METALLOPORPHYRIN CATALYZED OXIDATION OF CHLOROPHENOLS

by

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We Accept This Thesis As Conforming
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Date April 28, 1992
ABSTRACT

The use of water soluble, non-aggregating metalloporphyrins (meso-tetra(2,6-dichloro-3-sulphonatophenyl) porphyrin (TDCSPP) and meso-tetra(2,6-dichloro-3-sulfonatophenyl)-β-octachloroporphyrin (TDCS-β-Cl₈P) coordinated with iron or manganese) as catalysts for the peroxide oxidation of chlorophenols were investigated. The relative rates of chlorophenol oxidation with respect to several variables (catalyst, pH, oxidant, and chlorophenol structure) were determined. The rate was found to be pseudo-first order in the catalyst. The oxidation was most efficient using the iron porphyrins, at pH < 4. The oxidation rate was dependent on the oxidant. In order of decreasing rate, meta-chloroperoxybenzoic acid > potassium monoperoxysulfate > hydrogen peroxide > t-butylhydroperoxide. The oxidation rate was strongly dependent on both the number and the position of chlorine substitution on the phenol. In order of decreasing rate, 2,4-dichlorophenol > 2,4,5-trichlorophenol > 2-chlorophenol ≈ 4-chlorophenol > 3,4-dichlorophenol ≈ 2,4,6-trichlorophenol > 2,3,4,6-tetrachlorophenol ≈ 2,3,5,6-tetrachlorophenol > 3-chlorophenol > 3,5-dichlorophenol ≈ 2,3,4,5-tetrachlorophenol. The structures of some of the catalyzed reactions were elucidated. Products of phenoxy radical coupling, and quinones are typical. The results are discussed in the context of the possible use of these metalloporphyrins for pollution remediation.
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LIST OF ABBREVIATIONS

μmol micromole
abs absorbance
CP chlorophenol
DCP dichlorophenol
DNA deoxyribonucleic acid
FeTDCS-β-Cl₈PCI [iron(III)(meso-tetra(2,6-dichloro-3-sulfanatopheny1)-β-octachloroporphyrinato)] chloride
FeTDCSPPCl [iron(III)(meso-tetra(2,6-dichloro-3-sulphonatophenyl)porphyrinato)] chloride
HRP horseradish peroxidase
HPLC high performance liquid chromatography
HRMS high resolution mass spectrometry
LRMS low resolution mass spectrometry
mCBA meta-chlorobenzoic acid
mCPBA meta-chloroper oxybenzoic acid
mmol millimole
MnTDCSPPCl [manganese(III)(meso-tetra(2,6-dichloro-3-sulphonatophenyl)porphyrinato)] chloride
mol mole
nm nanometre
PCB polychlorinated biphenyl
PPM parts per million
rel. int. intensity relative to base peak (100%)
T temperature
t time
t-BuOH t-butyl alcohol
t-BuOOH t-butylhydroperoxide
<table>
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<tr>
<td>TCP</td>
<td>trichlorophenol</td>
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<tr>
<td>TDCS-β-Cl₅P</td>
<td>meso-tetra(2,6-dichloro-3-sulfanatophenyl)-β-octachloroporphyrin</td>
</tr>
<tr>
<td>TDCSPP</td>
<td>meso-tetra(2,6-dichloro-3-sulphonatophenyl) porphyrin</td>
</tr>
<tr>
<td>TeCP</td>
<td>tetrachlorophenol</td>
</tr>
<tr>
<td>TFA</td>
<td>trifluoroacetic acid</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
</tr>
<tr>
<td>TPP</td>
<td>meso-tetraphenyl porphyrin</td>
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<tr>
<td>tᵣ</td>
<td>retention time (chromatography)</td>
</tr>
<tr>
<td>TSPP</td>
<td>meso-tetra(4-sulphonatophenyl) porphyrin</td>
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<tr>
<td>UV</td>
<td>ultraviolet</td>
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<td>Vis</td>
<td>visible</td>
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1. INTRODUCTION

1.1 General Introduction

In 1988 ancient Inuit tissue, frozen for over 400 years, was analyzed for the presence of chlorinated dioxins. None of these toxic chemicals were detected. In contrast, modern human tissue samples have an average of 1 ppb dioxins\(^1\).

Another study, focusing on the measurement of chlorinated dioxins in core samples from lake sediments, illustrated that only sediments deposited after about 1938 contained any measurable quantities of these compounds\(^2\).

The implication of these data is that some aspects of recent human activities have led to the formation of these compounds. It has been suggested\(^2,3\) that the production and use of industrial quantities of chlorinated organic chemicals, which began around 1940, was the key transformation. These chlorinated materials subsequently entered the environment, both through use and through waste streams, in large quantities. Burning the contaminated wastes created dangerous and persistent chlorinated organic compounds (in particular, dioxins) and dispersed them widely. Within a very short period of time, the global environment has become contaminated with measurable quantities of potentially damaging chemicals.
This realization underscores the importance of acquiring a general understanding of the sources, the behaviour and the control of anthropogenic inputs into the environment. Following this theme, this thesis studies the use of water soluble metalloporphyrin catalysts for the oxidation of chlorophenols in aqueous wastes. Products of the oxidation reactions are described, and the relative rates of chlorophenol removal are reported. The technique is evaluated in terms of its viability as a new method for remediation of chlorophenol-containing aqueous wastes.
1.2 Chlorophenols

1.2.1 Sources and Scope of Environmental Contamination

The world wide production of chlorophenols exceeded an estimated 200 million kilograms in 1975\textsuperscript{[4]}, of which approximately half was pentachlorophenol. In Canada, during 1981, 5.3 million kilograms of chlorophenols was consumed. It was reported that 1.4 million kilograms (26\%) were eventually released into the environment\textsuperscript{[5]}. The general biocidal nature of chlorophenols led to the extensive use of technical mixtures of chlorophenols, in particular pentachlorophenol, as a wood preservatives\textsuperscript{[4]}.

The soil and water around many sawmills\textsuperscript{[6,7,8,9]} and wood preserving facilities\textsuperscript{[10,11]} is heavily contaminated with chlorophenols. A study (1987) of sawmills and lumber export terminals using chlorophenol treated wood in the lower mainland of British Columbia, found that storm water run-off from these facilities contained in excess of 100 \( \mu \text{g/L} \) total chlorophenols, concentrations which affect the growth and reproduction of fish\textsuperscript{[12]}.

Vast quantities of 2,4-dichlorophenol and 2,4,5-trichlorophenol have been made, as these compounds are the starting materials for the preparation of the important herbicides 2,4-dichlorophenoxyacetate (2,4-D) and 2,4,5-trichlorophenoxyacetate (2,4,5-T), widely used in agriculture. Since the initial biodegradation products of 2,4-D and 2,4,5-T are
2,4-dichlorophenol and 2,4,5-trichlorophenol, respectively, these two chlorophenols are particularly widespread environmental contaminants.\(^{13}\)

Chlorination of drinking water supplies leads to the formation of chlorophenols. Chlorine treatment of water containing two naturally occurring benzoic acids (p-hydroxybenzoic acid and vanillic acid) yielded 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol.\(^{14}\)

Chlorophenols are also generated as side products during many industrial processes. They have been detected in the waste of at least twelve industrial categories, including textiles, polymer manufacturing, metal refining, and coal conversion.\(^{15}\)

The presence of chlorophenols in the waste waters of pulp and paper bleach plants is particularly well documented.\(^{16,17,18,19}\) Treatment of pulp with chlorine to solubilise lignin (an intricate polymer containing phenylpropane moieties) naturally yields a complex mixture of chlorinated organic compounds including many chlorophenols.\(^{16}\) In a review of chemicals present in pulp mill effluent, researchers list 14 chlorophenol congeners. They reported a value of 2 g/tonne of effluent for 2,4-dichlorophenol.

A natural solution to the problem of generating chlorinated wastes is to use alternative bleaching agents. Although new chlorine free bleaching techniques are becoming industrially implemented, the majority of Canadian mills were built before 1975, and due to the high cost of retrofitting, these older mills will likely be dedicated to chlorine processes for some time.
Some chlorophenols are known to occur naturally. For example, 2,6-dichlorophenol is a sex pheromone for several species of tick\[^4\]. Compared to anthropogenic inputs, naturally occurring sources are negligible.

In general it can be said that chlorophenols are ubiquitous in the environment, having been detected in municipal sludges\[^20\], waste-waters\[^21\], soils\[^6,7,10\], groundwater\[^22\], surface water\[^23\], food\[^4\], animals\[^24\] and humans\[^4,25\].

1.2.2 Toxicity

In many early chlorophenol toxicity studies the effect of the presence of chlorinated dioxins, now known to be a common chlorophenol contaminant, was not evaluated. Due to the high toxicity of the dioxins the results of this early work is questionable. However, recent evaluations, using pure chlorophenol samples, have determined chlorophenols to be acutely toxic to a variety of organisms.

Increased acute toxicity with increased chlorine substitution was demonstrated for several species of fish. For example, two LC\(_{50}\) (24 hr) values (the concentration at which 50% of the sample population dies) for trout are 1.7 ppm for 2,4-dichlorophenol to 0.2 ppm for pentachlorophenol\[^27\]. Similar results were obtained for fathead minnows\[^28\].
Inhibition of bacterial growth also follows the general trend of increased toxicity with increased chlorine substitution\textsuperscript{[29,30]}. Values expressed as IC\textsubscript{50} (effective concentration causing 50% growth inhibition) were determined for 19 chlorophenols and varied from 700 ppm for 2-chlorophenol to 4 ppm for 2,3,4,5-tetrachlorophenol.

