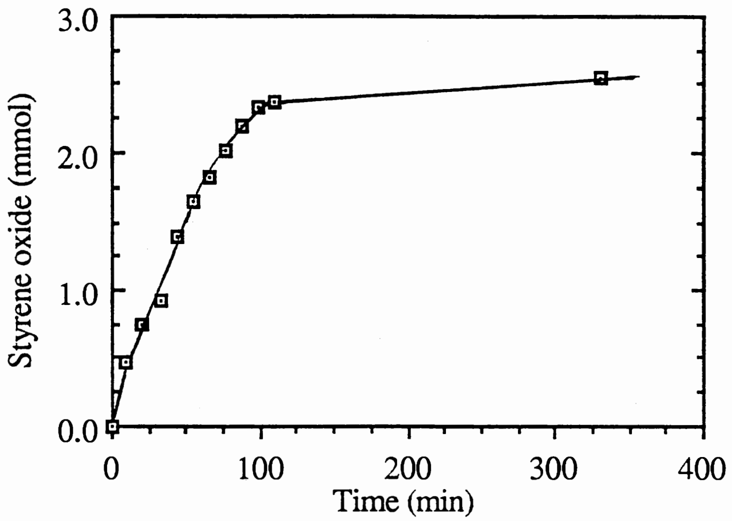


Figure 28. The time course epoxidation of 19.2 mmol of styrene. 1.50-1.51 mmol of NaOCl was added at 0, 11, 22, 33, 44, 55, 66, 78, 89, and 100 min, and 6.05 mmol of NaOCl was added at 111 min.

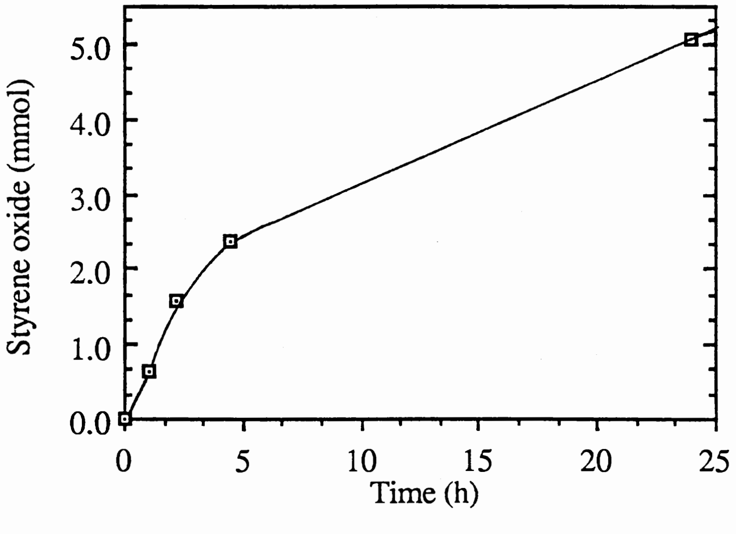


Figure 29. The time course of epoxidation of 23.4 mmol of styrene. 1.50 mmol of NaOCl was added at 0, 60, 130, and 270 min, and 3.0 mmol of NaOCl was added at 330 min.

Several different compounds were tested for catalytic activity, but only soluble porphyrin **65** was able to epoxidize styrene. $MnCl_2$, Mn (acetate)$_2$, and 5,10,15,20-tetrakis(4-sulfonatophenyl)porphinatomanganese(III) acetate (**54**) were inactive. The inactivity of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphinatomanganese(III) (**54**) was due to fast destruction of the porphyrin by NaOCl, observed as bleaching of its green-brown color in seconds under reaction conditions. Latex without porphyrin **65** was also inactive.

Epoxidation of Styrene Derivatives. The catalytic activity of latex-bound porphyrin **72** was tested for epoxidations of 4-chlorostyrene, 4-methylstyrene, α–methylstyrene, and β-methylstyrene. The substituted styrenes gave much lower conversions to epoxides than styrene under identical conditions, as shown in Table XXVI.

Table XXVI. Epoxidations of Styrene and Derivatives with NaOCl Catalyzed by Latex-Bound Porphyrin **72**[a,b]

substrate	substrate, mmol	epoxide,[c] %
styrene	1.16	71
α–methylstyrene	1.19	37
4-chlorostyrene	1.23	22
4-methylstyrene	1.25	18
β-methylstyrene	1.18	<5[d]

[a] Porphyrin **65** = 3.01 x 10^{-3} mmol [85% of porphyrin rings contain Mn(III)], [NaOCl] = 0.25 M, [NaOH] = 0.38 M, volume 6.0 mL, reaction time 1 h, and reaction mixtures were shaken. [b] 40.4 mg of latex L-10 (see Chapter II, Table VIII).
[c] Determined by GLC analysis. [d] Product was not identified.

Competitive epoxidations of styrene and one of the styrene derivatives using the same amount catalyst and oxidant produced more of styrene oxide (38-48%) and less of the substituted styrene oxide (13-19%) (Table XXVII).

Table XXVII. Competition Experiments of Styrene and Derivatives[a]

			GLC analysis	
styrene,[b] mmol	X-styrene	X-styrene,[c] mmol	styrene oxide, %	X-styrene oxide, %
1.23	α-methylstyrene	1.19	43	19
1.22	4-methylstyrene	1.17	38	15
1.20	4-chlorostyrene[d]	1.20	48	13

[a] Conditions were those of footnote *a* of Table XXVI. [b,c] Starting materials. [d] The peaks of styrene oxide and 4-chlorostyrene do not resolve on GLC chromatograms. The amounts of styrene oxide and 4-chlorostyrene were calculated by using the areas of styrene and 4-chlorostyrene oxide on GLC chromatograms.

Attempted Epoxidations of Alkenes. Epoxidation of 1-decene, 1-octene, cyclooctene, *cis*-stilbene, and undec-10-en-1-ol were attempted under conditions similar to those of the styrene epoxidation. No epoxide from 1-decene was observed, and only trace amounts of product, presumably epoxide, from 1-octene, cyclooctene, and *cis*-stilbene were detected by GLC.

More effort was made to improve the oxidation of cyclooctene because it has been used extensively to test the activity of catalysts for epoxidations.[69,82,83,104] A co-solvent in which cyclooctene is incompletely miscible, such as methanol or acetonitrile, did not change the outcome of the reactions much (Table XXVIII). Although CH_3CN helped the reaction proceed slightly better, there was a phase separation of the 50% CH_3CN-H_2O mixture (reaction 3, Table XXVIII). With 22 volume % of CH_3CN there was no phase separation (reaction 5). When the reaction was carried out at 70 °C, the porphyrin bleached in 5-10 min (reaction 4, Table XXVIII). Also no epoxide was obtained from 1-decene in 50% CH_3OH-H_2O.

Table XXVIII. Attempted Epoxidation of Cyclooctene[a]

expt.	cyclooctene, mmol	NaOCl, mmol	volume, mL	solvent	product[b]
1	1.21	1.50	6.0	H_2O	trace
2	1.13	1.50	10.5	50% CH_3OH-H_2O	trace
3[c]	1.39	1.50	10.5	50% CH_3CN-H_2O	4%
4[d]	1.35	1.50	6.0	H_2O	trace
5	1.29	1.50	6.8	22% CH_3CN-H_2O	6%

[a] Reactions were carried out with 2.99 x 10^{-3} mmol porphyrin **65** [85% of porphyrin rings contain Mn(III)], 40.4 mg of latex L-10 (see Chapter II, Table VIII), 1.50 mmol NaOCl, and 2.3 mmol NaOH. The reaction time was 1 h. [b] Product was not identified. Percentages given were not corrected with GLC response factors. [c] Phase separation occurred with 50% CH_3CN-H_2O at high ionic strength. [d] Reaction was carried out at 70 °C.

Attempted Oxidation of Styrene with Dioxygen. Metalloporphyrins are known to activate dioxygen and add oxygen to the double bond of an unsaturated hydrocarbon.[102-107,184]

Oxidation of styrene with dioxygen was investigated in the presence of a water-soluble manganese porphyrin catalyst with 1-methylimidazole as a ligand and $NaBH_4$ as the reducing agent. The preliminary results obtained semiquantitatively showed that both soluble porphyrin **65** and 5,10,15,20-tetrakis(4-sulfonatophenyl)porphinatomanganese(III) acetate (**54**) catalyze autoxidation of styrene in low yield (Table XXIX).

1-Phenylethanol in major and acetophenone in minor quantities were the oxidation products. Presumably acetophenone forms first, then is reduced to 1-phenylethanol by the reducing agent, $NaBH_4$. When water was the solvent, about 10% of 1.2 mmol styrene was converted to 1-phenylethanol in 1 h and turnover number of the catalyst was about 30. When methanol was used as solvent, reactions gave lower yields than those run in water, and usually both acetophenone and 1-phenylethanol were obtained. No improvement was achieved by working at higher dioxygen pressure (ca. 2 atm), with different reducing agent (ascorbic acid), at different pHs, and with latex-bound catalyst.

Visible Spectrophotometry of Soluble Porphyrin 65 and Latex-Bound Porphyrin 72. Absorption spectra of soluble porphyrin **65** and latex-bound porphyrin **72** were used to elucidate both the nature of manganese species in different media and the stability of the porphyrin in the presence of hypochlorite. Also the absorption spectra of porphyrin **65** and porphyrin **72** were obtained during the epoxidation of styrene to styrene oxide.

An aqueous solution of porphyrin **65** showed a similar absorption spectrum to those of 5,10,15,20-tetrakis(4-pyridyl)porphinatomanganese(III) in water at pH 7 and 5,10,15,20-tetrakis(4-carboxyphenyl)porphinatomanganese(III) in water at pH 14.[81] The Mn porphyrins 5,10,15,20-tetrakis(4-pyridyl)porphinatomanganese(III), 5,10,15,20-tetrakis(4-carboxyphenyl)porphinatomanganese(III), 5,10,15,20-tetrakis(N-methyl-4-pyridyl)porphinatomanganese(III), and 5,10,15,20-tetrakis(4-sulfonatophenyl)-porphinatomanganese(III) (**54**) gave identical spectra in water.[130] In other words the nature of the water solubilizing group and the solvent polarity do not affect the absorption spectrum.

Table XXIX. Manganese Porphyrin Catalyzed Oxidation of Styrene by Molecular Oxygen[a]

expt.	porphyrin[b]	porphyrin, mmol	$NaBH_4$,[c] mmol	1-MeIm,[d] mmol	styrene, mmol	O_2, atm	solvent	product, %
4	**65**	2.50 x 10^{-3}	0.28	0.25	1.25	0.93	H_2O	1-Phenylethanol, 9%
5	**65**	3.39 x 10^{-3}	0.35	0.49	1.27	0.96	CH_3OH	-
7[e]	**65**	3.63 x 10^{-3}	0.36	0.41	1.28	2.0	CH_3OH	-
8[f]	**65**	3.54 x 10^{-3}	0.35	0.54	1.25	2.3	H_2O	1-Phenylethanol, 11%
11	**65**	2.47 x 10^{-3}	1.25[g]	0.21	1.19	2.0	H_2O	-
12[h]	**65**	2.47 x 10^{-3}	0.36	0.40	1.24	2.0	H_2O	-
13[i]	**72**	2.47 x 10^{-3}	0.33	0.39	1.30	2.0	H_2O	1-Phenylethanol, 4%
9[j,k]	**54**	2.25 x 10^{-3}	2.53	1.75	3.11	2.0	CH_3OH	Acetophenone, 18%
10[k]	**54**	2.25 x 10^{-3}	2.59	1.90	3.51	2.0	H_2O	1-Phenylethanol, 4%
2[k,l]	**54**	2.20 x 10^{-2}	2.53	1.68	3.17	-	CH_3OH	1-Phenylethanol, 70% + Acetophenone, 30%

[a] Volume was 3 mL, and reaction time was 1 h unless otherwise indicated. [b] Porphyrin **65**: tetrasodium salt of 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) chloride; porphyrin **72**: latex-bound 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) chloride; porphyrin **54**: tetrasodium salt of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphinato(III) acetate. [c] Reducing agent. [d] 1-MeIm: 1-Methylimidazole unless otherwise indicated. [e] pH was 10.6. [f] pH

was 10.1 buffered with 0.063 mmol $Na_2B_2O_7$. Volume was 3.5 mL. [g] Reducing agent was sodium ascorbate. [h] Reaction was carried out in 0.38 M NaOH. [i] 40.4 mg of latex was present. [j] pH was 11.1. [k] Volume was 10 mL. [l] Molecular oxygen was bubbled into mixture. Reaction time was 2.5 h.

The titration of soluble porphyrin **65** (9.90 x 10^{-5} M) with NaOH from pH 7.0 to 11.9 caused only small changes the spectra with a small decrease of the intensity of the band at λ_{max} 464 nm. The concentration of soluble porphyrin **65** was chosen for spectroscopy as close as possible to that of porphyrin **65** under reaction conditions. At [NaOH] >0.01 M, the intensity of absorption at λ_{max} 464 nm decreased substantially. When [NaOH] = 1.03 M, there was a shift of the band from 464 mn to 467 nm (Figure 30). The extinction coefficient of the absorption spectrum of any water-soluble metalloporphyrin shows a strong pH dependence, whereas the spectrum of the water-soluble metal-free porphyrin analogue does not.[130] This pH dependence arises because two water molecules coordinated to manganese at the axial positions in neutral solution can be deprotonated in basic solution. The ligands are both water molecules at pH <7.5. The first pK_a transition corresponds to loss of a proton from one of these water molecules. The second transition involves loss of a proton from second water molecule. The pK_1 and pK_2 values for 5,10,15,20-tetrakis(4-sulfonatophenyl)porphinatomanganese(III) were 8.6 and 11.6 respectively.[130]

The absorption spectra of the solutions of porphyrin **65** buffered with sodium borate at pH 9.0 in the absence and in the presence of 0.22, 1.7, and 8.5 mg of latex per mL showed gradual decrease of the maximum absorbance, broadening, and shift toward longer wavelength (about 10 nm) of the major band as the amount of the latex increased (Figure 31).

The absorption spectrum of oxidized porphyrin **65** in the presence of NaOCl (0.065 M) in 0.38 M NaOH showed a broad band at λ_{max} 416 nm which is similar to the band of oxidized 5,10,15,20-tetrakis(4-carboxyphenyl)porphinatomanganese at λ_{max} 420 nm[81] (Figure 32). Soluble porphyrin **65** gave a short lived species at 432 nm. After porphyrin **65** in 0.39 M NaOH was treated with 1.32 x 10^{-2} M NaOCl, the spectrum obtained in the first minute showed a stronger band at λ_{max} 432 nm than at λ_{max} 415 nm (Figure 33). The second scan of this sample after 6 min showed stronger absorption at

415 nm than at 432 nm. The origin of this short lived at λmax 432 nm species is not known. However at low pH (pH 10.8) and in the presence of 1.32 x 10^{-2} M NaOCl, porphyrin **65** (1.32 x 10^{-5} M) gave no band at 432 nm. The spectrum of oxidized porphyrin **72** bound to different amounts of latex under the same conditions showed two distinct maxima at λmax 441-443 nm and λmax 422 nm (Figure 32). The two maxima were observed for the varying concentration of porphyrin **72** in the presence of constant amount of latex (Figure 34).

Manganese(III) porphyrins are oxidized with sodium hypochlorite to high valent manganese-oxo species. The oxidation products could be Mn(IV), Mn(V), and Mn(III) π-radical cation, or μ-oxo dimers of high valent manganese.[81] Some of the oxidation product is unstable and usually high alkali concentration is needed to stabilize to the manganese-oxo porphyrin.