The toxicity investigations also found a dependency of the toxicity on the position of chlorine substitution. Chlorophenols with chlorine in the 3 and 5 positions are often more toxic than expected solely on the basis of their degree of substitution. No rationalization was forwarded for this observation. However, based on the work in this thesis, there is some correlation between oxidative stability and toxicity. This will be discussed further in a subsequent section.

Toxicity to phytoplankton, zooplankton, and invertebrates has been studied\textsuperscript{[4]}. The IC\textsubscript{50} values are similar and in the region of 0.5 to 15 mg/L.

The mammalian carcinogenicity of 2,4,6- and 2,4,5-trichlorophenol has been evaluated by the International Agency for Research on Cancer\textsuperscript{[26]}. It was concluded that 2,4,6-trichlorophenol is an animal carcinogen, and that there were inadequate data for the assessment of the carcinogenicity of 2,4,5-trichlorophenol.

As well as being inherently toxic, the generation of highly toxic dioxins from the low temperature incineration of chlorophenols and from photolysis of chlorophenols in the
The presence of chlorobenzenes is well documented\textsuperscript{[31,32]}. The toxicity, and the widespread nature of the contamination, has led to the inclusion of four chlorophenols on the U.S. Environmental Protection Agency's list of 129 Priority Pollutants\textsuperscript{[41]}. It is known however, that partial oxidation of chlorophenols significantly decreases their toxicity\textsuperscript{[33]}.

1.2.3 Remediation of Chlorophenol Pollution

Much effort has been focused on methods of degradation or removal of chlorophenols for remediation of contaminated soils and waste water. Due to the complexity and variety of the waste, no single system has been developed which removes or degrades chlorophenols under all conditions. Several abatement techniques are discussed here.

1.2.3.1 Microbial Techniques

Biorestoration of contaminated sites is a promising technique\textsuperscript{[34,35,36,37,38]}. Biodegradation offers distinct advantages over other treatments, primarily the potential for complete mineralization of contaminants to carbon dioxide and inorganics, a most desirable result. The 'ecologically
sound’ nature of the technique, and the ability to treat soils in situ are other advantages often quoted.

Biodegradation of chlorophenols has been extensively studied, using both individual strains and mixed cultures of aerobic\textsuperscript{[39]} and anaerobic\textsuperscript{[40,41,42,43,44]} microorganisms. Since chlorophenols are used specifically as antimicrobial and antifungal agents, it was not a surprising discovery to find that biodegradation by native microorganisms is slow.

In a recent study, biodegradation of pentachlorophenol by native microorganisms in contaminated soil from a wood preserving facility was monitored\textsuperscript{[45]}. The soil was tilled and fertilized with appropriate nutrients. Over 90 days pentachlorophenol concentration decreased from 90 mg/kg soil to 25 mg/kg soil. The researchers considered this rate of degradation too slow for a full scale remediation strategy.

More efficient biodegradation was observed when pentachlorophenol was present in low concentrations. In soil amended with sewage sludge, $^{14}$C labelled pentachlorophenol (0.75 mg PCP/kg soil) was observed to be degraded to $^{14}$CO$_2$, with a half life of ten to fifteen days\textsuperscript{[20]}.

Soil heavily contaminated with a chlorophenol based fungicide (mostly 2,3,4,6-tetrachlorophenol) was isolated and monitored for chlorophenol degradation\textsuperscript{[46]}. After two years the total chlorophenol concentration decreased from 212 mg/kg to 15 mg/kg.
Genetic selection in vivo and genetic manipulations in vitro have allowed construction of bacteria strains which have wider biodegradation potentials than their natural counterparts. Several isolated cultures have been shown to utilize, under laboratory conditions, some chlorophenols as their carbon or energy source.

A Flavobacterium species has been shown to effectively degrade pentachlorophenol, utilizing this substrate as its sole source of carbon and energy\textsuperscript{(47,48)}. A solution of pentachlorophenol (50 mg/L) was completely mineralized within 48 hours. However, inoculation of contaminated soils with this species enhanced pentachlorophenol degradation, but the efficacy was not total and repeated culture applications were necessary for 80\% removal after 100 days\textsuperscript{(50)}.

As with most metabolic processes, the biochemical mechanism for bacterial metabolism of chlorophenols is highly specific. For example, the above mentioned Flavobacterium species was specific to pentachlorophenol and did not metabolize other chlorinated phenols; of the fifteen di- tri- and tetra- chlorophenols, only 2,4,6-trichlorophenol and 2,3,5,6-tetrachlorophenol were significantly degraded\textsuperscript{(49)}.

In contrast to the substrate specificity of bacteria, the basidiomycetes fungus Phanerochaete chrysosporium has the ability to degrade a wide variety of organic pollutants\textsuperscript{(51)}. The extractable pentachlorophenol in soils inoculated with P. chrysosporium decreased by 98\% over two months\textsuperscript{(52)}. It was determined that the major degradative pathway was not to CO\textsubscript{2},
but rather irreversible binding to soil organic matter was likely. Other researchers have found that basidiomycetes fungi methylate chlorophenol hydroxyl groups, producing chloroanisoles\(^{[53]}\). Chloroanisoles would be strongly bound to the soil organic matter, and thus less available for attack by fungal enzymes. The biotransformation of xenobiotic substrates into new, sometimes more recalcitrant, compounds is an important consideration. As with basidiomycetes fungi, the bacterium *Rhodococcus chlorophenolicus* generates chlorinated methoxyphenols as well as completely degrading chlorophenols\(^{[59,54]}\).

The use of microbes as a technology for remediation of contaminated sites or wastes faces other limitations. It has been suggested\(^{[55]}\) that environmental conditions such as extremes of pH and temperature, toxins, predators, competition from indigenous populations, nutrient limitations and, high concentrations of pollutants and their by-products, may inhibit growth, or kill microbial cells and prevent biodegradation. Practical difficulties such as maintaining active cells during transportation to polluted sites and limited mobility of the cells within the soil are other restricting factors.

1.2.3.2 Enzymatic Techniques

Enzymes have been reported to be less sensitive than bacteria to variations in pH, pollutant concentration, toxins, and temperature\(^{[55]}\). The use of enzymes could circumvent some of the drawbacks encountered by microorganisms. The function of enzymes *in vivo* is to perform
only one of many steps in the metabolism of a substrate. Thus, enzymatic treatments do not have the potential for complete mineralization of pollutants.

Enzymes which catalyze phenol oxidation (phenol oxidases, laccases, peroxidases) have been used to detoxify phenol solutions and industrial waste waters\[^{55}\]. Oxidation and polymerization of the phenols yields less soluble high molecular weight compounds which can be removed by filtration or sedimentation. The precipitates formed during the polymerization of 2,4-dichlorophenol were oligomers with average molecular weights of 800. As well, inorganic chloride was released during the reaction. Up to 20% of the chlorine initially associated with the phenol was released.

Extracellular laccases from the fungi *Rhizoctonia practicola* and *Tramates versicolor* as well as horseradish peroxidase and tyrosinase have been used as oxidation catalysts to detoxify aqueous chlorophenol solutions\[^{56,57,58}\].

2,4-dichlorophenol is completely removed from solution within 5 hours by horseradish peroxidase with hydrogen peroxide, but only 83% of 4-chlorophenol is removed after 15 hours. After 15 hours, the laccase from *T. versicolor* removed 90% of 2,4-dichlorophenol from solution, but under the same conditions, only 38% of the 2,4,5-trichlorophenol was removed. As with microorganisms, the enzymes appear to exhibit significant substrate specificity.
The activity of the enzymes is dependent on the pH of the solutions. The laccase enzyme from *R. practicola* was inactive towards oxidation of 2,4-dichlorophenol above pH 9 and below pH 4. Horseradish peroxidase must be between pH 5.5 and 8.5 to retain 90% or more of its activity.

Although the laccases are less effective than horseradish peroxidase, for potential large scale applications, the laccases have the advantage of utilizing molecular oxygen as the oxidant, whereas peroxidase requires more costly hydrogen peroxide.

Efficient dechlorination of 2,4,6-trichlorophenol by extracellular lignin peroxidases (ligninase) from *Phanerochaete chrysosporium* has been observed\(^{[59,60]}\). The researchers identified 2,6-dichlorobenzoquinone as the product of quantitative 4-dechlorination. 2,4-dichlorophenol was oxidized to 2-chloro-1,4-benzoquinone\(^{[61]}\).

Although enzymes are potentially more robust than microbes, enzymatic detoxification processes also show disadvantages. Thermal denaturation of enzymes is well known and can occur at temperatures as low as 40°C. Many inorganic and organic substances act as inhibitors of enzymes and can render them inactive. Phenol polymers, like those generated in some of the enzymatic reactions, are known to be generated by plants in response to cut wounds as a mechanism of protection, their purpose being to inhibit foreign enzymes. This may work against an enzymatic technique for detoxification of phenolic wastes. Technical confines such as enzyme extraction and purification, and practical obstacles like susceptibility
to degradation by microbial proteases inherent in the waste, may be limitations. Formation of minute amounts of dibenzo-p-dioxins and dibenzofurans during the peroxidase catalysed oxidation of chlorophenols has been tentatively determined\textsuperscript{62}. Generation of these highly toxic products may preclude the use of these techniques for waste clean-up.

1.2.3.3 Chemical and Physical Techniques

Aqueous solutions of iron (II) sulfate and hydrogen peroxide (Fenton's reagent) have been used to oxidize mono- and di-chlorophenols.

Researchers recovered stoichiometric quantities of chloride when using excess hydrogen peroxide, and with ferrous ion present in concentrations similar to that of the initial chlorophenol concentration\textsuperscript{37}. The half life of five of the lower chlorinated phenols ranged from six to twelve minutes. The ultimate fate of the aromatic ring was not elucidated.

Using a similar system, a 2,4-dichlorophenol solution and two phenolic industrial waste-waters were partially oxidized as a pretreatment step prior to biological treatment\textsuperscript{33}. The residual products of hydrogen peroxide oxidation were evaluated based on microorganism toxicity and biodegradability. It was found that the products were an order of magnitude less toxic than the initial solutions. Also, the oxidized material was much more readily consumed by municipal sludge.
Although formation of dioxins from low temperature burning of chlorophenols is known\textsuperscript{[63]}, high temperature rotary kiln incineration has been demonstrated to be effective for chlorophenol destruction\textsuperscript{[64]}. However many complex wastes contain material such as volatile metals, which are dangerous to incinerate.

Other, less widely applicable, techniques for chlorophenol destruction have been reported. Polymerization and dechlorination of pentachlorophenol by oxidation with copper (II) immobilized on smectite clay, was evaluated as a detoxication technology\textsuperscript{[65]}. Extended reaction in refluxing hexane was required, and oxidation was incomplete. Partial dechlorination of chloroaromatics using a semiconductor photoreactor has been reported\textsuperscript{[66]}. Using boiling nitric acid or permanganate does destroy chlorophenols but these conditions are considered too severe for general use\textsuperscript{[67]}. Many other degradation technologies have been reported. Microwave discharge, ozonation, photodecomposition, and physical adsorption are interesting techniques which hold some promise for future development\textsuperscript{[67,68]}. 
1.3 Chemistry of Phenol Oxidation

The oxidation of phenols has been extensively studied\textsuperscript{[69,70,71]}. Biosynthetic pathways to a wide range of natural products including tannins, lignins, pigments, alkaloids and antibiotics involve oxidation and coupling of phenols as key reactions. This same mechanism is implicated in other important biological processes such as the browning of damaged fruit surfaces, and the formation of complex soil humic materials.

Many oxidants have been used to effect phenol oxidation\textsuperscript{[72]}. The most widely used methods involve the use of a variety of inorganic salts and oxides (\textit{e.g.}, of lead, silver, manganese, copper, iron, cobalt, vanadium, thallium, cerium, iridium, and others), particularly lead dioxide, potassium ferricyanide, and ferric chloride. Organic reagents such as nitrites, quinones, peroxides and hydroperoxides have been used. Some other techniques include use of molecular oxygen, enzymes, photolysis, electrolysis, radiolysis and pyrolysis.

The removal of a single electron and a proton generates a phenoxy radical (Figure 1.1).

![Figure 1.1 Resonance Forms of the Phenoxy Radical](image-url)
ESR measurements\cite{73} demonstrate that the highest spin density is found on oxygen and on the \textit{para} carbon ($a_{\text{H}p}=10.1$ Gauss). The spin density is next highest at the \textit{ortho} carbons ($a_{\text{Ho}}=6.6$ Gauss), and the density is much smaller at the 1, 3, and 5 positions.

Two radicals can combine (Figure 1.2), and the dimers a to f may result. The dimers tautomerize rapidly in protic solvents to the stable aromatic compounds g to k. Oligomerization or polymerization is effected by oxidation of the dimers and further coupling with other phenoxy radicals.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{phenol_dimerization.png}
\caption{Products of Phenol Dimerization}
\end{figure}
An alternative fate of the phenoxy radical is possible\cite{59,74} (Scheme 1.1). A second one-electron oxidation, generating a cation, is followed by nucleophilic attack by solvent (water). Loss of the para substituent and a proton yields the benzoquinone. The use of oxygen-transferring oxidants, such as potassium nitrosodisulfonate (Fremy’s salt) or thallium trifluoroacetate also generate quinones in high yields\cite{74,75}. Quinone formation is most common in aqueous reactions with \textit{para}-substituted phenols. Oxidation of 2,6-disubstituted phenols leads to the formation of the \textit{para}-\textit{para} coupled dimer which can be further oxidized to an extended quinone.

\begin{center}
\textbf{Scheme 1.1} \textit{Phenol Oxidation to Form a Quinone}
\end{center}
1.4 Porphyrins

1.4.1 Structural Considerations

All porphyrins are derivatives of the parent methylene bridged tetrapyrrolic macrocycle, porphine (Figure 1.3). The numbering system for IUPAC nomenclature is shown, however non-IUPAC nomenclature is often used. The methylene bridge carbons (5,10,15,20) are also known as the meso- positions, and the peripheral pyrrolic carbons (2,3,7,8,12,13,17,18) are termed the β- positions.

![Figure 1.3 Structure of Porphine](image)

The ring is a conjugated π-system and a number of pathways through the ring involve 18 π-electrons which satisfies the Hückel ‘4n + 2’ rule for aromaticity. The ring is planar, rigid
and has $^1$H NMR chemical shifts typical of aromatic compounds$^{[76]}$. The ring is also a good tetradeutate ligand, readily coordinating metals through the four pyrrole nitrogens, to form metalloporphyrins. Most metals take up axial ligands to complete their coordination sphere. An important and interesting property of metalloporphyrins is that they can be reversibly oxidized; electrons can abstracted from the porphyrin ring, the chelated metal, or from both$^{[77,78]}$.

Metalloporphyrins occur widely in nature and are at the core of the essential processes of life, playing key roles in both plant photosynthesis and animal respiration. A particular metalloporphyrin, iron protoporphyrin IX (Figure 1.4), is the prosthetic group in many enzyme and metalloprotein systems (cytochrome P-450, peroxidases, catalases, haemoglobin, and others), and acts in mediation of a variety of redox reactions, oxygen transportation, and oxygen activation$^{[72]}$.

Figure 1.4 *Structure of Iron Protoporphyrin IX*
An approach to studying the fundamental chemistry of these important biological processes has been the use of synthetic metalloporphyrins as models\cite{80,81,82,83}. Use of protein free iron protoporphyrin IX for *in vitro* studies has not been successful as the porphyrin moiety is reactive, particularly at the *meso*-positions and the vinyl groups. *Meso*-tetraphenylporphyrin, TPP (Figure 1.5; $R_1=R_2=H$) is more stable than protoporphyrin IX, and, importantly, is readily prepared by simple synthetic sequences. Thus, TPP and derivatives, with a wide variety of coordinated metals, have been extensively studied.

\[ R_1 \quad N \quad HN \quad R_2 \]

Figure 1.5  *Structure of Meso-tetraphenylporphyrin* ($R_1=R_2=H$)
Beyond their biological relevance, the catalytic redox activity of metalloporphyrins may lead to their use as catalysts for synthesis or industry. The potential to perform important reactions which are catalyzed by enzymes, while avoiding the difficulties associated with complicated biological systems, is very exciting and promising.

Although capable of oxidizing unactivated alkanes and alkenes, oxidation reactions using metallated TPP are characterized by low turnovers\textsuperscript{[84,85]}. In the presence of molecular oxygen, iron (III) TPP dimerizes through a bridging oxygen atom, as shown in scheme 1.2\textsuperscript{[86]}. The $\mu$-oxo dimer is not catalytically active. This, coupled with oxidative destruction of the porphyrin, are the likely causes of the observed low turnovers.

Scheme 1.2 Formation of Porphyrin $\mu$-oxo Dimers
Through structural modification of the porphyrin periphery the chemical properties of the molecule can be substantially altered. Researchers in our laboratories and elsewhere have prepared modified porphyrins which are more robust and efficient oxidation catalysts than TPP\cite{84,87,88}.

Since the phenyl and porphyrin rings are sterically constrained to be essentially perpendicular to each other, the use of bulky substituents on the ortho-phenyl position (Figure 1.5, R2) sterically prevents formation of the \( \mu \)-oxo dimer\cite{89,90,91}. This non-aggregating behaviour increases catalytic activity\cite{84,92,93}.

Additional stabilization of the porphyrin ring towards oxidation can be accomplished via modification of the porphyrin ring (particularly at the pyrrolic \( \beta \)-position (Figure 1.5, R1) with electron withdrawing groups. Chlorination of the eight \( \beta \)-positions (Figure 1.5, R1=Cl, \( R_2=H \)), produces a positive shift of 0.41 V of the measured \( E_{1/2} \) for the first reduction, compared to TPP. The effect of chlorination at the ortho-phenyl positions on the \( E_{1/2} \) is much smaller, because electronic effects can only be inductively transmitted to the porphyrin ring\cite{94}.

Water solubility can be imparted by substitution with an ionic group. Examples include meso-carboxyphenyl, -sulfonatophenyl, -methylpyridinium, and -trimethylanilinium substituents.

Thus, by using bulky ortho- substituents and electron-withdrawing \( \beta \)-substituents, porphyrins
Figure 1.6 Structure of Chlorinated Water Soluble Metalloporphyrins. 

1a = [iron(III)(meso-tetra(2,6-dichloro-3-sulphonatophenyl) porphyrinato)] chloride; 2a = [iron(III)(meso-tetra(2,6-dichloro-3-sulfanatophenyl)-β-octachloroporphyrinato)] chloride; 2b = [manganese(III)(meso-tetra(2,6-dichloro-3-sulfanatophenyl)-β-octachloroporphyrinato)] chloride.
which have greatly increased stability towards oxidative degradation can be prepared. Following this rational, \textit{meso}-tetra(2,6-dichloro-3-sulfanatophenyl)porphyrin, 1, (TDCSPP), and \textit{meso}-tetra(2,6-dichloro-3-sulfanatophenyl)-\(\beta\)-octachloroporphyrin, 2, (TDCSP-\(\beta\)-Cl\(_8\)P), have been synthesized (Figure 1.6)\(^{(95)}\). The chloride complexes of three metallated derivatives (iron 1a, and 2a; manganese 2b) are the catalysts used for this study.