Epoxidation of styrene (0.22 M) with NaOCl in 0.38 M NaOH solution in the presence of soluble porphyrin catalyst **65** was carried out, and five samples were withdrawn from this reaction mixture after 3, 13, 27, 44, and 60 min. The spectrum of every sample showed the same pattern but the absorption intensity of the band at λ_{max} 419 nm decreased as the reaction progressed (Figure 35). After 3 h, λ_{max} had shifted to 464 nm. When latex-bound porphyrin **72** was used as catalyst in the epoxidation of styrene under similar conditions to the homogeneous reaction, the oxidized porphyrin **72** showed two maxima during the first 27 min, one at λ_{max} 423 nm and the other at λ_{max} 441 nm. The next spectrum taken after 44 min showed the disappearence of the 441 nm band and appearance of a new band at 472 nm (Figure 36). This new species was stable and did not revert to the original porphyrin **72** (λ_{max} 470 nm) or to the high valent porphyrin **72** (λ_{max} 442 and 421 nm).

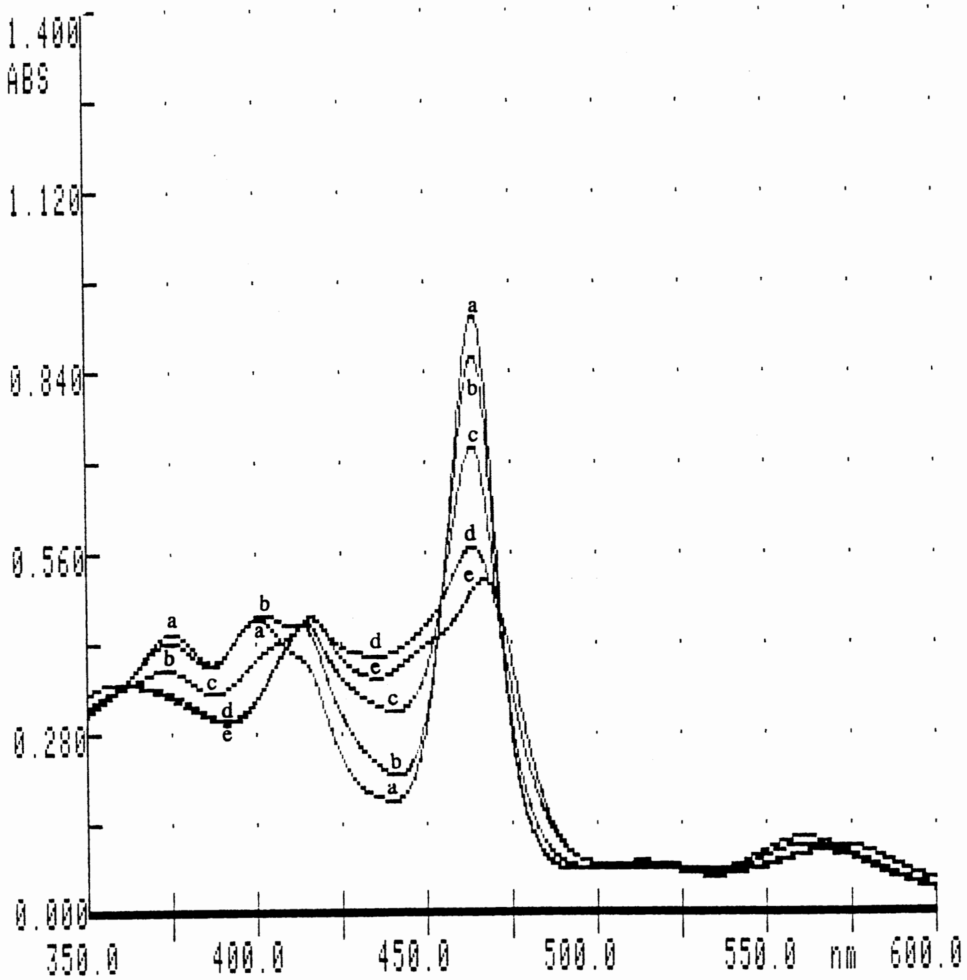


Figure 30. Absorption spectra of porphyrin **65** (9.90×10^{-5} M) as a function of NaOH concentration: (a), pH 7.0; (b), 0.01 M; (c), 0.06 M; (d), 0.38 M; (e), 1.03 M.

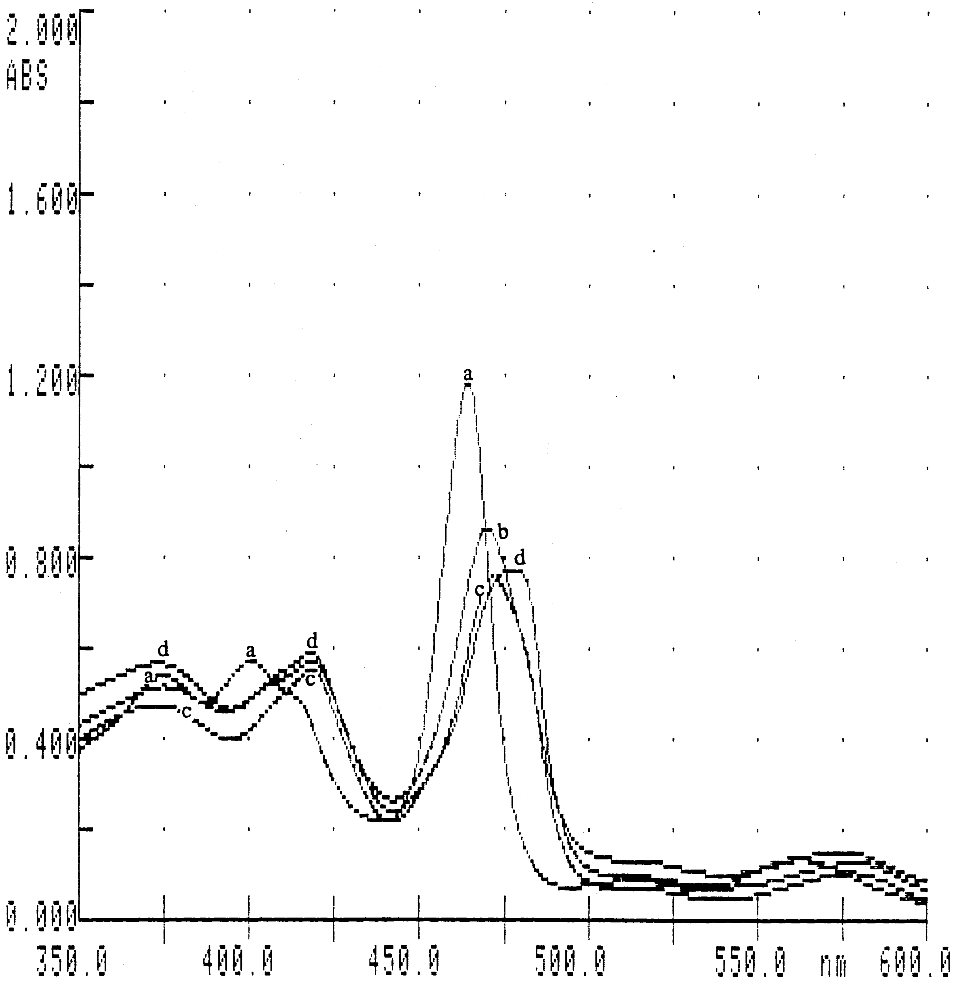


Figure 31. Absorption spectra of porphyrin **65** and **72** ([**65**] = 1.30 x 10^{-4} M) at pH 9.0 in the presence of 8.7 x 10^{-4} M sodium borate buffer and various amount of latex (L-10): (a), 0.0 mg mL^{-1}; (b), 0.22 mg mL^{-1}; (c), 1.7 mg mL^{-1}; (d), 8.5 mg mL^{-1}.

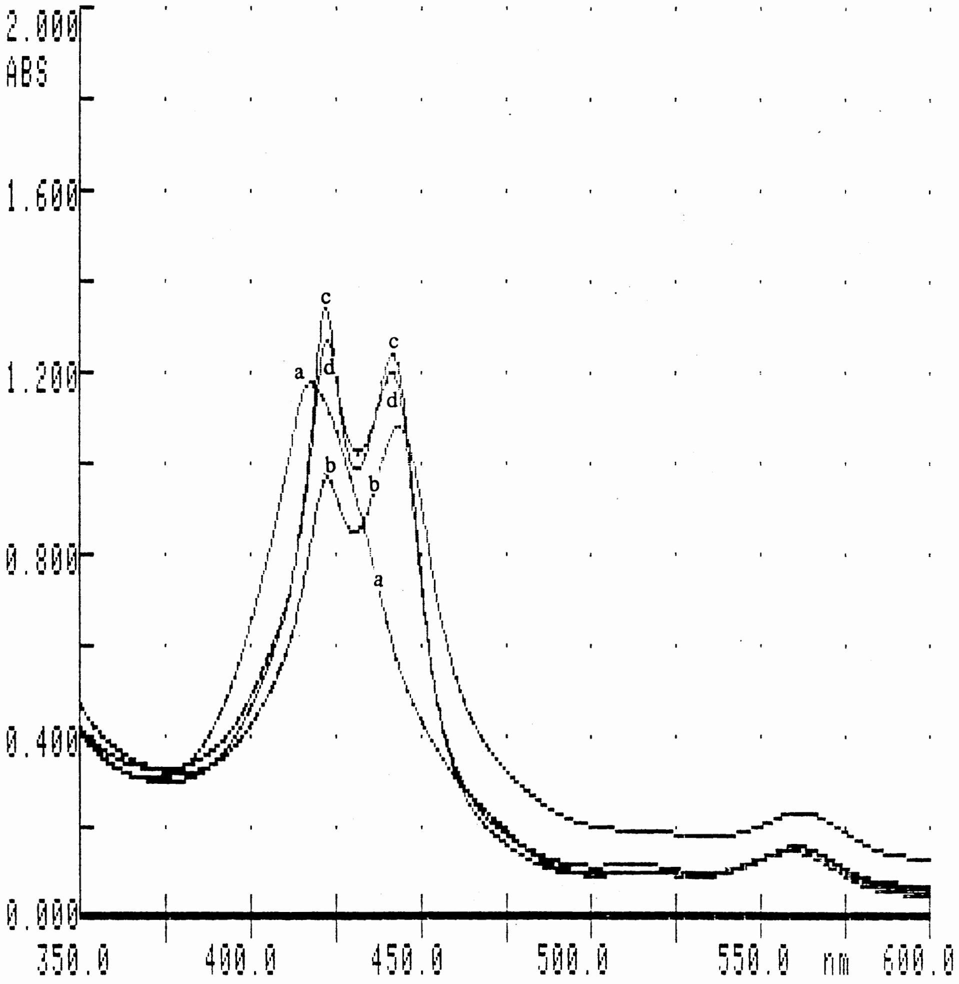


Figure 32. Absorption spectra of oxo-porphyrin **72** (**[65]** = 1.30 x 10^{-4} M) in 0.065 M NaOCl and 0.38 M NaOH in the presence of various amount of latex (L-10): (a), 0.0 mg mL^{-1}; (b), 0.22 mg mL^{-1}; (c), 1.7 mg mL^{-1}; (d), 8.5 mg mL^{-1}.

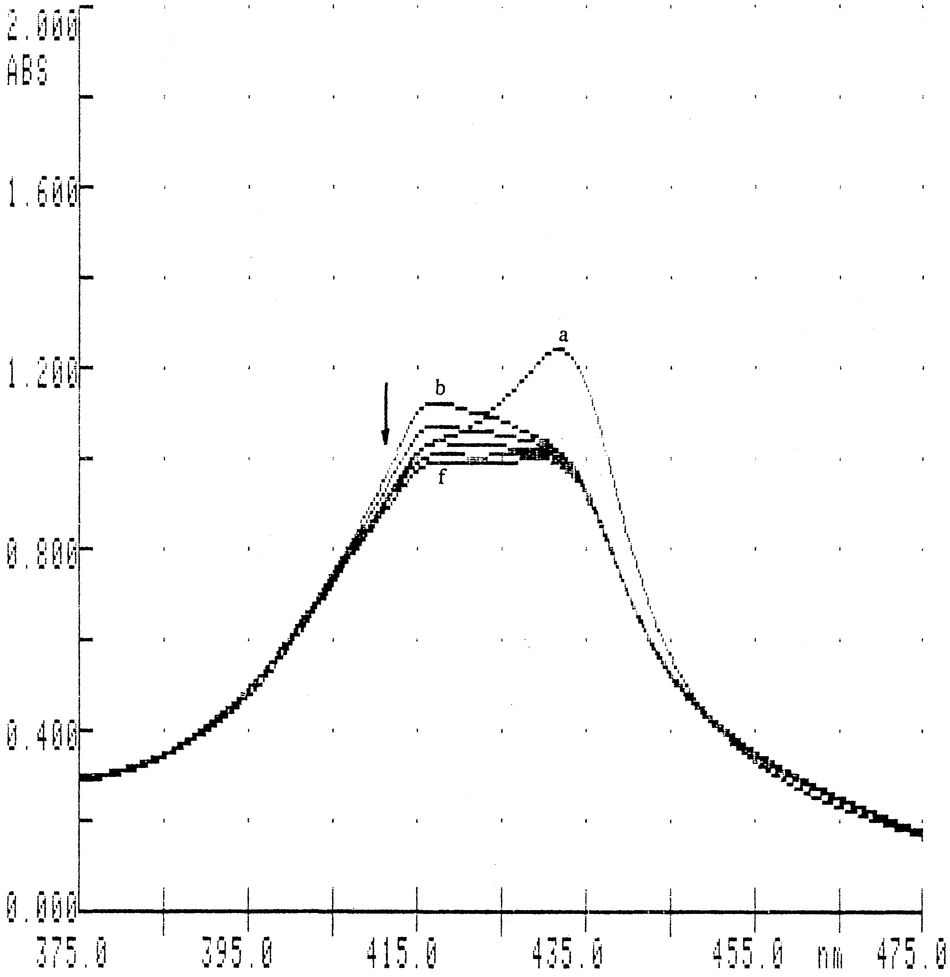


Figure 33. Absorption spectra of oxo-porphyrin **65** ([**65**] = 1.32 x 10^{-5} M) in the presence of 1.32 x 10^{-2} M NaOCl and 0.39 M NaOH as afunction of time: (a), 1 min; (b), 6 min; (c), 11 min; (d), 16 min; (e), 21 min; (f), 26 min.

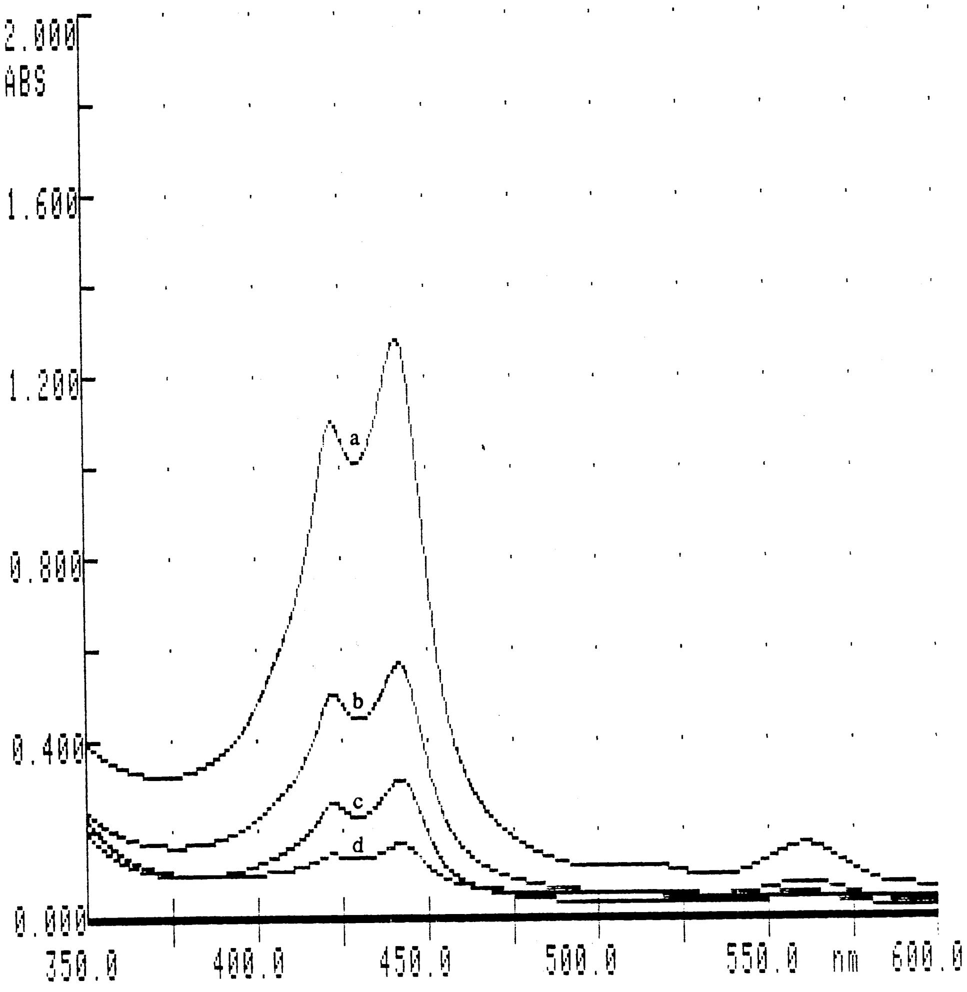


Figure 34. Absorption spectra of various concentrations of porphyrin **65** in the presence of 0.065 M NaOCl, 0.38 M NaOH, and 8.5 mg mL^{-1} latex (L-10): (a), 1.30 x 10^{-4} M; (b), 5.59 x 10^{-5} M; (c), 2.73 x 10^{-5} M; (d), 1.04 x 10^{-5} M.

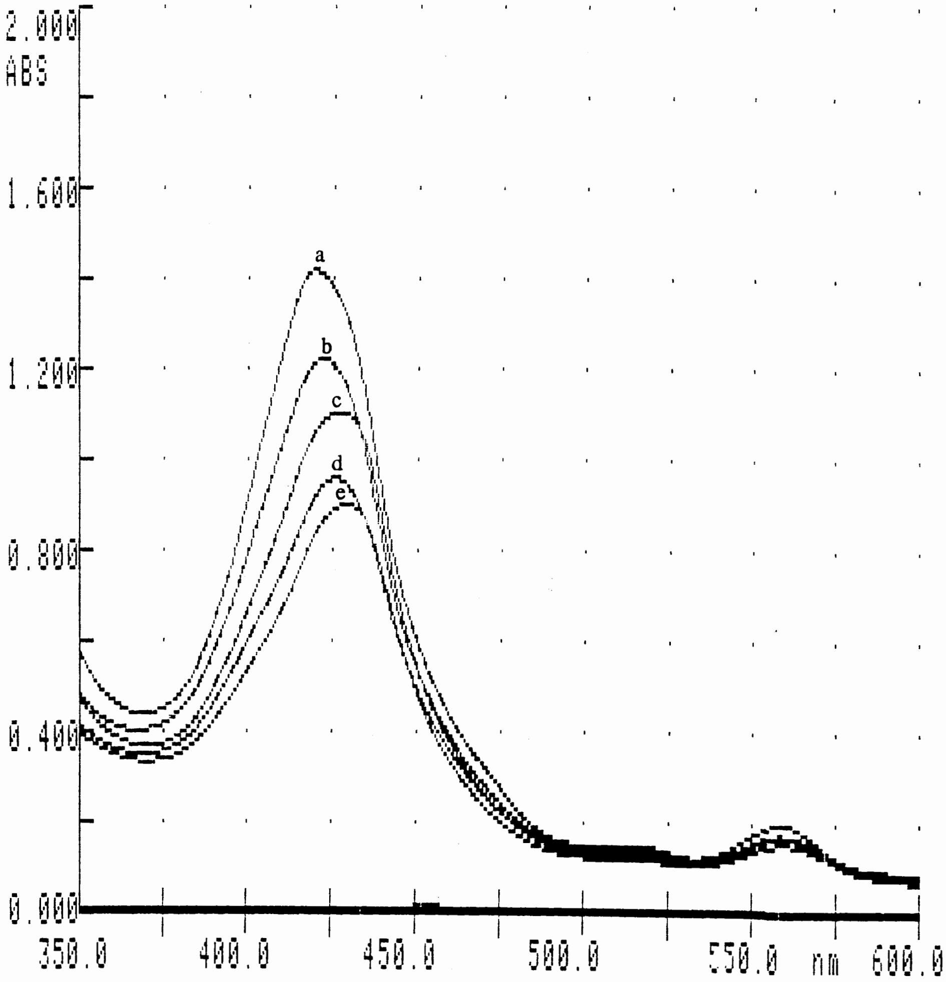


Figure 35. Absorption spectra of oxo-porphyrin **65** from sampling of styrene epoxidation mixture as a function of time: (a), 3 min; (b), 13 min; (c), 27 min; (d), 44 min; (e), 60 min. [**65**] = 2.0 ± 0.1 x 10^{-4} M, [NaOCl] = 0.25 M, [NaOH] = 0.38 M.

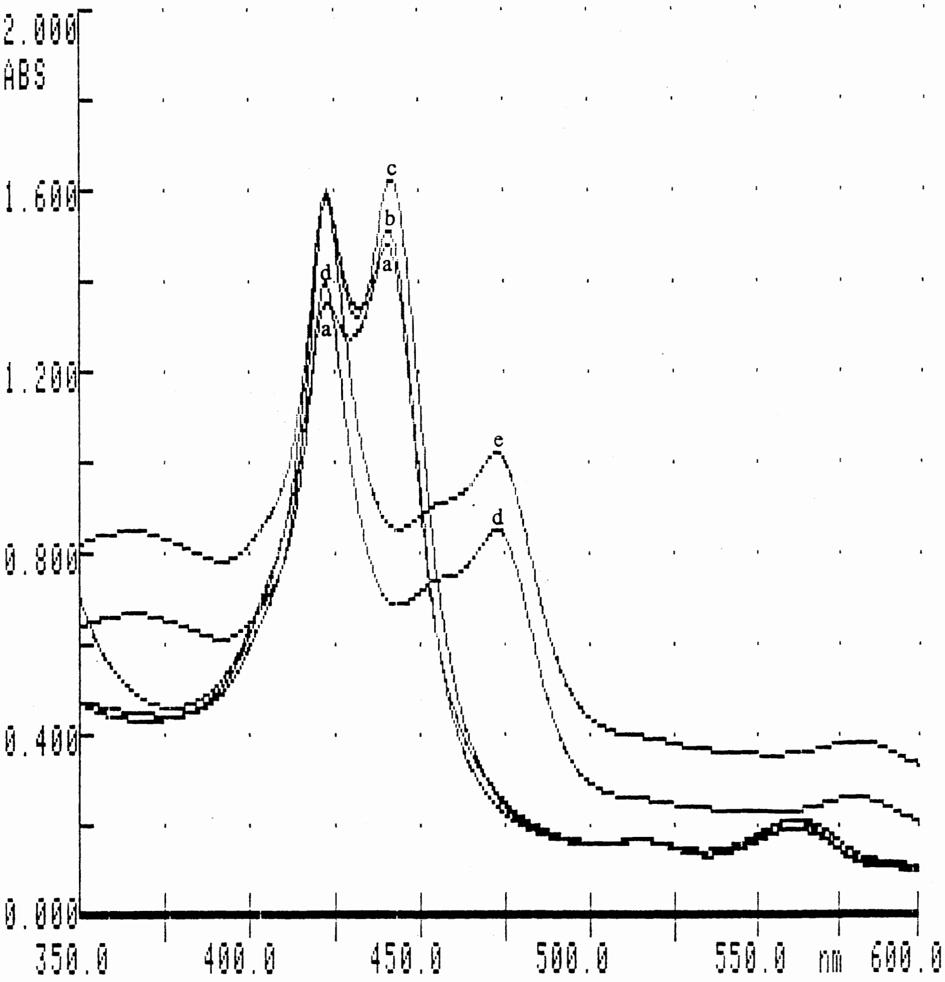


Figure 36. Absorption spectra of oxo-porphyrin **72** from sampling of styrene epoxidation mixture as a function of time: (a), 3 min; (b), 12 min; (c), 27 min; (d), 44 min; (e), 60 min. [**65**] = 2.0 ± 0.1 x 10^{-4} M, [NaOCl] = 0.25 M, [NaOH] = 0.38 M.

Stability Test of Soluble Porphyrin 65 and Latex-Bound Porphyrin 72: Since the instability of the oxidized product of soluble manganese porphyrin is pH dependent,[81,130,131] the stabilities of oxidized porphyrin **65** and porphyrin **72** were investigated at different NaOH concentrations. The spectral changes were followed to determine the stabilities of soluble porphyrin **65** and latex-bound porphyrin **72**. Absorption intensities were measured as the differences between absorbances at the 415-422 and 440-442 nm peak tops and a base line drawn tangent to the minima on each side of the peak. The rate of the disappearances and half-lives of the porphyrins were obtained from the data by using the least-square analysis and the error limits were estimated standard deviations of slopes.

The rate of the disappearance of oxo-porphyrin **65** was measured in the presence of 0.25 M NaOCl at pH 10.8. The first order plot gave the destruction rate constant 1.21 $\pm 0.03 \times 10^{-2}$ min^{-1} and the half-life 57 min (Figure 37).

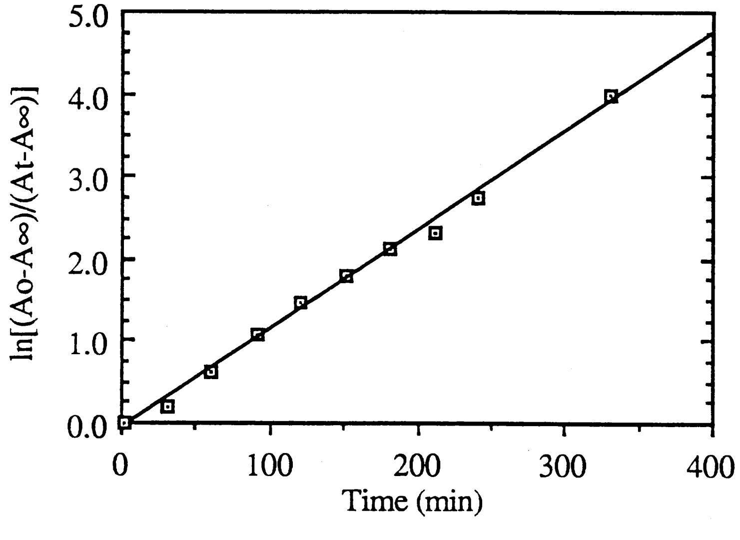


Figure 37. Plot of disappearance of soluble porphyrin **65** (1.33×10^{-5} M) with time in the presence of 0.25 M NaOCl at pH 10.8 at 30.0 °C. $A_{\infty} = 0.258$.

However the rate of disappearance of oxo-porphyrin **65** was much slower at high pH ([NaOH] = 0.38 M). The rate constant was 5.96 ± 0.35 x 10^{-4} min^{-1}, and the half-life was about 19.4 h (Figure 38).

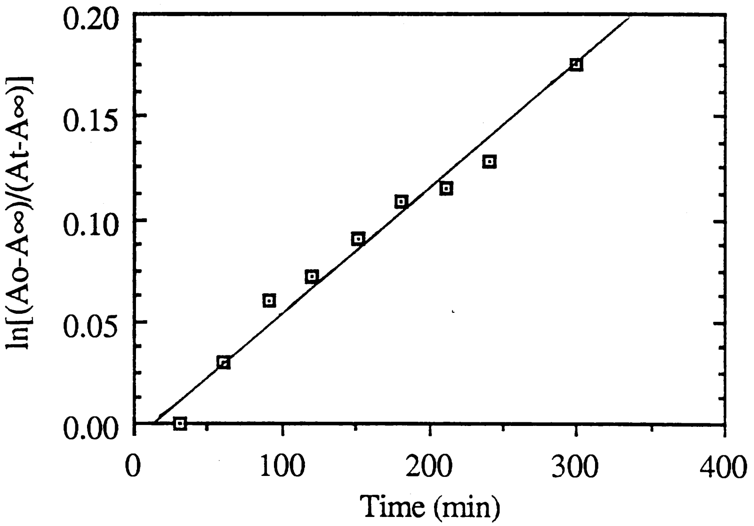


Figure 38. Plot of disappearance of soluble porphyrin **65** (1.33 x 10^{-5} M) with time in the presence of 0.25 M NaOCl in 0.38 M NaOH at 30.0 °C. $A_\infty = 0.491$. (The absorbance of 31 min was taken A_0, because the spectrum at 1 min did not fit the overall pattern).

The stability of latex bound oxo-porphyrin **72** in the presence of 0.25 M NaOCl at pH 10.8 was less than that of oxo-porphyrin **65**. Interestingly at this pH only one maximum was obtained at 421 nm for latex-bound oxo-porphyrin **72**. The rate constant of disappearance and half-life were 3.12 ± 0.14 x 10^{-2} min^{-1} and 22 min at pH 10.8 respectively (Figure 39). The latex-bound oxo-porphyrin **72** shows two maxima in 0.38 M NaOH.

When the concentration of NaOH was 0.38 M, one of the two bands at 442 nm disappeared much faster than the other band at 421 nm (Figure 40). The disappearance rate constants and half-lives were 1.67 ± 0.12 x 10^{-2} min^{-1} and 41 min for the band at λ_{max} 442 nm band and 8.58 ± 1.05 x 10^{-4} min^{-1} and 13.5 h for the band at λ_{max} 421 nm band (Figure 41).

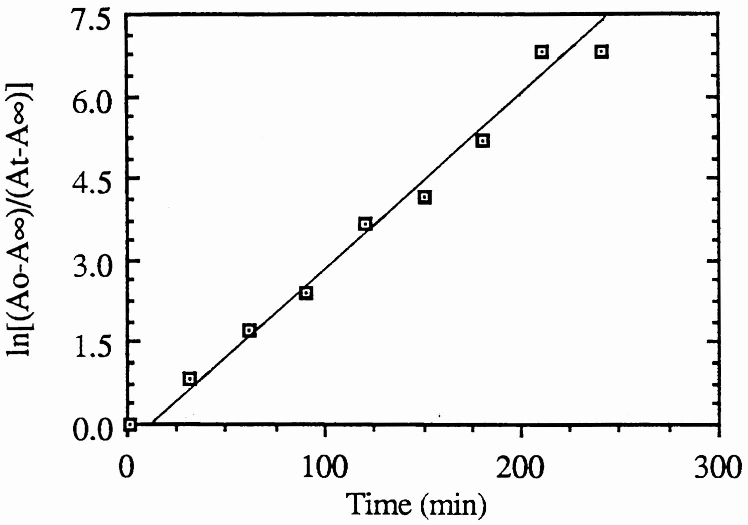


Figure 39. Plot of disappearance of latex-bound porphyrin **72** (1.33×10^{-5} M) with time in the presence of 0.18 mg latex per mL and 0.25 M NaOCl at pH 10.8 at 30 °C. A_∞ = 0.071.

Table XXX summarizes the rate constants and half-lives of Figures 37-39, 41.