\textit{1.4.2 Catalytic Mechanisms}

As mentioned earlier, metalloporphyrins can be reversibly oxidized. In solution, high valent, reactive species are generated by transfer of an oxygen atom to the metal center, forming an oxometal complex.

For example, for iron(III) porphyrins, both the product oxidized by one electron at the metal (oxoiron(IV) porphyrin), and the two electron oxidation product, one electron from the metal, and one electron from the \(\pi\)-cloud of the porphyrin moiety (oxoiron(IV) porphyrin \(\pi\)-radical cation) are known. These compounds have been obtained in their crystalline state and characterized by their chemical reactions, resonance Raman, EPR, EXAF, \(^1\text{H}\) NMR, and UV/Vis spectroscopy, and with electrochemical and magnetic techniques\(^{(96,97,98)}\).

Recently, an oxoiron(IV) porphyrin \(\pi\)-radical cation which is stable at a relatively high temperature was described. \textit{meso}-tetra(2,6-dichlorophenyl)-\(\beta\)-octaphenylporphyrin"
oxoiron(IV) was obtained and characterized spectroscopically at 8 °C\textsuperscript{96}. An example of a recently characterized oxoiron(IV) species is that of porphyrin 1a. The one electron oxidized species was stable for several hours in water at ambient temperatures\textsuperscript{97}.

Whereas there is consensus of opinion with respect to the mechanism of oxygen transfer from acyl hydroperoxides to iron(III) porphyrins, there is considerable debate as to the oxygen transfer mechanism with alkyl peroxides or hydrogen peroxide.

When the oxidant is an acyl hydroperoxide or peroxyacid, heterolytic cleavage of the O-O bond occurs, and the metalloporphyrin is oxidized by two electrons (equation 1).

\[
Porph Fe^{III} + YOOH \rightarrow Porph\,^+\,Fe^{IV}O + YOH \quad (1)
\]

For alkyl hydroperoxides a similar heterolytic cleavage has been proposed\textsuperscript{99,100}, however strong evidence (kinetic and product distribution studies) for homolytic O-O bond scission has been presented\textsuperscript{101,102,103,104}. Porphyrin 1a in water, and the non-sulfonated TDCPP Fe(III) in organic solvents, have typically been used for these studies. The porphyrin oxidation would thus proceed in two distinct steps (equations 2 and 3).

\[
Porph Fe^{III} + ROOH \rightarrow Porph\,Fe^{IV}O + RO' \quad (2)
\]

\[
Porph\,Fe^{IV}O + RO' \rightarrow Porph\,^{+\,+}\,Fe^{IV}O + RO' \quad (3)
\]
For hydrogen peroxide or alkyl hydroperoxides, the catalytic cycle of porphyrin oxidation and reduction can be summarized as in scheme 1.3. Initial one electron oxidation generates the oxoferryl porphyrin species. A second one electron oxidation produces the oxoferryl porphyrin π-radical cation. Two subsequent one electron transfers to a substrate regenerates the starting iron(III) porphyrin.

1.4.3 Reactions of Chlorinated Metalloporphyrins

The stability of the halogenated metalloporphyrins to oxidative degradation has led to substantial interest in their use as catalysts.

These catalysts have been used to effect alkene epoxidation. Norbornene was epoxidized in 85% yields with 10,000 turnovers using TDCPP FeCl\textsuperscript{[84,92]}\). Using hydrogen peroxide, styrene was epoxidized (93% yield) with TDCPP MnCl\textsuperscript{[105]}\). Also using this catalyst, epoxidation of several alkenes including cyclooctene and limonene, was studied under a variety of conditions\textsuperscript{[106]}.

Low temperature hydroxylation of alkanes by molecular oxygen is catalyzed by halogenated metalloporphyrins\textsuperscript{[107,108]}\). The catalyst was shown to be long lived, effecting over 12 000 turnovers in this industrially important reaction. Other oxidations such as hydroxylation of aromatic compounds\textsuperscript{[93,109]}\), and aldehyde conversion to carboxylic acids\textsuperscript{[110]}\), have been
Scheme 1.3 Proposed Catalytic Cycle of Metalloporphyrin Oxidation with Hydrogen Peroxide and Reduction by Substrate.
catalysed by these catalysts in organic solvents.

Catalyst 1a was used as a new route to quinones from methoxyarenes\(^{[111]}\). Catalyst 1a and 1b were used as a biomimetic analogue of ligninase, catalyzing oxidation reactions of lignin model compounds\(^{[112,113]}\). These catalysts were shown to be effective in alkyl peroxide pulp bleaching\(^{[114]}\).
2. RESULTS

2.1 Analysis of Products from the Oxidation of Chlorophenols

The reaction products of the oxidation of several chlorophenols were identified.

Chlorophenols were dissolved in water, catalyst and oxidant (usually hydrogen peroxide) were added, and the mixture stirred. The reactions were monitored by HPLC or by UV/Vis spectrophotometry. The reaction mixtures were extracted with organic solvent, separated by chromatography, and identified by NMR spectroscopy, and mass spectrometry. The details are discussed in the experimental section.

2.1.1 Products from the Oxidation of Monochlorophenol

The reaction products of 2-chlorophenol, 3-chlorophenol and 4-chlorophenol were similar. The product was typically a brown colloidal material which was insoluble in water. With a small excess of oxidant the yield of the precipitate was quantitative for 2- and 4-chlorophenol, by gravimetric analysis. HPLC demonstrated that no chlorophenol remained in solution (Figure 2.23). The yield of precipitate for 3-chlorophenol, under similar conditions, was approximately 20%. Individual compounds could not be isolated as chromatography was not successful.
HPLC of the colloidal precipitate demonstrated that it was a mixture of several components. The infrared spectra of the crude has absorbances assignable to alcohol O-H stretch (3300 cm$^{-1}$ br) and aryl ether C-O stretch (1223 cm$^{-1}$). Mass spectrometry of the crude material demonstrated strong m/e peaks at 508, 380, 254 (Figure 2.1). These can be tentatively assigned to the tetramer, trimer and dimer, respectively. Although characterization is not complete, experimental evidence suggests that the product of monochlorophenol oxidation is a mixture of phenolic oligomers. Figure 2.2 demonstrates two possible structures.

2.1.2 Products from the Oxidation of 2,4-Dichlorophenol

The formation of at least eight products by the oxidation of 2,4-dichlorophenol was observed by HPLC (Figure 2.24) and TLC. Several of these products were isolated and identified (Figure 2.3). All of the products were obtained in low yield ( < 15%).

The most abundant of the isolated products (15% yield) was 2-chloro-1,4-benzoquinone, 3. The mechanism of a two electron oxidation and nucleophilic attack by water at the 4-chloro position, as mentioned in the introduction, is probable.

Dimer coupling products and products arising from the oxidation of the dimers were isolated. Due to the presence of the chlorine at the 2- and 4- positions, coupling can only occur at the oxygen and the C6- position. Two electron oxidation of the phenol group of the
Figure 2.1  *Mass Spectrum of 2-Chlorophenol Oxidation Product*
Figure 2.2 Two Possible Products of 2-Chlorophenol Oxidation
Figure 2.3 Products of Oxidation of 2,4-Dichlorophenol
phenoxyphenol dimer (2-(2,4-dichlorophenoxy)-4,6-dichlorophenol), and subsequent nucleophilic attack by water is the proposed mechanism for the formation of 2-(2,4-dichlorophenoxy)-1,4-benzoquinone, 4. A similar mechanism to account for the formation of 2-(3-chloro-cyclohexa-3,6-diene-2,5-dione)-4,6-dichlorophenol, 5, is proposed.

The C-C bonded quinone dimer (2-(3-chlorocyclohexa-3,6-diene-2,5-dione)-6-chloro-1,4-benzoquinone, 6) was also a product of the oxidation. As before, oxidation of the phenol group of 5 to form the quinone moiety is the suggested mechanism.

Scheme 2.1 summarizes a possible reaction pathway of the oxidation of 2,4-dichlorophenol based on these products and previously suggested mechanisms\[59,69]\.

A product was isolated in insufficient quantities for complete characterization, but was tentatively identified as a trimer of the phenol, based on mass spectrometry. Other minor products (<5%) were formed as observed by HPLC, but were not isolated and identified. Products such as tetramers and other oligomers are likely.

2.1.3 Products from the Oxidation of 2,4,6-Trichlorophenol

The product from the oxidation of 2,4,6-trichlorophenol was 2,6-dichloro-1,4-benzoquinone, 7 (Figure 2.4). This product was obtained in 94% yield.
Scheme 2.1 Reaction Pathways of 2,4-Dichlorophenol Oxidation
Figure 2.4 Products of 2,4,5- and 2,4,6-Trichlorophenol Oxidation
When the reaction is done under conditions of high substrate concentration, a second product was detected by HPLC. This product was minor and could not be isolated in sufficient yield for complete characterization. Based on mass spectroscopy a possible structure is the diphenooquinone (8).

2.1.4 Products from the Oxidation of 2,4,5-Trichlorophenol

The formation of at least seven products from the oxidation of 2,4,5-trichlorophenol can be observed by HPLC (Figure 2.25) and TLC.

Two of the products were isolated and identified (Figure 2.4). The two electron oxidation product, 2,5-dichloro-1,4-benzoquinone, 9, was isolated in 10% yield. 2-(2,4,5-trichlorophenoxy)-3,6-dichloro-1,4-benzoquinone, 10, was also identified. This product presumably arises from the oxidation of the phenoxyphenol dimer as illustrated in the case of 2,4-dichlorophenol.