Table XXX. Rate Constants of Disappearance and Half-Lives of Porphyrin **65** and Porphyrin **72**

porphyrin		k (min^{-1})	$t_{1/2}$
65	pH 10.8	$1.21 \pm 0.03 \times 10^{-2}$	57 min
65	[NaOH] = 0.38 M	$5.96 \pm 0.35 \times 10^{-4}$	19.4 h
72	pH 10.8	$3.12 \pm 0.14 \times 10^{-2}$	22 min
72	[NaOH] = 0.38 M	$8.58 \pm 1.05 \times 10^{-4}$ $1.67 \pm 0.12 \times 10^{-2}$	13.5 h 41 min

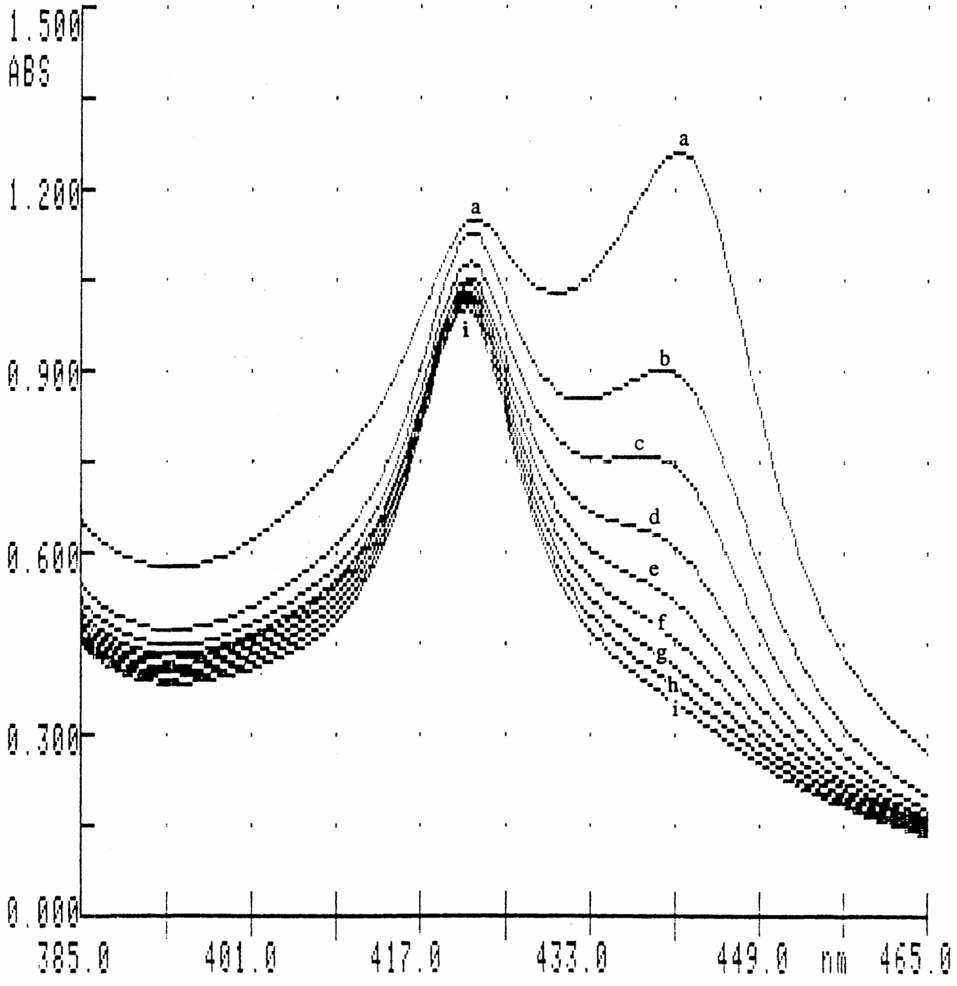


Figure 40. Absorption spectra of porphyrin **72** ([**65**] = 1.32 x 10^{-5} M) in the presence of 0.25 M NaOCl, 0.38 M NaOH, and 0.18 mg mL^{-1} latex as a function of time: (a), 1 min; (b), 31 min; (c), 61 min; (d), 91 min; (e), 121 min; (f), 151 min; (g), 181 min; (h), 211 min; (i), 241 min.

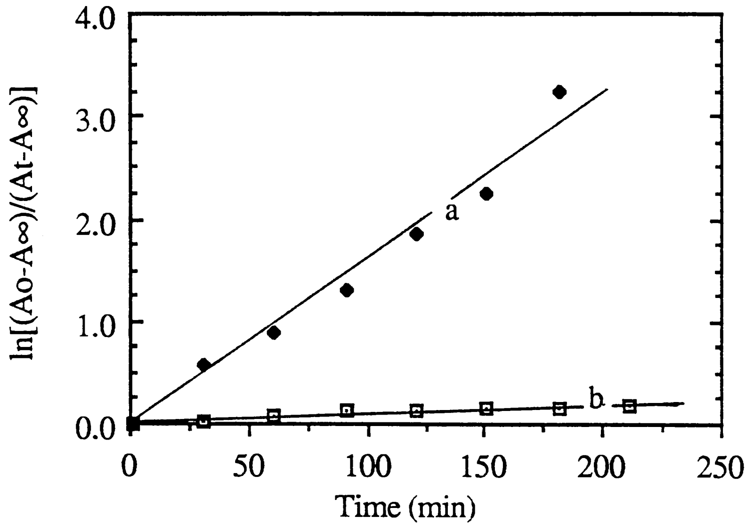


Figure 41. Plot of disappearance of latex-bound porphyrin **72** (1.33×10^{-5} M) with time in the presence of 0.18 mg latex per mL and 0.25 M NaOCl in 0.38 M NaOH: (a), $A_\infty = 0.417$; (b), $A_\infty = 0.287$.

Since the rate of disappearance of the band at 442 nm was extremely fast in the first 30 min, the change was followed in small time intervals. The spectra of a dispersion of porphyrin **72** in NaOH in the presence of NaOCl was obtained nine times at 36 sec time intervals. The first scan started 10 sec after the addition of NaOCl and lasted 24 sec. Eight more scans were carried out at 36 sec time intervals. The first trace showed two maxima that appeared λ_{max} 442 nm and λ_{max} 421 nm. Immediately the band at 442 nm started decreasing and the band at 421 nm started building up. Figure 42 shows the absorption changes with time. In two minutes, the interconversion of these Mn porphyrin complexes were completed and then the changes in both bands slowed down.

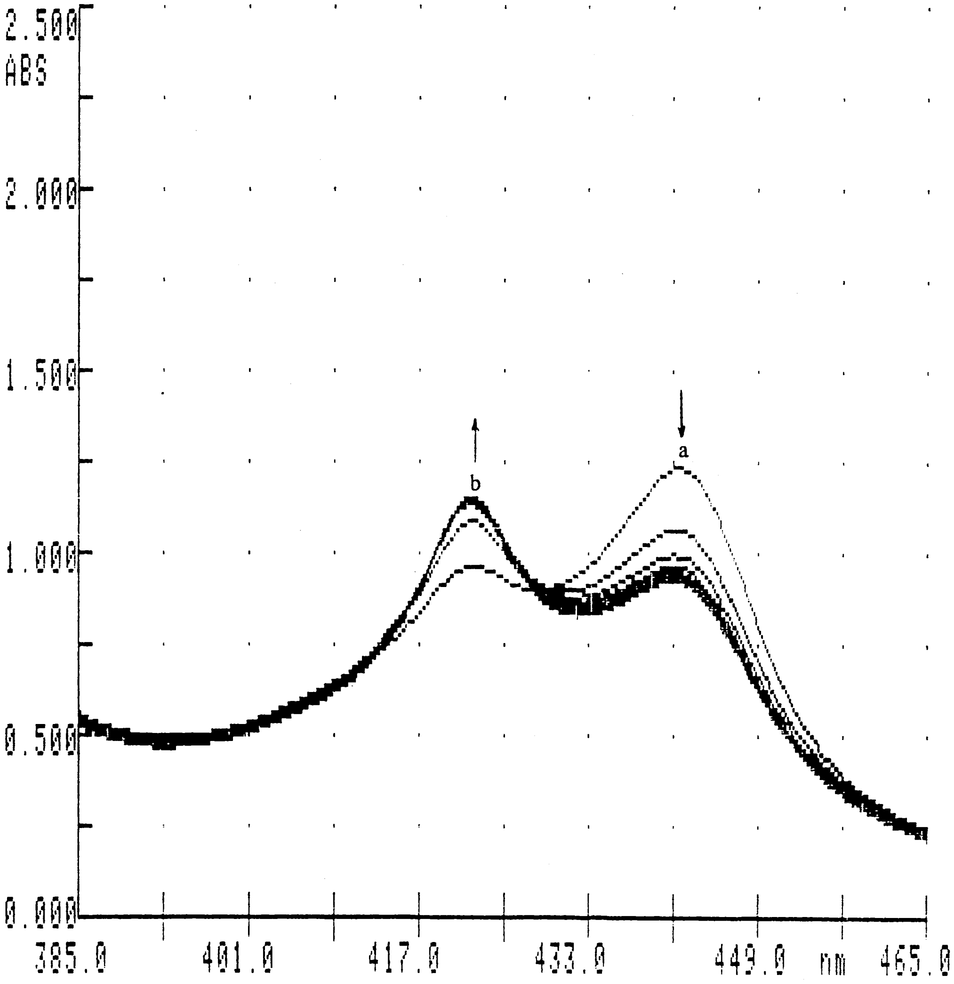


Figure 42. Absorption spectra of porphyrin **72** ([**65**] = 1.16 x 10^{-5} M) in the presence of 0.22 M NaOCl, 0.38 M NaOH, and 0.16 mg mL^{-1} latex as a function of time: (a), 442 nm; 17, 53, 89, 125, 161, 197, 233, 269, 305 sec; (b), 421 nm; 23, 59, 95, 131, 167, 203, 239, 275, 311 sec.

The absorption spectra of latex-bound porphyrin **72** in 0.38 M NaOH in the presence of 0.25 M NaOCl and 5.4 x 10^{-2} M styrene were followed for 100 min. The expected band shift from 441 nm to 472 nm which was observed with samples taken from the reaction mixtures was not observed in this case. The large excess of styrene apparently prevents or slows down the formation of the green species which is responsible for the band shift. This result is in agreement with the observations from the epoxidations with excess styrene. Due to dispersion of styrene in the reaction mixture, the absorbance scale of the spectra shifted. If the mixture rested for a while before running, low absorptions were observed (Figure 43).

A similar study was carried out in the absence of latex. Spectra taken over 60 min (Figure 44) showed that bleaching was slower than when latex was present.

Visible Spectrophtometry of 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphinatomanganese(III) Acetate (54). The bleaching rate of porphyrin **54** was extremely fast and could not be followed with the spectrophotometer. In the presence of NaOCl and at pH >13, total disappearance of the Mn porphyrin took only 3-3.5 min, whereas at pH <11, no porphyrin **54** was left after a 50 s spectrophotometer scan.

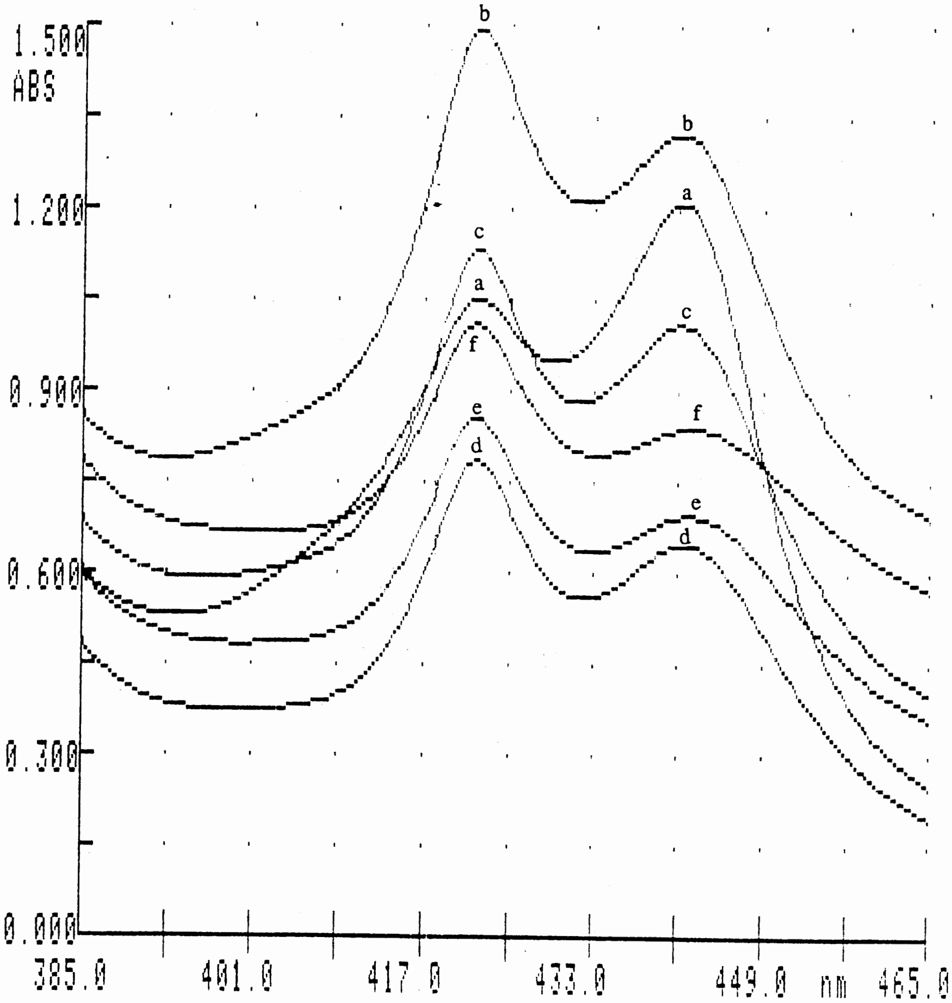


Figure 43. The spectral changes of porphyrin **72** (1.33 x 10^{-5} M) in the presence of 0.18 mg latex per mL and 0.25 M NaOCl in 0.38 M NaOH: (a), 1 min; (b), 14 min; (c), 27 min; (d), 41 min; (e), 52 min; (f), 60 min.

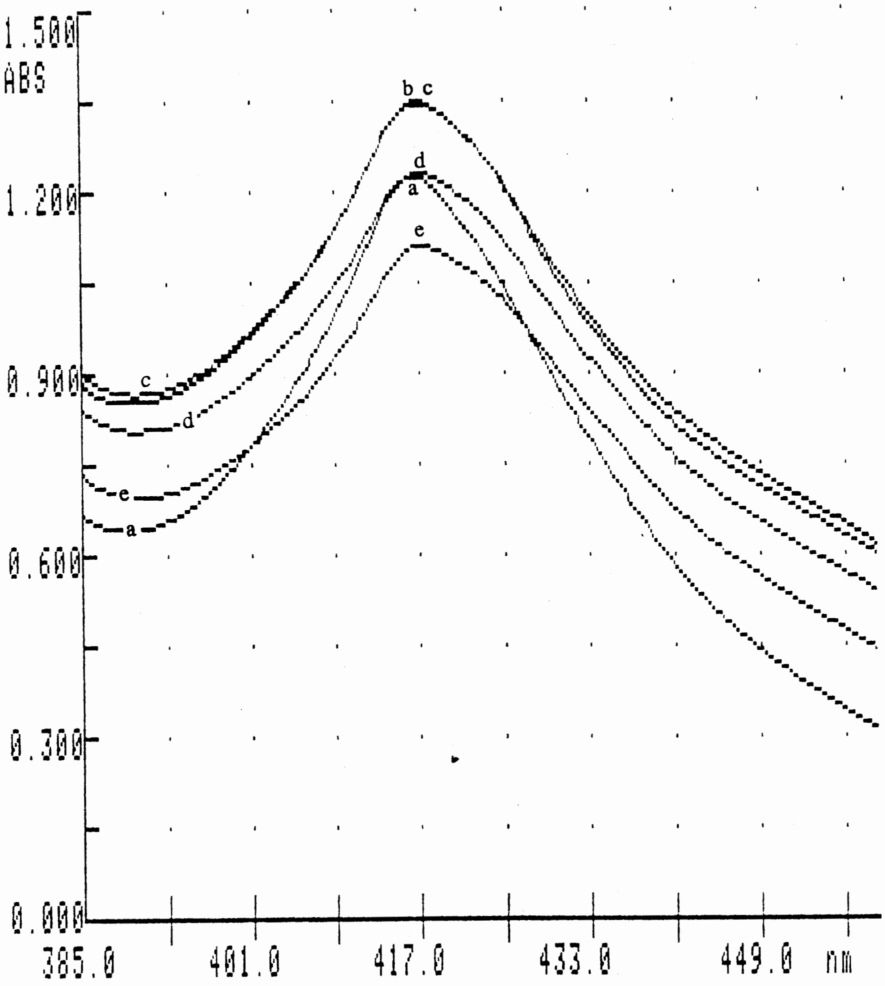


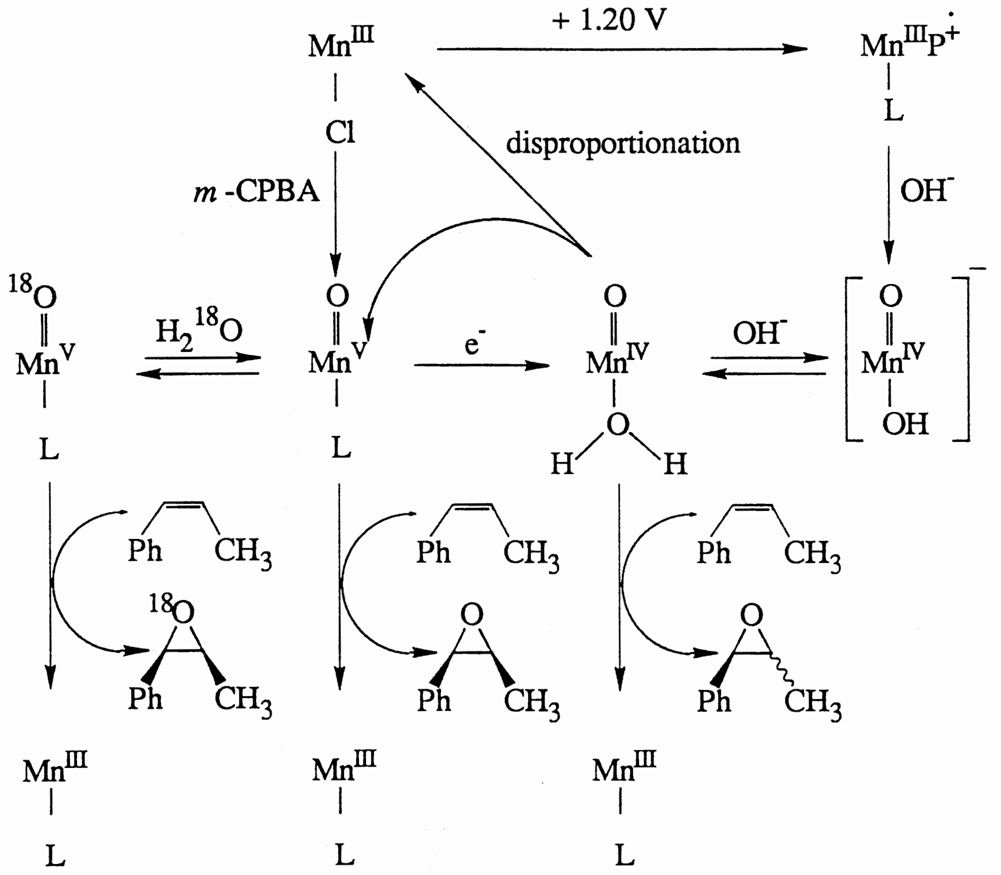
Figure 44. The spectral changes of porphyrin **65** (1.33×10^{-5} M) in the presence of 0.25 M NaOCl and in 0.38 M NaOH: (a), 1 min; (b), 14 min; (c), 28 min; (d), 45 min; (e), 60 min.

Discussion

The catalysis of alkene epoxidation by oxo-porphyrin **65** in homogeneous solutions and in the presence of a latex was the goal of this study. Water-insoluble styrene was chosen to epoxidize with NaOCl in highly alkaline (>0.1 M NaOH) solution. As in the case of Co(II)PcTs catalyzed oxidation of 2,6-di-*tert*-butylphenol in Chapter II, latex-bound porphyrin **72** showed higher activity than the soluble porphyrin catalyst **65** (Table XVII). The oxidizing agent in the styrene epoxidation is hypochlorite anion, which is attracted by positively charged quaternary ammonium sites of the latex and competes with OH^- and Cl^- for the positively charged sites not used by the Mn porphyrin. In a typical reaction mixture, the number of quaternary ammonium sites is 0.153 mmol and about 5% of these sites are consumed by the porphyrin. This leaves 0.145 mmol of quaternary ammonium sites for ClO^-, OH^-, and Cl^- ions. The external mixture contains 1.50 mmol of OCl^-, 2.28 mmol of OH^-, and about 1.65 mmol of Cl^- (1.50 mmol from the bleach solution and 0.153 mmol as the counter ion of the quaternary ammonium sites). Ion exchange selectivity of these ions is $ClO^- > Cl^- > OH^-$. Therefore more ClO^- than Cl^- or OH^- is bound to the latex.

The key intermediate in the alkene epoxidation by a manganese porphyrin is proposed to be a high-valent oxo-manganese complex.[82,89,90,94,96,99,100,185-187] Groves[99,100] isolated oxo-5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphinatomanganese(IV) and identified oxo-5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphinatomanganese(V) by spectra at low temperatures when 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphinatomanganese(III) chloride was treated with *m*-chloroperoxybenzoic acid, and showed that these complexes can transfer oxygen to *cis*- and *trans*-*β*-methylstyrene (Scheme VI).

Scheme VI. Proposed Mechanism of Oxo-5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)-porphinatomanganese and Transfer of Oxygen to *cis*-*β*-methylstyrene[99]



Carnieri[81] showed electrochemically and spectroscopically that hypochlorite oxidation of 5,10,15,20-tetrakis(4-carboxyphenyl)porphinatomanganese(III) acetate, 5,10,15,20-tetrakis(4-sulfophenyl)porphinatomanganese(III) acetate, 5,10,15,20-tetrakis-(*N*-methyl-4-pyridyl)porphinatomanganese(III) acetate, and 5,10,15,20-tetrakis(4-pyridyl)porphinatomanganese(III) acetate in aqueous solution gives oxo-Mn(IV) and oxo-Mn(V) complexes. In that study, oxo-5,10,15,20-tetrakis(4-carboxyphenyl)porphinatomanganese(IV) was identified by spectra in the form of dimeric μ-oxo complex (eq. 28). The second oxidation of the Mn porphyrin with hypocholorite involves dissociation of the μ-oxo dimer (eq. 29). In aqueous alkaline solution the oxo-Mn(V) porphyrin did not react with added Mn(III) porphyrin to give oxo-Mn(IV) porphyrin.

$$2\,\mathrm{Mn(III)P} \quad + \quad \mathrm{OCl^-} \quad \rightleftharpoons \quad \mathrm{Mn(IV)P\text{-}O\text{-}Mn(IV)P} \quad + \quad \mathrm{Cl^-} \qquad (28)$$

$$\mathrm{Mn(IV)P\text{-}O\text{-}Mn(IV)P} \quad + \quad \mathrm{OCl^-} \longrightarrow 2\,\mathrm{Mn(V)P{=}O} \quad + \quad \mathrm{Cl^-} \qquad (29)$$

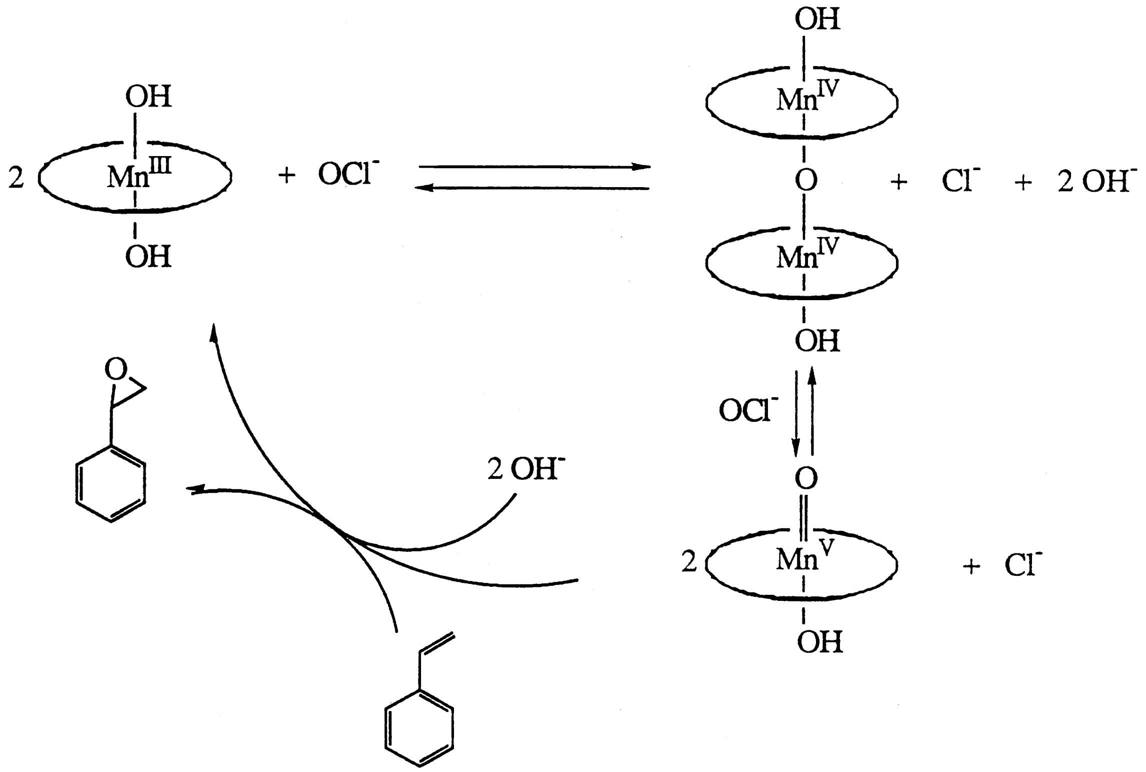
However the reaction between Mn(V) and Mn(III) porphyrins was reported in a wet-dichloromethane medium for water insoluble 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphinatomanganese(III) chloride to give the oxo-Mn(IV) porphyrin[185] with a second-order rate constant of $2 \times 10^8\ M^{-1}s^{-1}$. Nonbornene, *cis*-cyclooctene, and cyclohexene were epoxidized with the oxo-Mn(V) porphyrin complex. The rate constant for formation of oxo-Mn(V) porphyrin from the Mn(III) porphyrin and ClO^- was $(3.8 \pm 1.8) \times 10^5\ M^{-1}s^{-1}$.

Based on these earlier observations, the oxo-Mn(V) porphyrin must be the active species in the epoxidation of styrene in aqueous phase (Scheme VII) and its formation should follow the same steps as the oxidation of 5,10,15,20-tetrakis(4-carboxyphenyl)-porphinatomanganese(III) with hypochlorite.[81] The oxo-Mn(V) complex transfers oxygen to styrene. The mechanism of oxygen transfer from the oxo-manganese to an olefin is still in debate and could proceed via direct transfer, a radical, a cation, or an oxametallacycle.[82] There is evidence for all of these intermediates in certain cases, and the nature of the intermediate likely depends on electron density of the alkene, steric bulk of the alkene, and structure of the porphyrin.[82,88,90,94,100,176,186,188-192]

In the literature, there are reports that the activity of polymer-bound metalloporphyrins is higher than that of soluble porphyrins because the polymer prevents the formation of inactive μ-oxo porphyrin complexes.[90] However it is not known if the latexes used in this study promote such a site isolation of porphyrin **65** and inhibit the formation of μ-oxo dimers.

Latexes crosslinked with 1% and 5% divinylbenzene and prepared with either sodium dodecylsulfate or hexadecyltrimethylammonium bromide gave roughly the same conversion of styrene (71-81%) in 1 h. As the amount of latex was reduced and the amount of catalyst was kept constant, the conversion of styrene was decreased (Table XVIII). Several reasons account for this observation such as less styrene in polymer, less quaternary sites to attract hypochlorite ions, and possible change in the aggregation state of the Mn porphyrin. When less catalyst was bound to a latex, the conversion of styrene decreased (Table XIX), but not as much as would be expected if conversion was directly proportional to the catalyst concentration.

Scheme VII. Proposed Catalytic Cycle for Styrene Epoxidation by NaOCl Catalyzed by Soluble Porphyrin **65** and Latex-Bound Porphyrin **72**



Two phase epoxidations of alkenes are very much influenced by a pyridine or imidazole ligand,[82,89,94] but no effect of pyridine or 1-methylimidazole was observed in the aqueous phase epoxidation (Table XXI). Presumably OH^- coordinates strongly at the axial positions of the Mn porphyrin and prevents coordination of 1-methylimidazole or pyridine to the central atom. The epoxidation was not very sensitive to the amounts of reagents or catalyst in the reaction mixture (Table XXII).

Due to the presence of strong oxidant and polymer in the reaction mixtures, the kinetics of the reaction could not be investigated easily by GLC. Limited kinetic information shows fast initial epoxidation (Figure 27) followed by a rate decrease that coincides with the change of the color of the reaction mixtures from red-brown to green, which may be the result of formation of inactive Mn porphyrin complex. Since this color change is unique to the latex-bound catalyst, the fast epoxidation may use up available styrene around the catalyst quickly and lead to change in the state of oxo Mn porphyrin. The color change was not observed when there was excess styrene present in the reaction mixture (Figure 28). The reusability of the catalyst is limited by its instability. As shown in Figure 28, the epoxidation of styrene ceased after 100 min due to total decomposition of the catalyst, even though large excesses of styrene and hypochlorite were available. The decomposition of the catalyst was slowed down and more styrene oxide was obtained when the oxidant was added in longer time intervals (about 1h) than 10 min (Figure 29). These results show that the catalyst loses its activity in a short time and without catalyst the reaction does not take place.

Shaking the reaction mixtures with a wrist-shaker and stirring them with magnetically gave comparable results (Table XX). However sonication gave very poor yield due to inefficient mixing of styrene and the aqueous phase. So mass transfer affects the activity of the catalyst. Styrene must be transported from the bulk phase through the aqueous phase to the catalyst particle surface and then diffuse from the particle surface to the active sites within the particle. Apparently sonication fails to mix styrene with aqueous phase which contains the catalyst and oxidant.

pH higher than 9.5 does not affect the epoxidation of styrene directly, but as the pH decreases, the stability of water-soluble as well as water-insoluble porphyrin decreases because of oxidative decomposition and increase of the concentration of HOCl which causes faster oxidation of the porphyrin. The stability of the Mn porphyrin is discussed in the later part of this section.

Styrene derivatives, *α*–methylstyrene, *β*-methylstyrene, 4-methylstyrene, and 4-chlorostyrene, epoxidized slower than styrene. Single substrate as well as competition reactions showed that the reactions are governed by several factors such as the transfer of the substrate to the catalytic sites, electron density of the vinyl group and steric factors during the oxygen transfer stage. Lower epoxide yields from 4-chlorostyrene and 4-methylstyrene than from styrene (Table XXVI) indicate that the electron density does not control the reaction. If the styrene acts as an electron pair donor to the Mn(V)=O, the relative reactivity should be 4-methylstyrene >styrene >4-chlorostyrene. The lower epoxide yields from 4-chlorostyrene, 4-methylstyrene, and *α*–methylstyrene than from styrene, and almost no epoxide from *β*-methylstyrene, may be attributed to the steric factors as well as to the mass transfer limitations of the substrate. Since the transition state of epoxidation and relative solubilities of styrene, 4-chlorostyrene, 4-methylstyrene, *α*–methylstyrene, and *β*-methylstyrene in water are not determined, the factors cited are only speculation.