Other products were not isolated but likely structures (analogous to the products of 2,4-dichlorophenol oxidation) include: the phenoxyphenol dimer, the C-C bonded biphenyl dimer, the oxidized biphenyl products; the quinone and diquinone dimers, as well as trimers and oligomers.
2.1.5 Products from the Oxidation of Tetrachlorophenols

Oxidation of 2,3,5,6-tetrachlorophenol results in two main products as detected by HPLC (Figure 2.26). Because the ortho positions are blocked by the chlorine substituents, coupling can occur only at the oxygen and the para positions. As might be expected from the mechanism, 4-(2,3,5,6-tetrachlorophenoxy)-2,3,5,6-tetrachlorophenol, 11, and 4,4'-dihydroxytetrachlorobiphenyl, 12, were obtained (Figure 2.5). By comparison of HPLC retention times and UV spectra at the HPLC detector of the reaction mixture and standard sample, a minor amount of tetrachloroquinone, 13 was detected.

As judged by HPLC, there is primarily one product from the oxidation of 2,3,4,6-tetrachlorophenol. It was produced in low yield (<15%) and this product was not completely characterized, but the UV spectrum of the peak at the HPLC detector has a strong absorbance at 270 nm, characteristic of the quinones. The product is likely 2,3,6-trichloro-1,4-benzoquinone.

2.1.6 Oxidation of Pentachlorophenol

The oxidation of pentachlorophenol is an unusual case.

Figure 2.6 demonstrates the HPLC traces taken during the reaction. Initially, the peak
Figure 2.5  Products of 2,3,5,6-Tetrachlorophenol Oxidation
Figure 2.6  *HPLC Traces Taken During Reaction of Pentachlorophenol.*

A, $t=0$; B, $t=2$ hrs; C, $t=12$ hrs; D, $t=22$ hrs.
corresponding to pentachlorophenol ($t_r=5.2$ min) decreases and a new peak ($t_r=15.6$ min) appears, and begins to increase in intensity. After approximately 3 hours the pentachlorophenol peak intensity stops decreasing and slowly begins increasing, and correspondingly, the new peak starts to decrease in intensity. After 24 hours, the pentachlorophenol peak returns to near it’s original intensity, and the new peak diminishes to the baseline. Similar observations, or no oxidation of pentachlorophenol is seen with the three catalysts (1a, 2a, 2b), used with several oxidants (t-butylhydroperoxide, meta-chloroperoxybenzoic acid, and hydrogen peroxide), over a range of pH values and temperatures. In all cases, only pentachlorophenol was recovered upon attempted isolation of the new product. When the above oxidants are used without catalyst, the HPLC trace does not change over 24 hours.

A possible explanation for this observation is as follows. Oxidation generates the phenoxy radical intermediate. Since both the ortho and the para positions are occupied by chlorine substituents, only the O-O coupling takes place. This peroxide is unstable and, through reaction with residual hydrogen peroxide or water, the phenol is regenerated. That is, the formation and decomposition of the aryl peroxide is an equilibrium process. When the hydrogen peroxide concentration is high, the phenol is oxidized. When the hydrogen peroxide concentration decreases, decomposition of the dimer to the phenol is favoured.
2.2 Kinetic Studies

The rate of oxidation of 11 chlorophenols was examined by monitoring HPLC peak integration of the substrate with time (Figure 2.7 demonstrates the linearity of the HPLC detector response to chlorophenol concentration). The effect of pH, oxidant type, and catalyst type was evaluated. The HPLC conditions are detailed in the experimental section.

2.2.1 Effect of the Catalyst

The effect of adding the metalloporphyrin catalyst 1a on the oxidation of 4-chlorophenol is clearly demonstrated in figure 2.8.

From this graph the initial rate of disappearance \((V_0)\) of 4-chlorophenol was obtained by calculating, via computer, the slope of the line at \(t=0\). Table 2.1 summarizes these initial rates.

A plot of catalyst concentration against initial rate (absolute value) generates a straight line (Figure 2.9, \(r^2 = 0.996, \text{slope} = 182\)). The reaction is pseudo-first order in the catalyst.
Figure 2.7  Relationship of HPLC Integrator Response (at 270 nm) and 2-Chlorophenol Concentration.
<table>
<thead>
<tr>
<th>Catalyst Concentration (mmol/L)</th>
<th>Initial Rate (d[% consumed]/d(min))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.049</td>
</tr>
<tr>
<td>0.00292</td>
<td>0.73</td>
</tr>
<tr>
<td>0.00586</td>
<td>1.33</td>
</tr>
<tr>
<td>0.0293</td>
<td>5.98</td>
</tr>
<tr>
<td>0.0586</td>
<td>10.70</td>
</tr>
</tbody>
</table>
Figure 2.8  Effect of Catalyst Concentration on Oxidation of 4-Chlorophenol.

Conditions: catalyst 1a; initial chlorophenol concentration 5.8 mmol/L; hydrogen peroxide 28.4 mmol/L; pH=2.1, T=23°C; detection by HPLC 270nm.
Figure 2.9  Relationship Between Initial 4-Chlorophenol Oxidation Rate and Catalyst Concentration.

Conditions: catalyst 1a; initial chlorophenol concentration 5.8 mmol/L; hydrogen peroxide 28.4 mmol/L; pH=2.1, T=23°C; detection by HPLC 270nm.
2.2.2 Relative Chlorophenol Oxidation Rates

By measuring chlorophenol disappearance, graphs 2.10 to 2.14 were generated. The pH, the initial chlorophenol concentration, oxidant, and catalyst concentration were constant. From these graphs, the initial rate of disappearance (V₀) was obtained by calculating, via computer, the slope of the line at t=0. Table 2.2 summarizes these initial rates.

<table>
<thead>
<tr>
<th>Chlorophenol</th>
<th>Initial Rate (d[% consumed]/d(min))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Chlorophenol</td>
<td>6.20</td>
</tr>
<tr>
<td>3-Chlorophenol</td>
<td>2.66</td>
</tr>
<tr>
<td>4-Chlorophenol</td>
<td>5.98</td>
</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td>11.96</td>
</tr>
<tr>
<td>3,4-Dichlorophenol</td>
<td>4.78</td>
</tr>
<tr>
<td>3,5-Dichlorophenol</td>
<td>0.79</td>
</tr>
<tr>
<td>2,4,5-Trichlorophenol</td>
<td>8.48</td>
</tr>
<tr>
<td>2,4,6-Trichlorophenol</td>
<td>5.16</td>
</tr>
<tr>
<td>2,3,4,5-Tetrachlorophenol</td>
<td>0.98</td>
</tr>
<tr>
<td>2,3,4,6-Tetrachlorophenol</td>
<td>3.57</td>
</tr>
<tr>
<td>2,3,5,6-Tetrachlorophenol</td>
<td>3.34</td>
</tr>
</tbody>
</table>
Figure 2.10  *Kinetics of Oxidation of Monochlorophenols.*

*Conditions:* catalyst 1a (FeTDCP), 0.026 mmol/L; initial chlorophenol concentration 5.2 mmol/L; hydrogen peroxide 10.9 mmol/L; pH=2.1, T=23°C; detection by HPLC 270nm.
Figure 2.11  *Kinetics of Oxidation of Dichlorophenols.*

*Conditions: catalyst 1a (FeTDCPPhCl), 0.026 mmol/L; initial chlorophenol concentration 5.2 mmol/L; hydrogen peroxide 10.9 mmol/L; pH=2.1, T=23°C; detection by HPLC 270nm.*
Figure 2.12 *Kinetics of Oxidation of Trichlorophenols.*

*Conditions:* catalyst 1a (FeTDCSPPCl), 0.026 mmol/L; initial chlorophenol concentration 5.2 mmol/L; hydrogen peroxide 10.9 mmol/L; pH=2.1, T=23°C; detection by HPLC 270nm.
Figure 2.13  Kinetics of Oxidation of Tetrachlorophenols.

Conditions: catalyst 1a (FeTDCSPPCI), 0.026 mmol/L; initial chlorophenol concentration 5.2 mmol/L; hydrogen peroxide 10.9 mmol/L; pH=2.1, T=23°C; detection by HPLC 270nm.
Figure 2.14  Comparison of Oxidation Rates of Several Chlorophenols.

Conditions: mole ratio catalyst/chlorophenol/hydrogen peroxide II 1/200/210; catalyst 1a (FeTDCSPPCI); initial chlorophenol concentration 5.2 mmol/L; pH=2.1, T=23°C; detection by HPLC 270nm.
Oxidation rate depends on the number and position of chlorine substituents. *Meso*-substitution deactivates the phenol to oxidation. *Meso*-substituted mono- and di-chlorophenols are much more slowly oxidized than those not *meso*-substituted. Reactivity to oxidation in order of decreasing rate is: 2,4-dichlorophenol > 2,4,5-trichlorophenol > 2-chlorophenol ≈ 4-chlorophenol > 3,4-dichlorophenol ≈ 2,4,6-trichlorophenol > 2,3,4,6-tetrachlorophenol ≈ 2,3,5,6-tetrachlorophenol > 3-chlorophenol > 3,5-dichlorophenol ≈ 2,3,4,5-tetrachlorophenol.

2.2.3 Effect of the Type of Oxidant

Oxidation of 2,4,6-trichlorophenol was monitored by UV/Vis spectroscopy. The product of this oxidation is 2,6-dichlorobenzoquinone which has a distinct absorbance at 272 nm and can easily be monitored during the reaction (Figure 2.15). The type of oxidant has a large effect on the oxidation rate, qualitatively, *meta*-chloroperoxybenzoic acid >> Oxone® (potassium monoperoxy sulfate) >> hydrogen peroxide ≈ t-butyl hydroperoxide (Figure 2.16).