The heterogeneity of these reaction mixtures and the possible variations between polymer and substrate make the interpretation of the results especially the nature of the step of oxygen transfer to alkene difficult.

The inactivity of the latex-bound porphyrin **72** and soluble porphyrin **65** toward epoxidation of 1-decene, 1-octene, cyclooctene, *cis*-stilbene, and undec-10-en-1-ol cannot be explained by structural differences between the alkenes and benzyltrimethylammonium latex, because the catalyst acts synergistically with the latex. Low alkene solubility in the latex may be responsible for their lower reactivity. However, the addition of CH_3OH and CH_3CN to the reaction mixtures of cyclooctene did not give much improved results (Table XXVIII).

On the basis of the results of visible spectrophotometry presented here it is clear that the oxidative destruction of the porphyrin is much faster in aqueous ClO^- reactions than in biphase reactions where porphyrin is in the organic phase and is exposed only to very low concentration of inorganic oxidant during the phase-transfer catalyzed reaction. Any manganese porphyrin catalyst could undergo side reactions during epoxidation of an alkene with an oxidant. An oxo-Mn porphyrin can react with an olefin, form a μ-oxo dimer with another Mn-porphyrin, or be destroyed oxidatively.

Soluble porphyrin **65** and latex-bound porphyrin **72** became more stable in the presence of hypochlorite as pH increased. The formation of HOCl (pK_a 7.54),[182] a powerful oxidant, was limited by increasing the pH. Porphyrin **65** is more stable than most porphyrins because the 2,6 chloro substituents on the phenyl moieties of the porphyrin block the access by oxidant to the *meso* position of the porphyrin from the top and bottom of the porphyrin ring. So 2,6-dichloro substitution to the porphyrin gave enough stability to study some epoxidations in an aqueous phase. But 5,10,15,20-tetrakis(4-sulfonatophenyl)porphinatomanganese(III) acetate was destroyed by hypocholorite in a minutes even at pH >13, presumably via oxidation at the unprotected *meso* positions.

The presence of colloidal quaternary ammonium exchange resin speeds up the oxidative degradation of the manganese porphyrin. The anion OCl^-, an oxidant and nucleophile, binds to the excess quaternary ammonium sites of the latex. This increase of the OCl^- concentration in the vicinity of the Mn porphyrin is likely the cause of the faster oxidative destruction. Phase transfer catalysts were also reported to decrease the stability of the manganese porphyrins.[82]

The reason why the absorption spectrum of oxo-porphyrin **72** at pH >13 shows two bands at 421 and 442 nm is not known (Figure 32 and 34). So far, in the literature no such a spectrum was reported for any porphyrin in water or organic solvent. The band at shorter wavelength is strongly suspected to be due to the oxo-Mn(V) porphyrin, analogous to the band of Mn(V) in homogeneous medium. The absorption spectra of manganese(IV) porphyrin and manganese(V) porphyrin are reported to have only a 2 nm difference in their λ_{max}, and ESR spectra and magnetic susceptibility measurements were used to determine the formal oxidation state.[81] In the case of oxo-porphyrin-catalyzed epoxidations, the amount of OCl^- used was 1000 times the amount of porphyrin, and the oxidation states of the manganese in oxo-porphyrin **65** and oxo-porphyrin **72** are believed to be +5 due to the excess OCl^-. From the spectroscopic evidence, the species that absorbs at 442 nm forms first, and then partially transforms to the 421 nm species in *ca.* 3 min (Figure 42). So the 442 nm species must be an intermediate between porphyrin **72** and oxo-porphyrin **72**, possibly the OCl^- adduct of porphyrin **72**. The disappearence of this band follows different routes in the absence and presence of styrene. In the absence of styrene, the band disappears with a half life of 41 min (Figures 40 and 41), either by conversion to the 421 nm species or by oxidative degradation. In the presence of styrene, under the usual reaction conditions, this species is present for the first 20-30 min, and reaction mixture is red-brown. Suddenly the color changes to green and the band of the species at 442 nm shifts to 472 nm (Figure 36). *N*-alkylated porphyrins are known to be greeen.[64,78,176] This 472 nm band may be due to either an *N*-alkylated Mn porphyrin or the original porphyrin **72**. The major band of the latex bound porphyrin **72** appears at 477-469 nm, depending on the amount of latex used.

Dioxygen in the presence of $NaBH_4$ was less active than hypochlorite for the epoxidation of styrene catalyzed by soluble porphyrin **65**, latex-bound porphyrin **72**, and porphyrin **54**. Although the turnover number 30 obtained in the styrene epoxidation is far inferior to the turnover numbers observed in the cytochrome P-450 enzymatic reactions, the result is comparable to the results obtained from various metalloporphyrin-O_2-reducing agent-solvent systems. Mansuy[193] obtained 60 and 8 turnover frequencies [mol of oxygenated product/(mol of Mn(III)porphyrin x h)] in the formation of styrene oxide and 2-phenylethanal from 1 mL of styrene in 1 mL of benzene under 1 atm of dioxygen catalyzed by 5,10,15,20-tetraphenylporphinatomanganese(III) chloride in the presence of sodium ascorbate and trioctylmethylammonium chloride in 1 M tris-HCl buffer at pH 8.5 at 20 °C for 10 h.

Shimizu[106] reported the epoxidation of styrene (0.4 mL, ~3.4 mmol) with dioxygen catalyzed by 5,10,15,20-tetrakis(4-sulfonatophenyl)porphinatomanganese(III) and 5,10,15,20-tetraphenylporphinatomanganese(III) in the presence of $NaBH_4$ and *N*-methylimidazole in methanol for 3 h at 30 °C. When the catalyst was 5,10,15,20-tetrakis(4-sulfonatophenyl)porphinatomanganese(III), the turnover frequency was approximately 22 and the oxygenated products of styrene were styrene oxide (1%), acetophenone (1.6%), 1-phenylethanol (45.2%), and 2-phenylethanol (0.4%). When the catalyst 5,10,15,20-tetraphenylporphinatomanganese(III) was used, the turnover frequency of 13 was obtained and the products of styrene were acetophenone (0.4%) and 1-phenylethanol (35.7%).

Styrene (4.3 x 10^{-3} M) was epoxidized in a polymerized vesicle dispersion[97] under 1 atm pressures of dioxygen and hydrogen in the presence of 5,10,15,20-tetrakis[4-(hexadecyloxy)phenyl]porphinatomanganese(III) acetate, *N*-methylimidazole, methylene blue, and Pt at 20 °C. The turnover frequency [mol of oxygenated product/(mol of Mn(III)porphyrin x h)] was 1.3 was obtained and the product was 1,2-dihydroxy-1-phenylethane.

The oxidation products of styrene by dioxygen in this research were acetophenone and 1-phenylethanol (Table XXIX), which were the major products observed as well from the autoxidation of styrene in methanol,[106] but they were different from the autoxidation of styrene in biphase mixtures[193] and in vesicles.[97]

The epoxidation of arylalkenes with sodium hypochlorite in water catalyzed by soluble and latex-bound manganese porphyrins could be extended to several areas. Since the polystyrene-based ion exchange latexes failed to promote epoxidations of aliphatic alkenes, other latexes could be prepared for that purpose. This might be achieved by with either less hydrophilic latexes than the ones used here or latexes with long alkyl chains, or fewer quaternary ammonium sites. The interaction between latex and 5,10,15,20-tetrakis-(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) chloride and oxidized states may be investigated by using UV/visible, ESR, and stopped-flow spectroscopic techniques to find the nature of the porphyrin species that is present in the colloidal system. Using literature results about porphyrin stability, an oxidatively resistant manganese catalyst might be prepared and tested. Milder oxidants, such as hydrogen peroxide and dioxygen, rather than hypochlorite might be used in epoxidations to reduce porphyrin destruction. Catalytic activity must be improved if a large scale application is considered.

Experimental Section

Materials. Deionized, glass distilled water was used for all experiments. Pyrrole 99% (Aldrich) was distilled under reduced pressure at 98 °C, and the colorless distillate was stored under argon over 4-Å molecular sieves at 4-5 °C and protected from ambient lighting. Boron trifluoride etherate (Alfa) was distilled under reduced pressure (1.5 mm Hg/27 °C) and stored under argon over 4 Å molecular sieves at 4-5 °C. 2,6-Dichlorobenzaldehyde 99%, and *p*-chloranil 99%, and manganese acetate tetrahydrate (all from Aldrich) were used as received. Manganese chloride tetrahydrate was obtained from Mallinckrodt. Ion-exchange resins Amberlite® IR-120 and Dowex® 50-X8 were obtained from Rohm and Haas Co. and J. T. Baker Chem. Co. respectively. Reagent grade $CHCl_3$ (Fisher) was distilled over K_2CO_3[125,126] (ca. 50 g per L of $CHCl_3$) using a fractionating column while passing argon, stored under argon over 4 Å molecular sieves, and protected from ambient lighting (recently it was found[179] that ethanol in $CHCl_3$ was essential in the synthesis of 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin and a simple distillation did not remove ethanol from $CHCl_3$). The tetrasodium salt of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin was obtained from Strem Chemicals and used as received. 4-

Methylstyrene was obtained from Mobil Chem Co. and distilled under reduced pressure. 4-Chlorostyrene and α-methylstyrene were obtained from Aldrich and passed through 10-cm alumina columns. Styrene was washed with 0.1 N NaOH, and distilled under reduced pressure. Clorox® bleach was obtained from a local supermarket and its OCl^- content was determined by iodometric titration.[194] 1-Octene (Aldrich), 1-decene (Fluka), and cyclooctene (Fluka) were used as received. Silica gel (I.D. Grade 62, 60-200 mesh) was obtained from E. M. Science.

Analyses and Instrumentations. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Before analyses, porphyrins **65**, **71**, and **72** were dried under vacuum at 60 °C for 4 h. The NMR spectra were taken on a Varian XL-300 spectrometer using $(CH_3)_4Si$ or $(CH_3)_3Si(CH_2)_2COO^- Na^+$ as internal standard. The infrared spectra were obtained with a Perkin-Elmer 681 instrument. Mass spectra were taken at the Oklahoma State University Mass Spectrometry Facility using a VG Analytical ZAB-SE instrument using fast atom bombardment (FAB) method of ionization. Gas chromotography was performed with a Hewlett-Packard 5840A instrument equipped with a 6 ft x 1/8 in Tenax® packed column from Supelco Inc. and a thermal conductivity detector and interfaced with a Hewlett-Packard 5840A terminal. UV/visible spectra were obtained with a Varian DMS-200 spectrophotometer equipped with thermostated cell holders and with a VWR 1140 model variable temperature circulating bath. One mm and one cm pathlength cells were used for 10^{-4} and 10^{-5} M porphyrin samples. After 5 min from insertion of the cells into the holders, the reference cell temperature was measured by inserting a 0.05 °C graduated thermometer (meets NBS specifications). The reference cell in cell holder contained water in homogeneous solution studies and the same concentration of latex when latex-bound Mn porphyrin was scanned.

5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphyrin (70). The preparation of porphyrin **70** requires dry conditions. Chemicals as well as glassware were dried carefully. The presence of as little as 0.18 µL of water per mL of CH_2Cl_2 in the solution causes a shift in the equilibrium toward the open-chain polypyrrylmethanes, while the larger quantity of water (5 µL per mL of CH_2Cl_2) buffers the acid catalyst BF_3 etherate and terminates the reaction.[125] A 2-L three neck round-bottomed flask and a reflux condenser were dry in a drying oven at 130-135 °C for 24 h. They were set up hot while passing dried argon through them. The setup was dried one more time heating with a heat gun. A Drierite® drying tube was attached to the top of the condenser while the setup cooled.

The conditions described here were used in the preparation-2 in Table XVI. The well-dried flask fitted with a condenser, a gas inlet port, and an addition port was charged with 1 L of distilled $CHCl_3$. The solvent was stirred with an egg-shaped stirring bar (ca. 2.5-cm). Distilled pyrrole (680 mg, 10.1 mmol) via a syringe, 2,6-dichlorobenzaldehyde (1.768 g, 10.1 mmol) as a solid, and distilled BF_3 etherate (561 mg, 4.0 mmol) via a syringe were added to the flask at about 5 min intervals. The mixture was stirred at 22 °C under argon for 21 h (not optimized), and the flask was shielded from ambient lighting.

In order to convert porphyrinogen to porphyrin, an oxidizing agent, *p*-chloranil (1.863 g, 7.6 mmol, 3 equiv per porphyrinogen, 0.75 equiv per pyrrole) in powder form was added all at once, and the mixture was refluxed for 3 h under air (not optimized). *p*-Chloranil also oxidizes open-chain polypyrrylmethanes to polypyrrylmethenes. After the reaction mixture cooled, BF_3 etherate was hydrolyzed with water, and the aqueous phase was separated. The organic phase then was rotary evaporated to dryness. All the components of the crude product except porphyrin **70** were methanol soluble. Methanol was added to the crude dry product, until no big particles remained on the bottom of the drying flask. During gravity filtration of this slurry through a Whatman 42 (12.5 -cm) filter paper, a purple-bluish residue, in which porphyrin **70** was the major compound, was collected on the filter paper, scraped off the paper with a spatula, and kept aside. The filtrates were refiltered 3-4 times until no more purple residue collected on the filter paper.

Each filtration took about 0.5 h. The ^{1}H NMR spectrum of the purple-bluish residue had peaks of porphyrin **70** and of impurities at 1.48, 1.23, and 0.84 ppm, and the TLC in 30% ethyl acetate-petroleum ether showed spots of impurities (R_f = 0.32-0.69) along with the intense yellow-green spot of porphyrin **70** (R_f = 0.0). When the TLC was developed in dichloromethane, the spot of porphyrin **70** moved with the solvent front (R_f = 0.91), and the impurities tailed (R_f = 0.28-0.0). Further purification was done with column chromatography.

The purple-bluish residue recovered from filtration was dissolved in CH_2Cl_2 and adsorbed on about 5 g of silica gel in a dish, which was mixed with a glass rod for homogeneous adsoption and warmed with a hot plate to evaporate the solvent. The damp silica gel was poured onto a 60 x 2.5 cm column of silica gel packed in CH_2Cl_2. The column was washed with CH_2Cl_2 to elute the red-brown band of the porphyrin **70**. The TLC analysis of the eluate showed a single yellow spot which moved with the solvent front in CH_2Cl_2 and stayed at the origin in 33% ethyl acetate-petroleum ether. The porphyrin **70** was recovered by evaporating the solvent and dried under vacuum at 65-70 ^{o}C for about 12 h. The ^{1}H NMR spectrum of the product showed three small impurity peaks at 0.8-1.7 ppm along with expected porphyrin **70** peaks.