2.2.4 Effect of Catalyst Type

For the oxidation of 2-chlorophenol, with hydrogen peroxide, at pH 2.1, the iron catalysts 1a and 2a are more effective than the manganese catalyst 2b. Figure 2.17 compares 2-chlorophenol consumption using the three catalysts.
Figure 2.15 Change in UV Spectrum During Oxidation of 2,4,6-Trichlorophenol to 2,6-Dichlorobenzoquinone. Catalyst 1a (FeTDCSPPCl), oxidant hydrogen peroxide, pH=2.1. Measurement interval of 2.0 minutes.
Figure 2.16  Oxidation of 2,4,6-Trichlorophenol to Quinone with Different Oxidants.  

Conditions: catalyst 1a (FeTDCSPPCl), 5 μmol/L; initial trichlorophenol concentration 2.5 mmol/L; oxidant 12.2 mmol/L; pH=4.5; T=22°C; detection by UV 272nm.
Figure 2.17  Effect of Catalyst Type on Oxidation of 2-Chlorophenol.

Conditions: catalyst, 30 μmol/L; initial chlorophenol concentration 5.9 mmol/L; hydrogen peroxide 29.3 mmol/L; T=22°C; detection by HPLC, 270 nm.
2.2.5 Effect of pH

For the hydrogen peroxide oxidation of 2-chlorophenol, with 1a and 2a as catalysts, the rate of reaction is strongly dependent on solution pH, as can be seen in figures 2.18, and 2.19. In both cases, oxidation is fastest at pH 2.1. Rate decreases at higher pH, although no simple trend is evident. The mCPBA oxidation of 2,4,6-trichlorophenol with 2b as the catalyst is fastest at pH 4.5, and slower at the other investigated pH values (Figure 2.20). Again, no trend is obvious. Solution pH was adjusted using phosphate buffers.

2.2.6 Effect of Generating a Quinone

Quinones are known to be oxidants. Dicyanodichloroquinone (DDQ) is a common mild oxidant in organic chemistry. To determine if the quinones generated in the reaction themselves can oxidize the phenol substrates, 2,6-dichloroquinone was added to a solution of 2,4,6-trichlorophenol and meta-chloroperoxybenzoic acid. As can be seen in figure 2.21, the quinone with the oxidant does not oxidize the trichlorophenol. Upon addition of catalyst \( t=8 \) min, the phenol is quickly oxidized.
Figure 2.18  Effect of pH on the Oxidation of 2-Chlorophenol.

*Conditions:* catalyst 1a (FeTDCSPPCl), 30 μmol/L; initial chlorophenol concentration 5.9 mmol/L; hydrogen peroxide 29.3 mmol/L; T=22°C; detection by HPLC 270nm.
Figure 2.19  *Effect of pH on the Oxidation of 2-Chlorophenol.*

*Conditions:* catalyst 2a (FeTDCSP-β-Cl₈PCI), 30 μmol/L; initial chlorophenol concentration 5.9 mmol/L; hydrogen peroxide 29.3 mmol/L; T=22°C; detection by HPLC, 270nm.
Figure 2.20  Effect of pH on the Oxidation of 2,4,6-Trichlorophenol.

Conditions: catalyst 2b (MnTDCSP-β-Cl₈PCl), 2.5 µmol/L; initial chlorophenol concentration 1.3 mmol/L; mCPBA 2.5 mmol/L; T=22°C; detection by UV, 272nm.
Figure 2.21  Effect of Added Quinone to Oxidation of 2,4,6-Trichlorophenol.  
Conditions: initial chlorophenol concentration 1.3 mmol/L; mCPBA 2.5 mmol/L; 2,6-dichlorobenzoquinone (0.1 mmol/L). At t=8 min, catalyst 1a was added (3.0 µmol/L), and rapid oxidation of trichlorophenol to quinone was evidenced by increase in UV absorbance. pH=2.1; T=23°C.
2.3 Effect of Catalyst on Product Distribution

To determine if the catalyst affects the type of product formed in the oxidation of 2,4,6-trichlorophenol by meta-chloroperoxybenzoic acid, four similar reactions were run, in which the catalyst was varied. The four reactions contained: no catalyst (A), iron(III) meso-tetra(3-sulfonatophenyl)porphyrin chloride (B), catalyst 1a (C), and catalyst 2a (D).

The reaction products were analyzed by HPLC after 24 hours. Figure 2.22 shows the conversion of 2,4,6-trichlorophenol, $t_r = 12.2$ min, to 2,6-dichlorobenzoquinone, $t_r = 7.1$ min (meta-chloroperoxybenzoic acid and meta-chlorobenzoic acid co-elute at $t_r = 6.0$ min). In the reactions catalyzed by 1a and 2a, the conversion to the quinone was 100%. These catalysts greatly increased the reaction rate; in the un-catalyzed reaction 96% of the 2,4,6-trichlorophenol remained after 24 hours. Although not as effective as the chlorinated porphyrins 1a and 2a, sulfonated TPP also increased the reaction rate. 60% of the 2,4,6-trichlorophenol remained after 24 hours.

In all cases, oxidation of 2,4,6-trichlorophenol produced only 2,6-dichlorobenzoquinone.
Figure 2.22  HPLC of Reaction Mixture of 2,4,6-Trichlorophenol with mCPBA After 24 h. Top trace 220 nm, bottom trace 270 nm. A: no catalyst; B: FeTSP; C: 1a (FeTDCSPPCl); D: 2a (FeTDCSP-β-Cl8PCI). Conditions: initial phenol concentration 5.0 mmol/L; mole ratio catalyst/phenol/oxidant // 1/500/1500; pH=2.1.
2.4 Experimental

2.4.1 Chemicals and Instrumentation

Reagent grade chlorophenols and quinones were obtained from \textit{Aldrich} or \textit{Pfalz and Bauer} and purified by chromatography when necessary. Metalloporphyrins 1 and 2 were kindly supplied by T. Wijesekera and D. Dupre. Phosphate buffers were used to control pH.

All high performance liquid chromatography was performed using a \textit{Waters} Gradient controller, \textit{Waters} Model 994 diode array UV detector, with a \textit{Waters} C-18 microBondapak reverse phase column (30cm x 0.39cm). All chromatography was done at ambient temperature with a flow rate of 1.0 mL/min. Detection was typically set to 220 nm and 270 nm. HPLC solvent conditions: Monochlorophenols; 50% water / 50% acetonitrile / 0.1% TFA. Di- and Trichlorophenols; 45% water / 55% acetonitrile / 0.1% TFA. Tetrachlorophenols; 35% water / 65% acetonitrile/ 0.1% TFA. Pentachlorophenol; 20% water / 80% acetonitrile / 0.1% TFA.

A \textit{Hewlett Packard} Model 8459 diode array spectrophotometer was used for UV/Vis spectrometric studies. Mass spectrometry (electron impact ionization, 150-220°C) was performed by Dr. G. Eigendorf and coworkers using a \textit{Kratos} MS50 (high resolution) or a \textit{AEI} MS9 (low resolution) spectrometer. NMR spectra were recorded at room temperature,
with TMS internal standard, on a Varian XL 300 spectrometer. Melting points (uncorrected) were determined using a Thomas Model 40 micro hot stage.

Preparative TLC was performed using a Harrison Model 7924T Chromatotron® (rotating plate) with Merck PF_{254} silica gel adsorbent.
2.4.2 Oxidation of Monochlorophenols

Typical reaction conditions:

A 250 mL round bottom flask was charged with 75 mg (5.8 x 10^{-4} mol) 2-chlorophenol, 200 mL pH 2.1 phosphate buffer (0.05 M), 1.51 mg 1a (1.03 x 10^{-6} mol), (mole ratio catalyst/substrate: 1/500).

As the mixture was stirred, 120 µL 30% hydrogen peroxide solution (1.44 x 10^{-3} mol) was added (mole ratio oxidant/substrate: 2.5/1).

The mixture was stirred and monitored by HPLC (Figure 2.23). A brown precipitate was produced, which was removed by filtration on a fine glass frit (yield 74 mg, 99%). Reverse and normal phase TLC of the material produced streaks; no individual products could be isolated.

Characterization of products:

LRMS m/z (rel. int.): 510 (4.8), 508 (8.8), 506 (6.9), 384 (27.4), 382 (83.8), 380 (85.6), 256 (43.6), 254 (69.3)
Figure 2.23 *HPLC Traces of 2-Chlorophenol ($t_0=6.1$ min) Oxidation Products.*

A: $t=0$, B: $t=2$ hrs. Reaction conditions described in section 2.4.2.
2.4.3 Oxidation of 2,4-Dichlorophenol

Typical reaction conditions:

A 500 mL round bottom flask was charged with 94 mg (5.7 x 10^4 mol) 2,4-dichlorophenol, 200 mL pH 2.1 phosphate buffer (0.05 M), 1.34 mg la (1.03 x 10^{-6} mol), (mole ratio catalyst/substrate: 1/550).

As the mixture was stirred, 120 μL 30% hydrogen peroxide solution (1.44 x 10^{-3} mol) was added (mole ratio oxidant/substrate: 2.5/1).

The reaction was monitored by UV. When the absorbance at 260 nm no longer increased (about two hours), the reaction mixture was extracted four times with dichloromethane. The organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness to yield 86 mg (91%) of a yellow viscous oil. Analysis by TLC and HPLC (Figure 2.24) showed that the product was a mixture of at least eight compounds. The mixture was separated by Chromatotron® chromatography.
Characterization of products:

2-chloro-1,4-benzoquinone:

\[
\text{H-NMR (acetone-}d_6\text{)} \delta: \quad 6.82 \text{ (dd, 1H, J}_a^b = 10.2 \text{ Hz, J}_a^c = 2.4, H_a); \quad 6.93 \text{ (d, 1H, J}_b^a = 10.2 \text{ Hz, H}_b; \quad 7.02 \text{ (d, 1H, J}_c^a = 2.4 \text{ Hz, H}_c}
\]

LRMS m/z (rel. int.): \quad 144 (35.6), 142 (100.0), (M'); \quad 116 (27.6), 114 (66.2), (M' - CO)

HRMS: \quad \text{Calculated for C}_6\text{H}_3\text{Cl}: 141.9822. \quad \text{Found: 141.9831.}

Melting point: \quad \text{Found: 55-6°C, reported}^{[125]}: 57°C.