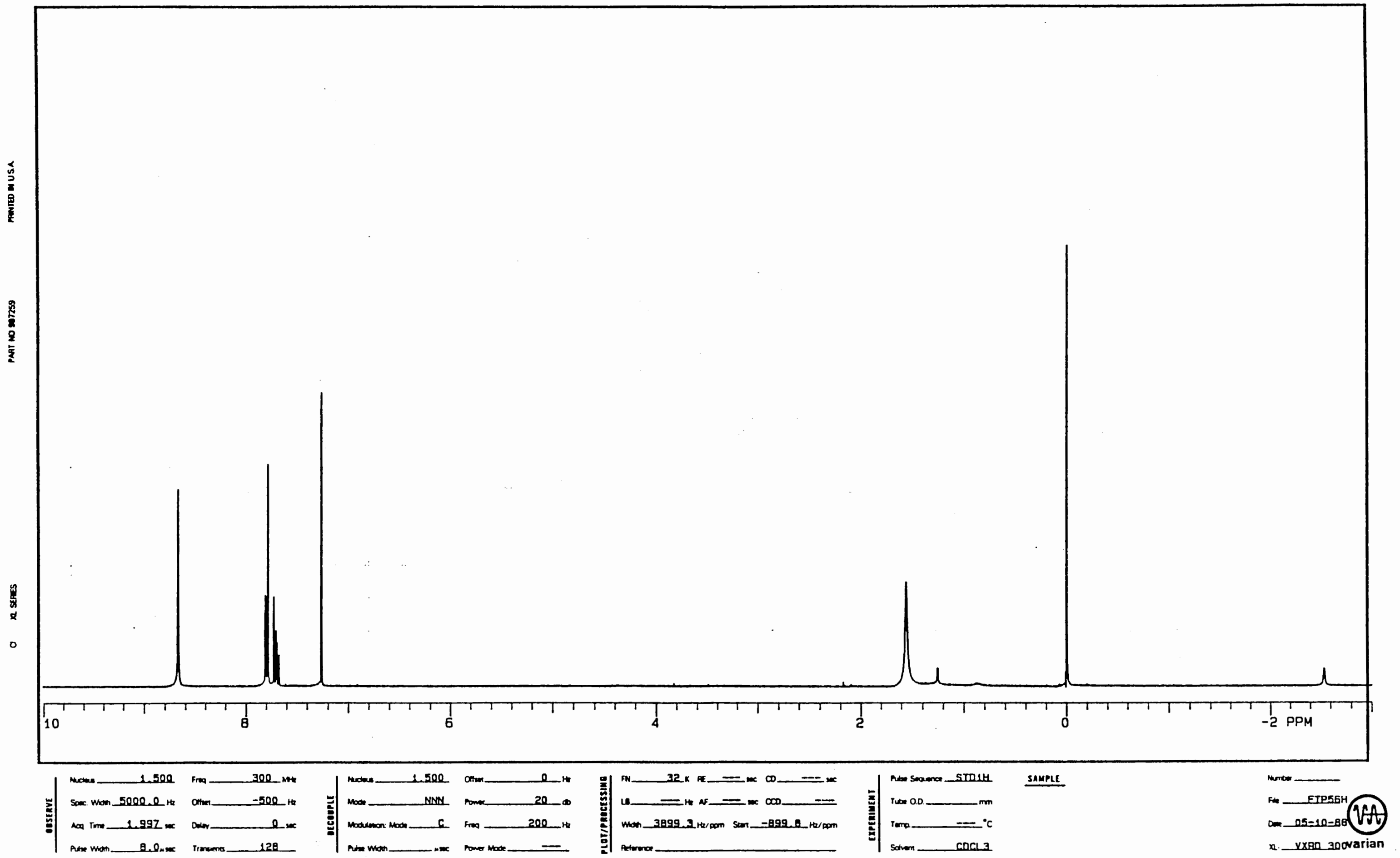
In order to remove these impurities, a second chromatography and crystallization were performed. The silica column (45 x 2.5 cm) was prepared as in the first chromatography, and 50% ethyl acetate-petroleum ether was used as initial eluent to remove impurities. Finally, the column was washed with ethyl acetate, in which porphyrin **70** has little solubility, and CH_2Cl_2 was used to remove porphyrin **70** from the column. The CH_2Cl_2 eluate was evaporated on a rotary evaporator. After the residue had been dissolved in warm $CHCl_3$, porphyrin **70** was crystallized from $CHCl_3$/n-heptane by refrigerating for 2 days. Crystals formed were recovered by gravity filtration and vacuum dried at 60 ^{o}C for 18 h. The yield was 16% based on 2,6-dichlorobenzaldehyde. The ^{1}H NMR spectrum of porphyrin **70** after crystallization showed an impurity peak at 1.56, smaller peak at 1.25 , and trace at 0.85 ppm which have not been identified (Figure 45). ^{1}H NMR ($CDCl_3$, $(CH_3)_4Si$) δ 8.67 (s, 8H, *β*–pyrrole-H), 7.79 (d, *J* = 8.4 Hz, 8H, *m*-Ph-H), 7.70 (t, *J* = 8.0 Hz, 4H, *p*-Ph-H), -2.53 (N-pyrrole-H), 1.56 (s, unassigned). IR (KBr) 3420 (N-H stretch), 3300, 3080 (=C-H stretch), 1545 (C=C stretch), 1420, 1330, 1180, 960, 795, 770, 705 cm^{-1}. MS (FAB, DMSO/glycerol): m/e 891 (36), 855 (9, -Cl), 819 (5, -2Cl), 748 (7, -4Cl), 536 (6), 369 (17), 277 (100), 263 (29), 235 (26); most abundant in isotopic cluster calcd. for $C_{44}H_{22}N_4Cl_8$, 890.79. Anal. Calcd. for $C_{44}H_{22}N_4Cl_8$ (FW 890.31): C, 59.36; H, 2.49; N, 6.29; Cl, 31.86. Found: C, 59.55; H, 2.55; N, 6.18; Cl, 32.12.

Table XVI gives quantitative information about starting materials, reaction times, and yields of seven preparations of porphyrin **70**.

5,10,15,20-Tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrin (71). $H_2TSPPCl_8H_4$ (**71**) was prepared by the method of Fleischer.[180] Porphyrin **70** (238 mg, 0.27 mmol) in powder form and concd. H_2SO_4 (7 mL) in a 25-mL single neck round-bottomed flask equipped with a condenser and an egg-shaped stirring bar were heated for 6 h with a 185 ± 5 °C oil bath. The flask was cooled to room temperature (ca. 25 °C) and stirred for 24 h. The mixture was cautiously diluted with stirring in a hood with 40-45 mL of distilled water to precipitate the porphyrin. If dilution is done with more water, the precipitate dissolves and a green homogeneous solution of the porphyrin is obtained. The resulting green precipitate, which is the HSO_4^- salt of the sulfonated diacid of porphyrin **70**,[180] was filtered through a 60-mL 40F fritted funnel connected to a water aspirator in 2-3 h. The light green filtrate was discarded. The solid **71** containing a small amount of water and H_2SO_4 was dissolved in methanol, transferred to a recovery flask, and evaporated. Acetone, in which the sulfonated porphyrin has little solubility, was used to extract water and H_2SO_4 three times. After vacuum drying at 65 °C for 18 h, 291 mg of product **71** was obtained. Yield was 87% (based on porphyrin containing 3.5 SO_3^-

and 4 H_2O) (Figure 46). The ^1H NMR spectrum of the sulfonated porphyrin **71** indicated 3.5 SO_3^- group substitution per porphyrin ring and the substitutions mostly occurred at the 3 position of the phenyl groups. Distorted multiplet NMR spectrum peaks of protons of the sulfonated porphyrin **71** were the evidence for several isomers as well as restricted motions of the 2,6 dichlorosubstituted phenyl groups around C_1-C_{ipso} bond. The sulfonated porphyrin **71** was highly hygroscopic. ^1H NMR (CD_3OD, TMS) ∂ 9.03 (m, 8H, β–pyrrole-H), 8.63 (m, 4H, *p*-Ph-H), 8.05 (m, 4.5-5H, *m*-Ph-H), 5.87 (s, H_2O), 3.27 (s, CHD_2OD), 1.30 and 0.87 (impurity). MS (FAB, dithiothreitol-dithioerythritol): m/e 1212 (6, -2Cl), 1134 (12), 1057 (15, -$C_6H_2Cl_2SO_3H$), 1050 (10), 891 (39, -3.5 SO_3H x 4 H_2O), 759 (18), 697 (33), 565 (100). Anal. Calcd. for $C_{44}H_{18.5}N_4Cl_8$ x 3.5 SO_3H x 4H_2O (FW 1242.6): C, 42.53; H, 2.43; N, 4.51; Cl, 22.83; S, 9.03. Found: C, 42.29; H, 2.63; N, 4.69; Cl, 22.71; S, 9.05.

When the precipitate was filtered off using a Whatman 42 ashless (12.5-cm) filter paper instead of the fritted funnel, it was contaminated presumably by filter paper which may have been attacked by dilute H_2SO_4.



OBSERVE
Nucleus 1.500
Spec. Width 5000.0 Hz
Acq. Time 1.997 sec
Pulse Width 8.0 µsec
Freq 300 MHz
Offset -500 Hz
Delay 0 sec
Transients 128

DECOUPLE
Nucleus 1.500
Mode NNN
Modulation Mode C
Pulse Width µsec
Offset 0 Hz
Power 20 db
Freq 200 Hz
Power Mode ---

PLOT/PROCESSING
FN 32 K RE --- sec CD --- sec
LB --- Hz AF --- sec CCD ---
Width 3899.3 Hz/ppm Start -899.8 Hz/ppm
Reference

EXPERIMENT
Pulse Sequence STD1H
Tube O.D. mm
Temp. --- °C
Solvent CDCL3

SAMPLE

Number
File FTP56H
Date 05-10-88
XL VXR0 300 varian

Figure 45. ^1H NMR spectrum of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**70**).

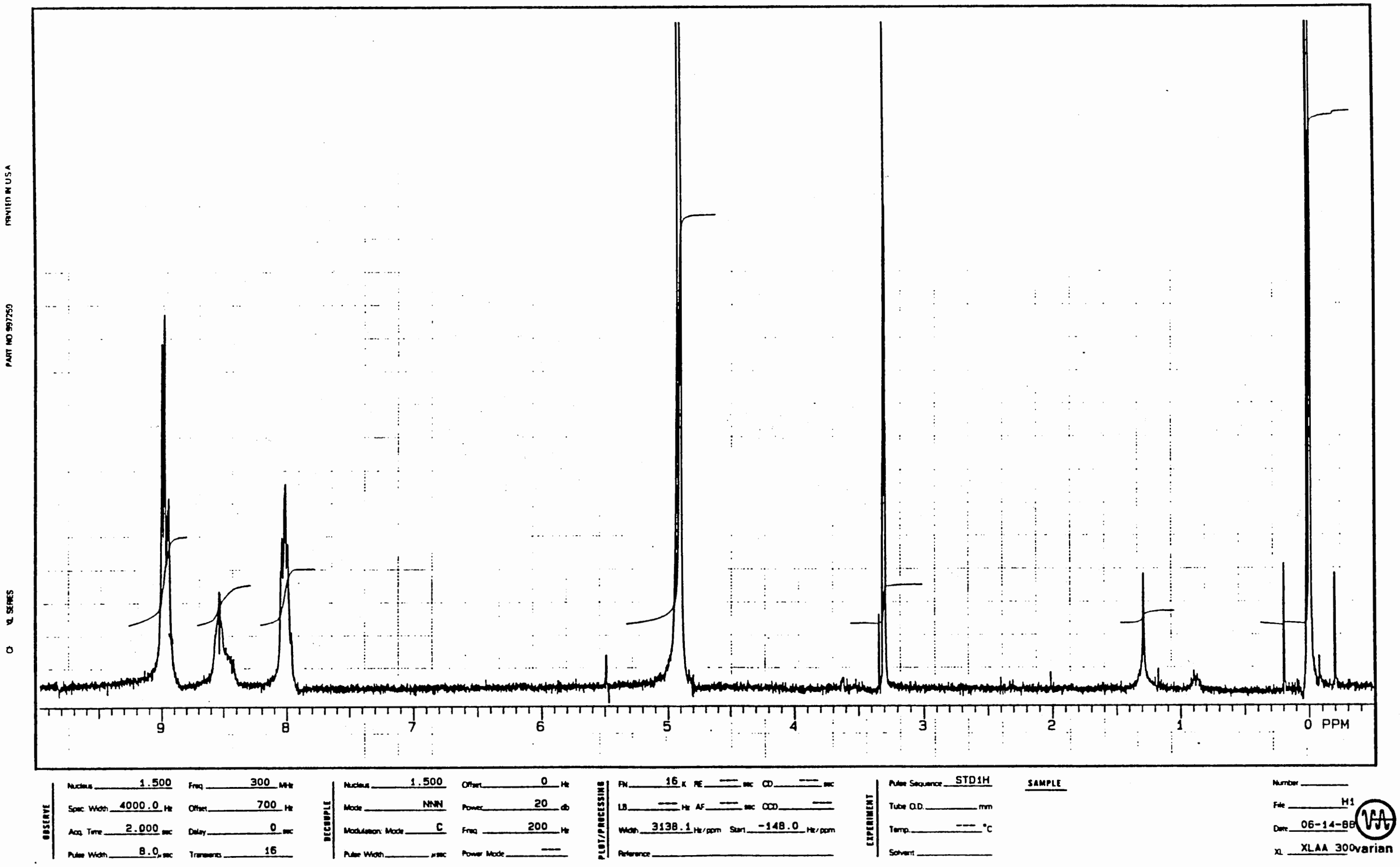


Figure 46. ^{1}H NMR spectrum of 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrin (**71**).

Tetrasodium Salt of 5,10,15,20-Tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) Chloride (65). Method 1: $H_2TSPPCl_8H_4$ (**71**) in H^+ form (280.6 mg, 0.23 mmol) and $MnCl_2 \cdot 4H_2O$ (396.3 mg, 2.0 mmol) were dissolved in 20 mL of distilled water in a 100 -mL round-bottomed flask equipped with a condenser and an egg-shaped stirring bar. The pH of the mixture was adjusted to 8.7 with 1 N NaOH solution. The mixture was heated for 24 h with an 85 ± 2 °C oil bath. Every 7-8 h, the pH was checked and raised from 6.0-6.5 to 8.5-9.0 with 1 N NaOH solution. The pH after reaction stopped was 6.7, and 1 N NaOH was added to pH 8.7. The mixture was evaporated to dryness, then dissolved in methanol, and filtered through a 60 -mL 40F fritted funnel to remove methanol-insoluble or slightly soluble salts. A 20 x 1 cm Dowex 50-X8® column was converted to Na^+ form with NaOH and washed with distilled water extensively until the pH of eluate dropped to 6.5. The solution of porphyrin **65** in methanol was passed through the column. The sulfonic acid groups of the manganese porphyrin **65** eluting from the column were already converted to the sodium salt. Since the column used in the purification was a cation exchange column in Na^+ form, the chloride anions from $MnCl_2$ were eluted as NaCl along with the manganese porphyrin **65**. The eluate was rotary evaporated to dryness, and the residue was dried in a vacuum desiccator at 65 °C for 18 h. The residue was Soxhlet extracted twice with HPLC grade methanol, and the product was recovered by rotary evaporation and dried in a vacuum desiccator at 65 °C for 24 h. Yield was 355 mg (0.22 mmol, 96%). The elemental analysis of this batch gave about 85% manganese incorporation and presence of 1 mol of NaCl per porphyrin. The odd numbers of H, Cl, and Mn in the calculated formula are due to partial metalation and sulfonation of the porphyrin. Anal Calcd. for $C_{44}H_{16.9}N_4Cl_{8.85}Mn_{0.85}$ x 3.4 SO_3Na x 12 H_2O x NaCl (FW 1587.0): C, 33.30; H, 2.60; N, 3.53; S, 6.87, Mn, 2.94. Found: C, 32.83; H, 2.32; N, 3.05: S, 6.70; Mn, 2.95.