Yield: \quad 15\%
2-(2,4-dichlorophenoxy)-6-chloro-1,4-benzoquinone:\n
\[ \text{\(\Delta NMR (acetone-d_6) \delta:\)} \]
\[ 5.83 (d, 1H, J_{ab} = 1.8 \text{ Hz}, H_a); 7.11 (d, 1H, J_{ba} = 1.8 \text{ Hz} H_b); \]
\[ 7.44 (d, 1H, J_{cd} = 9.0 \text{ Hz}, H_c); 7.54 (dd, 1H, J_{dc} = 9.0 \text{ Hz}, J_{dc} = \]
\[ 2.4 \text{ Hz}, H_d), 7.72 (d, 1H, J_{ed} = 2.4 \text{ Hz}, H_e) \]

\[ \text{LRMS m/z (rel. int.):} \]
\[ 308 (3.7), 306 (16.6), 304 (32.3), 302 (23.4), (M^+); 271 (1.7), \]
\[ 269 (65.8), 267 (100), (M^+ - Cl); 243 (3.8), 241 (23.0), 239 \]
\[ (35.6), (M^+ - Cl - CO) \]

\[ \text{HRMS:} \]
\[ \text{Calculated for } C_{12}H_{25}Cl_3O_3: 301.9304. \text{ Found: 301.9280.} \]

\[ \text{Yield:} \]
\[ 10\% \]
2-(3-chloro-cyclohexa-3,6-diene-2,5-dione)-4,6-dichlorophenol\textsuperscript{126}:

\[
\begin{align*}
\text{Cl} & \quad \text{OH} \\
\text{H}_d & \quad \text{H}_b \\
\text{Cl} & \quad \text{H}_c \\
\end{align*}
\]

\(^1\text{H-NMR (acetone-}d_6\text{)} \delta:\)

\[
\begin{align*}
7.00 \ (d, \ 1H, J_{ab} = 2.4 \ Hz, \ H_a); \ & 7.23 \ (d, \ 1H, J_{ba} = 2.4 \ Hz, \ H_b); \\
7.28 \ (d, \ 1H, J_{cd} = 2.4 \ Hz, \ H_c); \ & 7.55 \ (d, \ 1H, J_{dc} = 2.4 \ Hz, \ H_d); \\
8.9 \ (br, \ s, \ 1H, \ H_e) \\
\end{align*}
\]

LRMS m/z (rel. int.): 308 (11.2), 306 (31.6), 304 (39.7), (M\(^+\))

HRMS: Calculated for C\(_{12}\)H\(_5\)Cl\(_2\)O\(_3\): 301.9304. Found: 301.9297.

Yield: 9%
2-(3-chlorocyclohexa-3,6-diene-2,5-dione)-6-chloro-1,4-benzoquinone: (chloroquinone dimer)\(^{[127]}\):

![](image)

\(^1\)H-NMR (acetone-\(d_6\)) \(\delta\): 7.27 (d, 1H, \(J_{ab} = 2.1\) Hz, \(H_a\)); 7.49 (d, 1H, \(J_{ba} = 2.1\) Hz, \(H_b\))

LRMS m/z (rel. int.): 286 (12.6), 284 (57.3), 282 (82.2), (M\(^+\)); 258 (1.2), 256 (6.6), 254 (9.9), (M\(^+\) - CO)

HRMS: Calculated for C\(_{12}\)H\(_4\)\(^{35}\)Cl\(_2\)O\(_4\): 281.9487. Found: 281.9480.

Yield: 8%
2-(2,4-dichlorophenoxy)-4,6-dichlorophenol:

LRMS m/z (rel. int.): 328 (10.1), 326 (47.6), 324 (100.0), 322 (76.6), (M⁺)

2,4-dichlorophenol trimer:

LRMS m/z (rel. int.): 488 (3.5), 486 (7.8), 484 (9.3), 482 (4.8), (M⁺); 450 (2.1), 448 (2.8), 446 (1.1), (M⁺ - Cl)
Figure 2.24  *HPLC Traces of 2,4-Dichlorophenol (t=8.2 min) Oxidation Products.*

A: t=0, B: t=3 hrs. Reaction conditions described in section 2.4.3.
2.4.4 Oxidation of 2,4,5-Trichlorophenol

Typical reaction conditions:

A 500 mL round bottom flask was charged with 150 mg \((7.6 \times 10^{-4}\ mol)\) 2,4,5-trichlorophenol, 200 mL pH 2.1 phosphate buffer \((0.05\ M)\), 15 mL acetonitrile, 2.0 mg \((1.53 \times 10^{-6}\ mol)\) 1a, (mole ratio catalyst/substrate: 1/500).

As the mixture was stirred, 1.50 mL 3% hydrogen peroxide solution \((1.55 \times 10^{-3}\ mol)\) was added (mole ratio oxidant/substrate: 2.1/1).

After two hours, the reaction mixture was extracted four times with dichloromethane. The organic phase was dried over anhydrous magnesium sulfate, filtered and evaporated to dryness to yield 145 mg \((97\%)\) of a yellow viscous oil. Analysis by TLC and HPLC (Figure 2.25) showed that the product was a mixture of at least seven compounds. The mixture was separated by Chromatotron® chromatography.
Characterization of products:

2,5-dichloro-1,4-benzoquinone:

\[
\begin{align*}
\text{Cl} & \quad \text{O} \\
\text{H}_a & \quad \text{H}_a \\
\text{H}_a & \quad \text{Cl} \\
\text{O} & 
\end{align*}
\]

\(^{1}H\)-NMR (acetone-d\(_6\)) \(\delta\): 7.32 (s)

LRMS m/z (rel. int.): 180 (12.5), 178 (65.7), 176 (88.6), (M\(^{+}\)); 152 (5.4), 150 (29.6), 148 (46.8) (M\(^{+}\) - CO)

HRMS: Calculated for C\(_6\)H\(_2\)\(^{35}\)Cl\(_2\): 175.9432. Found: 175.9440.

Melting point: Found: 158-160\(^{\circ}\)C, reported\(^{[128]}\): 161-2\(^{\circ}\)C

Yield: 16\%
2-(2,4,5-trichlorophenoxy)-3,6-dichloro-1,4-benzoquinone[

\[
\begin{align*}
\text{\textsuperscript{1}H-NMR (acetone-d}_6\text{)} \delta: & \quad 6.32 \text{ (s, } 1\text{H, } H_a); \quad 7.69 \text{ (s, } 1\text{H, } H_c); \quad 7.94 \text{ (s, } 1\text{H, } H_e) \\
\text{LRMS m/z (rel. int.):} & \quad 376 \text{ (3.6), 374 (9.7), 372 (14.8), 370 (9.8), (M+); 341 (11.2),} \\
& \quad 339 \text{ (48.6), 337 (100), 335 (78.9) (M+ - Cl); 311 (16.6), 309} \\
& \quad (33.3), 307 \text{ (27.7) (M+ - Cl - CO)} \\
\text{HRMS:} & \quad \text{Calculated for } C_{12}H_3^{35}\text{Cl}_5O_3: 369.8525. \text{ Found: 369.8542.}
\end{align*}
\]
Figure 2.25  HPLC Traces of 2,4,5-Trichlorophenol ($t_1$=14.9 min) Oxidation Products.

A: $t=0$, B: $t=3$ hrs. Reaction conditions described in section 2.4.4.
2.4.5 Oxidation of 2,4,6-trichlorophenol

**Typical reaction conditions:**

A 500 mL round bottom flask was charged with 500 mg \(2.53 \times 10^{-3}\) mol) 2,4,6-trichlorophenol, 200 mL pH 2.1 phosphate buffer (0.05 M), 50 mL acetonitrile, 6.7 mg \(5.13 \times 10^{-6}\) mol) 1a, (mole ratio catalyst/substrate: 1/500), 650 mg \(3.76 \times 10^{-3}\) mol) mCPBA (mole ratio oxidant/substrate: 1.5/1).

The reaction was monitored by UV at 272 nm. When the absorbance at 272 nm no longer increased (about two hours), the reaction mixture was extracted four times with dichloromethane. The organic phase was dried over anhydrous magnesium sulfate, filtered and evaporated to dryness to yield 420 mg (94%) of a bright yellow solid. Analysis by TLC and HPLC (Figure 2.22) showed that the product was a single compound. The material was recrystallized from acetone/water (3/1).
Characterization of products:

2,6-dichloro-1,4-benzoquinone:

\[ \text{O} \quad \text{Cl} \quad \text{Cl} \quad \text{O} \]

\(^1\text{H}-\text{NMR (acetone-d}_6\text{)} \delta: \quad 7.21 \text{ (s)}\]

LRMS m/z (rel. int.): \quad 180 (6.2), 178 (28.7), 176 (41.3), (\text{M}^+); 152 (0.8), 150 (6.3),
\quad 148 (10.0), (\text{M}^+ - \text{CO})

HRMS: \quad \text{Calculated for C}_6\text{H}_2^{35}\text{Cl}_2: 175.9432. \text{ Found: 175.9430.}

Melting point: \quad \text{Found: 119-120}^\circ\text{C, reported}^{[125]}: 120-1^\circ\text{C}

Yield: \quad 94\%
Tetrachlorodiphenoquinone:

![Chemical Structure]

LRMS m/z (rel. int.): 324 (9.1), 322 (32.8), 320 (52.6), 318 (28.0), (M'); 287 (4.3), 285 (16.2), 283 (21.0), (M' - Cl)
2.4.6 Oxidation of 2,3,5,6-tetrachlorophenol

Typical reaction conditions:

A 250 mL flask was charged with 100 mg (4.31 x 10^-4 mol) 2,4,5,6-tetrachlorophenol, 75 mL pH 2.1 phosphate buffer, 75 mL acetonitrile, 1.13 mg (8.62 x 10^-7 mol) 1a, (moles catalyst/moles substrate: 1/500), 1.20 mL (1.06 x 10^-3 mol) 3% hydrogen peroxide solution (mole ratio oxidant/substrate: 2.5/1).