Method 2: $H_2TSPPCl_8H_4$ **(71)** in H^+ form (221.7 mg, 0.18 mmol) and $MnCl_2 \cdot 4H_2O$ (307.4 mg, 1.55 mmol) were dissolved in 20 mL of distilled water in a 100-mL round-bottomed flask equipped with a condenser and an egg-shaped stirring bar. The pH of the mixture was adjusted to 9.0 with 0.5 N NaOH solution. The mixture was heated for 24 h with an 85 ± 2 °C oil bath. During the reaction, the pH was raised three times to 9 with 0.5 N NaOH. After the reaction stopped, 0.5 N NaOH solution was added until the pH was 11.5. The brown mixture was evaporated to dryness, and the residue was dissolved in methanol. The solution was passed through a 40 x 1 cm column of Amberlite® IR-120 (H^+ form) ion exchange resin, and eluted into a receiver containing 0.62 mmol of NaOH solution to neutralize the sulfonic acid groups of the manganese porphyrin. The neutralized filtrate was evaporated to dryness on a rotary evaporator, dissolved in methanol, and filtered through a 60-mL 40F fritted funnel connected to a water aspirator. The filtrate was rotary evaporated to dryness, and the residue was Soxhlet extracted twice with HPLC grade methanol. Porphyrin **65** was recovered and dried in a vacuum desiccator at 65 °C for 18 h. The elemental analysis of manganese porphyrin from this purification showed 65% metal incorporation and the presence of 11 mols NaCl per porphyrin. The odd numbers of H, Cl, and Mn in the calculated formula are due to partial metalation and sulfonation of the porphyrin. Anal. Calcd. for $C_{44}H_{17.2}N_4Cl_{8.65}Mn_{0.65} \times 3.5\ SO_3Na \times 12\ H_2O \times 11\ NaCl$ (FW 2164.0): C, 24.42; H, 1.92; N, 2.59; Cl, 32.19; S, 5.19; Na, 15.40; Mn, 1.65. Found: C, 24.55; H, 2.08; N, 2.22; Cl, 32.31; S, 4.91; Na, 17.70; Mn, 1.65.

5,10,15,20-Tetrakis(4-sulfonatophenyl)porphinatomanganese(III) Acetate (54). Tetrasodium 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin · 12 H_2O in Na^+-form (341 mg, 0.275 mmol) and $Mn(CH_3CO_2)_2 \cdot 4H_2O$ (675 mg, 2.75 mmol) were dissolved in 20 mL of distilled water in a 100-mL round-bottomed flask equipped with a condenser and an egg-shaped stirring bar. The pH of the mixture was adjusted to

8.1 with 0.5 N NaOH solution. The mixture was heated for 26 h with an 85 ± 2 °C oil bath. During the manganese incorporation into 5,10,15,20-tetrakis(4-sulfonatophenyl)-porphyrin, the pH was adjusted three times to 8.4-9.4 with 0.5 N NaOH. After the reaction stopped, 0.5 N NaOH solution was added until the pH was 12.3.

The green mixture was evaporated to dryness on a rotary evaporator, dissolved in methanol, and then passed over a 30 x 1 cm column of Amberlite® IR-120 (H^+ form) cation exchange resin. The pH of the eluate was adjusted to 7.1. The mixture was evaporated on a rotary evaporator. Further purification was accomplished by precipitating the porphyrin **54** from a methanol solution by the addition of excess amount acetone. The precipitate was dissolved in methanol and reprecipitated with acetone six times.The product was vacuum dried at 60 °C for 16 h. Yield was 0.173 mmol, 63% for the porphyrin **54**. The manganese content of this porphyrin was not analyzed.

Determination of NaOCl Content of Commercial Bleach. Iodometric titration[194] was used for determination of the ClO^- content of commercial bleach solution. Clorox® (10 mL, 10.71 g) was diluted to the mark in a 200 mL volumetric flask, and 50 mL of it was taken in a 250 mL Erlenmeyer flask. After addition of about 2 g of KI and 10 mL of glacial acetic acid to the Erlenmeyer, the solution was titrated against 0.102 M solution of $Na_2S_2O_3$, which was standardized against 8.98 x 10^{-3} M KIO_3 solution, until the solution became pale yellow. Then a few mL of fresh starch solution was added. Titration was continued until dark-blue solution became colorless. Each measurement was done 3 times and the results were averaged.The redox equations below were used to determine the hypochlorite content of the bleach. [ClO^-] of Clorox® bleach was 5.34% by weight and 0.768 M.

Standardization of $Na_2S_2O_3$:

$$IO_3^- + 8\,I^- + 6\,H^+ \longrightarrow 3\,I_3^- + 3\,H_2O \qquad (30)$$

$$I_3^- + 2\,S_2O_3^{-2} \longrightarrow 3\,I^- + S_4O_6^{-2} \qquad (31)$$

Determination of sample:

$$ClO^- + 3I^- + 2H^+ \longrightarrow Cl^- + I_3^- + H_2O \quad (32)$$

I_3^- titrated with $S_2O_3^{-2}$ as in eq. 31.

General Procedures for Epoxidation of Styrene. Method 1: A 25 mL single neck round-bottomed flask was charged with pentadecane (internal standard, 60.9 mg), and latex (1.0 mL, 40.4 mg). While the flask was sonicated, a stock solution of 1.78×10^{-3} M porphyrin **65** (1.25 mL, 2.22×10^{-3} mmol) was added via a pipette. If a reaction was carried out without latex, the sonication step was omitted, and 1.0 mL of distilled water was added in place of the latex. Finally NaOH (0.76 mL, 2.30 mmol) and distilled water (0.90 mL) were added via pipettes. The flask was equipped with a stirring bar and an adapter fitted with a septum and glass stopcock and was flushed with argon. Styrene (125 mg, 1.20 mmol) was added to the flask through the septum via a syringe. Finally argon-purged Clorox® bleach solution (1.95 mL, 1.50 mmol) was added via a syringe. The pH of Clorox® bleach was 11.3. The flask was protected from ambient lighting by covering with a black sheet and its contents were stirred for 1 h at ambient temperature.

Method 2: A 20-mL test tube was first charged with pentadecane (internal standard, 59.2 mg) and latex (1.0 mL, 40.4 mg). While the flask was sonicated, a stock solution of 1.78×10^{-3} M porphyrin **65** (1.25 mL, 2.22×10^{-3} mmol) was added slowly to the test tube via a pipette. If a reaction was carried out without latex, the sonication step was omitted, and 1.0 mL of distilled water was added in place of the latex. After addition of NaOH (0.76 mL, 2.30 mmol) and distilled water (0.90 mL), the test tube was sealed with a septum and wrapped with teflon tape. After the test tube was purged with argon, styrene (124.6 mg, 1.20 mmol) was added via a syringe. Then the test tube was wrapped with a black sheet to protect it from ambient ligthing and was clamped to a wrist-action shaker. Finally argon-purged Clorox® bleach solution (1.95 mL, 1.50 mmol) was added through the septum via a syringe. The pH of Clorox® bleach was 11.3. The tube contents were shaken for 1 h at ambient temperature.

The reaction mixture was transferred into a 12-mL conical tube with a screw cap. A few mL of diethyl ether was added to the tube. The tube was shaken vigorously and centrifuged with a bench top centrifuge, and the top organic phase was transferred to another flask with a disposable pipette. This process was repeated 4-6 times until no styrene or product peak was seen on GLC chromatograms of the last extract of the reaction mixture. The combined extract was analyzed quantitatively with GLC. Response factors of 0.99 and 0.91 relative to pentadecane were used for styrene and styrene oxide. The products were identified by ^{1}H NMR spectroscopy.

Competition Experiments. Method 2 was followed with two different arylalkenes (1.20 ± 0.03 mmol each) in the reaction mixtures.

Preparation of NaOCl Solution. NaOCl solution was prepared according to the procedure described by Audrieth.[195] A 500 mL round-bottomed three neck flask equipped with a thermometer was charged with 16.3 g (0.41 mol) of NaOH pellets and 75 mL of degassed distilled water under argon. The flask was put in an ice bath and small ice pieces prepared from distilled water were added to the flask to lower the temperature around to 0 °C. Slowly Cl_2 gas was bubbled through the alkaline solution for 4 h while the temperature was kept at 0 °C. The solution contained 2.09% NaOCl by weight and 0.297 M NaOCl.

Oxidation of Styrene with Dioxygen. General Procedure: A 25-mL round-bottomed flask with a magnetic stirrer was charged with porphyrin **65** (1.15 mL, 2.50×10^{-3} mmol), 0.25 mmol of imidazole, and 0.28 mmol of $NaBH_4$. After addition of styrene (1.25 mmol), the 3 mL of mixture was kept under 0.93 atm of dioxygen for 1 h. Organic components were extracted with diethyl ether. In the case of methanol solvent, the extraction solvent was *n*-heptane. Products were analyzed by GLC by comparing with autentic samples of all possible oxygenated products of styrene and by ^{1}H NMR.

Stability of Porphyrin 65, Porphyrin 72 and Porphyrin 54 in the Presence of NaOCl. Absorption Spectra of Soluble Porphyrin 65 and Latex-Bound Porphyrin 72. Porphyrin **65** solutions (1.31×10^{-4} M) at neutral pH, in 0.38 M NaOH solution, and in 0.25 M NaOCl and 0.38 M NaOH were prepared and their absorption spectra were obtained. Also absorption spectra of porphyrin **65** in the presence of different amounts of latex at pH 9.0 were taken (Figure 31). Porphyrin **65** (0.74 mL, 2.62×10^{-4} mmol) solutions were added slowly via a pipette to a latex containing a certain amount of polymer while it was sonicated. The sonication continued about 5 min. Addition of sodium borate (0.58 mL, 1.74×10^{-3} mmol) solution, and dilution to 2.0 mL gave a dispersion that was 8.70×10^{-4} M in borate and pH 9.0. The final mixtures contained 0, 0.22, 1.7, and 8.5 mg of polymer per mL. The spectra were recorded.

Oxidation of porphyrin **65** by 0.065 M NaOCl was studied at constant Mn porphyrin concentration (1.31×10^{-4} M) with variable latex concentration (0-8.5 mg per mL) (Figure 32) and at variable Mn porphyrin concentration (1.05×10^{-5}-1.31×10^{-4} M) with constant latex concentration (8.5 mg per mL) (Figure 34) in 0.38 M NaOH solution. In the first case, porphyrin **65** (0.74 mL, 2.62×10^{-4} mmol) was added slowly via a pipette to a latex containing a certain amount of polymer (0.42 mL, 17.0 mg) while it was sonicated. Then 0.25 mL of 3.05 N NaOH, 0.42 mL of water, and 0.17 mL of 0.768 M NaOCl were added. A small sample from this mixture was transferred to a spectrophotometer cell, and the spectrum was obtained. In the second case, the latex concentration was 8.5 mg per mL, and the Mn porphyrin concentrations were 1.01×10^{-5}, 2.72×10^{-5}, 5.65×10^{-5}, and 1.31×10^{-4} M.

Spectrophotometry of Reacting Mixtures. Test tube styrene epoxidations with soluble porphyrin **65** and latex-bound porphyrin **72** catalysts were carried out to study the absorption spectra of oxo-porphyrin **65** and latex bound oxo-porphyrin **72** during the reactions (Figure 35 and 36). Samples (200 μL) from reaction mixtures were withdrawn with a syringe at 3, 13, 27, 44, and 60 min after addition of styrene and diluted to 500 μL with water. The UV/visible spectrum of every sample was obtained immediately using a 0.1-cm path-length spectrophotometer cell. The samples were handled under air and light during preparation.

Titration of Porphyrin 65 with NaOH. Porphyrin **65** (1.54 mL, 2.03 x 10^{-4} mmol) solutions were diluted to 2.0 mL with different concentrations of NaOH solutions (Figure 30). The pH's of the solutions were measured with the pH-meter equipped with a Corning® semi-micro combination electrode. The UV/visible spectra of these porphyrin **65** solutions (1.02 x 10^{-4} M) were taken at pH 7.0, 9.2, 9.9, 10.3, 11.3, 11.6, and 11.9. For high pH experiments, porphyrin **65** (1.32 mL, 1.98 x 10^{-4} mmol) solutions were diluted to 2.0 mL with NaOH solutions of different concentrations to achieve final NaOH concentrations of 1.03, 0.38, 0.06, and 0.01 M.

Stability of Soluble Porphyrin 65 and Latex-Bound Porphyrin 72 in NaOCl-NaOH. The changes of the absorption spectra of soluble porphyrin **65** and latex-bound porphyrin **72** in the presence of NaOCl at pH 10.8 and at pH >13 ([NaOH] = 0.38 M) were followed and the changes of the absorbance at λ_{max} were used to calculate the rate of disappearance.

A solution of porphyrin **65** (1.0 mL, 4.20 x 10^{-5} mmol) was diluted to 2.12 mL with water, and treated with NaOCl (1.02 mL, 0.78 mmol) at pH 10.8. The solution was transferred to a spectrophotometer cell at 30.0 ± 0.1 ^{o}C, and its spectrum was obtained in 1 min after the addition of NaOCl. The cell was kept in the cell holder and a spectrum was obtained every 30 min for 4 h to determine the rate of destruction of oxo-porphyrin **65**.

Using the 1st order rate law, the rate constant for disappearance and the half-life of the Mn porphyrin were calculated.

A similar study to the one described above was carried out with the same concentrations of porphyrin **65** and NaOCl at high NaOH concentration (0.38 M).

In the stability investigations of latex-bound porphyrin **72**, first porphyrin **65** (1.0 mL, 4.20 x 10^{-5} mmol) was added slowly via a pipette to the latex (0.52 mL, 0.56 mg) while it was sonicated. Then water (0.60 mL) and NaOCl (1.02 mL, 0.78 mmol) were added to the mixture of porphyrin **72**. The mixture at pH 10.8 was transferred to a spectrophotometer cell, and its spectrum was obtained in 1 min after the addition of NaOCl at 30 ± 0.1 °C. The cell was kept in the cell holder and the UV/visible spectrum was obtained every 30 min for 4 h to determine the rate of destruction of latex-bound porphyrin **72**. Using 1st order rate law, the disappearance constant and half life of the latex-bound porphyrin **72** were calculated.

A similar study to the one described above was carried out with the same concentrations of latex-bound porphyrin **72** and NaOCl at high NaOH concentration (0.38 M).

Stability of 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphinato-manganese Acetate (54) in NaOCl-NaOH Solution. In a qualitative test, the color of the solution of porphyrin **54** turned from red-brown at neutral pH to green at 13.1 due to changes of the ligands on porphyrin **54**. However in the presence of 0.18 M NaOCl, porphyrin **54** (4.38 x 10^{-4} M) bleached quickly. The color changed from red brown to light yellow in seconds. The stability of porphyrin **54** did not improve in the pH range of 8.8-13.1. In the absence of NaOCl, the porphyrin **54** was stable at neutral pH for months and at least the observed time of 18 h at pH 13.1. The attempts to determine the bleaching rate of porphyrin **54** quantitavely using the spectrophotometer failed because of extremely fast bleaching of the porphyrin **54**. In the first experiment porphyrin **54**

(1.32×10^{-5} M) in the solution of 0.38 M NaOH in the presence of 0.25 M NaOCl lost its color in 3.5 min whereas in the absence of externally added NaOH, the bleaching was so fast that during the first scan of the sample no 420 nm absorption maximum of porphyrin **54** was observed.

Binding of Porphyrin 65 to Colloidal Quaternary Ammonium Exchange Resins. Porphyrin **65** (1.25 mL, 2.22×10^{-3} mmol) solution was added slowly via a pipette to a latex (1.0 mL, 6 mg, $n_{N^+R_4\,Cl^-} = 2.53 \times 10^{-2}$ meq) while it was sonicated. The ratio of SO_3^- to N^+R_4 was 0.3 in the dispersion. The sonication was continued about 15 min. Then the dispersion was ultrafiltered through a 0.1 μm cellulose acetate/nitrate membrane filter (47 mm in diameter) (Millipore) using an all glass ultrafiltration system (Millipore).

The red-brown residue was washed with distilled water and the filtrate was added up to 25 mL. The absorption spectrum of the filtrate showed 0.04% of the original porphyrin **65** in the filtrate. However there was about 5 nm shift to $\lambda_{max} = 468$ nm in the spectrum relative to the $\lambda_{max} = 463$ nm spectrum of the original porphyrin **65** solution.

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