After two hours, the reaction mixture was extracted four times with dichloromethane. The organic phase was dried over anhydrous magnesium sulfate, filtered and evaporated to dryness to yield 96 mg (96%) of a yellow solid. Analysis by TLC and HPLC (Figure 2.26) showed that the product was a mixture of two main compounds. The mixture was separated by Chromatotron® chromatography.
Characterization of products:

4-(2,3,5,6-tetrachlorophenoxy)-2,3,5,6-tetrachlorophenol:

LRMS m/z (rel. int.): 468 (2.2), 467 (4.0), 466 (12.9), 465 (8.4), 464 (22.8), 463 (10.4), 462 (45.7), 461 (9.3), 460 (38.1), 459 (3.6), 458 (13.2), (M^+)

HRMS: Calculated for C_{12}H_{3}^{35}Cl_{3}O_{3}: 457.7562. Found: 457.7571.

Yield: 10%
4,4'-dihydroxyoctachlorobiphenyl:

LRMS m/z (rel. int.): 466 (0.4), 464 (3.2), 462 (6.2), 460 (4.1), 458 (1.6), (M*)

HRMS: Calculated for C₁₂H₂³⁵Cl₈O₂: 457.7562. Found: 457.7568.

Melting Point: Found: 230-235°C, reported[130]: 235-238°C

Yield: 11%
Figure 2.26  HPLC Traces of 2,3,5,6-Tetrachlorophenol (\(t_r=6.1\) min) Oxidation Products.

A: \(t=0\), B: \(t=4\) hrs. Reaction conditions described in section 2.4.6.
3. DISCUSSION

3.1 Discussion of Results of Oxidation Product Analysis

The products of chlorophenol oxidations are phenoxy radical coupling products or quinones. Coupling, followed by subsequent oxidation, generates phenol-quinone dimers or quinone-quinone dimers.

Analyzing the products of the oxidation reactions aids in evaluating the potential use, and limitations, of this technique for remediation of chlorophenol pollution.

The efficient conversion of 2- and 4-chlorophenol to a water insoluble material which can be removed by filtration is a potentially useful characteristic of the catalyzed oxidation reactions. Removing the chlorophenols by polymerization and filtration would isolate and concentrate this waste which could then be subsequently treated by a second technique for ultimate destruction. Incineration may work as a secondary process as well as biological treatment, although there is some evidence which suggests that polymeric substrates are less available to microorganisms and thus less biodegradable.

Chlorophenols other than monochlorophenols are converted to dimers and oxidized dimers. Some of the products are partially water soluble which would make removal from water more
difficult than simply filtering. However, it has been shown that partially oxidized chlorophenol mixtures are more readily biodegradable than the chlorophenols themselves\cite{33}. It is relevant to note that quinones are known intermediates in chlorophenol metabolism by some bacteria and fungi. Oxidative treatment of these chlorophenols may be useful as a waste pretreatment, making biological treatment more effective.

The possibility that these new products could be more environmentally damaging than the starting chlorophenols cannot be discounted. The product from 2,4,6-trichlorophenol oxidation, 2,6-dichlorobenzoquinone, has been demonstrated to cleave DNA\cite{115}. Chlorinated hydroxybiphenyls (one product of the coupling reactions) are thought to be one of the initial products of PCB metabolism, and are implicated in chick embryo toxicity\cite{116}.

These porphyrin catalyzed oxidations cannot be considered to be an accurate mimic of biological metabolic processes which are complex and involve many enzyme systems. However, some of the oxidation products are the same as those of some microbial transformations of chlorophenols. \textit{P. chrysosporium} was found to produce chloroquinone and 2,6-dichloroquinone as metabolites of 2,4-dichlorophenol and 2,4,6-trichlorophenol, respectively\cite{61}. \textit{Rhodococcus} bacteria generate quinones as an initial step in chlorophenol metabolism.
3.2 Discussion of Kinetic Results

3.2.1 Effect of pH

Iron porphyrins 1a and 2a catalyzed chlorophenol oxidation most effectively at pH 2. This observation is in agreement with results obtained by other researchers examining the kinetics of water soluble iron porphyrin (tetra(2,6-dimethyl-3-sulfantophenyl)porphyrin) catalysis of hydrogen peroxide oxidation of 2,2'-azinobis(3-ethylbenzthiazolinsulfonic acid) (ABTS)\textsuperscript{[88]}. This observation can been rationalized by considering several related factors.

Hydrogen peroxide can compete with chlorophenol as a substrate for the oxidized metalloporphyrin. As pH increases, hydrogen peroxide oxidation ("catalase-type" reaction) (reaction 4) is favored over substrate oxidation ("peroxidase-type" reaction) (reaction 5). Other researchers found that the yield of oxidized substrate (ABTS\textsuperscript{**}) was 100% at pH 1 and dropped rapidly to less than 20% at pH 8, with a concomitant increase in production of oxygen\textsuperscript{[88,117]}.

\[
Porph^{**} \text{Fe}^{IV}O + H_2O_2 \rightarrow Porph \text{Fe}^{III} + H_2O + O_2 \quad (4)
\]

\[
Porph^{**} \text{Fe}^{IV}O + 2 \text{PhOH} \rightarrow Porph \text{Fe}^{III} + 2 \text{PhOH}^{**} \quad (5)
\]
Researchers studying the formation of ferryl porphyrins (iron porphyrins oxidized by only one electron) found that these compounds are more readily formed at higher pH values\textsuperscript{[97]}. It is known that, in contrast to the species oxidized by two electrons, the species oxidized by one electron is not a good substrate oxidant\textsuperscript{[118]}.

Thus one may expect higher pH to disfavour phenol oxidation when considering the porphyrin behavior. However, considering the phenol substrate, one may expect higher pH to favour oxidation. The deprotonated chlorophenoxy anion, having higher electron density, would be expected to be more readily oxidized than the corresponding phenol. With porphyrin catalyzed oxidations, higher pH does not favour chlorophenol oxidation. It is probable that the effect of pH on metalloporphyrin chemistry (lower pH is more favourable) is the overriding factor in the overall oxidation rate.

3.2.2 Effect of the Coordinated Metal

At low pH, the iron catalysts 1\textit{a} and 2\textit{a} are more effective than the manganese porphyrin 2\textit{b}. Two factors may account for this observation.

Manganese porphyrins are known to have a higher oxidation potential than the corresponding iron porphyrins\textsuperscript{[101,119]}. Slower conversion of the manganese porphyrin to the activated oxidized species could explain slower substrate oxidation.
Secondly, as with iron porphyrins the manganese porphyrin can catalyze hydrogen peroxide decomposition. The relationship between pH and the "catalase-type" versus "peroxidase-type" reactions of manganese porphyrins is opposite to that of the iron porphyrins. That is hydrogen peroxide oxidation is favoured over substrate oxidation at lower pH values\textsuperscript{119}. This also may contribute to the observed slower chlorophenol oxidation for the manganese porphyrin 2b compared to iron porphyrins 1a and 2a.

### 3.2.3 Effect of the Oxidant Type

In the general reaction of metalloporphyrin oxidation by a peroxide oxidant, ROOH, RO\(^-\) can be considered to be a leaving group (reaction 6).

\[
\text{Porph} \text{Fe}^{III} + \text{ROOH} \rightarrow \text{Porph}^{\ast} \text{Fe}^{IV} \text{O} + \text{RO}^{-} \quad (6)
\]

Reaction of metalloporphyrins with ROOH is therefore facilitated by electron withdrawing R groups. That is, the rate increases with decreasing pK\(_a\) of ROH\textsuperscript{120,121}. For the peroxides used in this study, ROH pK\(_a\) values increase mCBA < KSO\(_4\)H < H\(_2\)O < t-BuOH which corresponds with the observed relative oxidation rates, mCPBA > KSO\(_4\)OH (Oxone\textsuperscript{®}) > H\(_2\)O\(_2\) > t-BuOOH.
3.2.4 Effect of Chlorophenol Structure

In this study, the relative rates of chlorophenol oxidation were determined to be, in order of decreasing rate: 2,4-dichlorophenol > 2,4,5-trichlorophenol > 2-chlorophenol ≈ 4-chlorophenol > 3,4-dichlorophenol ≈ 2,4,6-trichlorophenol > 2,3,4,6-tetrachlorophenol ≈ 2,3,5,6-tetrachlorophenol > 3-chlorophenol > 3,5-dichlorophenol ≈ 2,3,4,5-tetrachlorophenol.

The most notable feature of the relative chlorophenol oxidation rates obtained in this study is the inhibiting effect of meso-chlorines. The electron withdrawing chlorine would be expected to deactivate the phenol to oxidation in general. ortho- and para-chlorines could contribute to phenoxy radical stabilization through resonance, thus moderating their deactivation compared to meso-chlorines.

A quantitative relationship between structure and relative oxidation rate was not determined. The rates do not correlate with Hammet substituent constants.

It is interesting to compare the relative chlorophenol oxidation rates obtained here, with their relative toxicity to bacteria. Researchers measured the effective inhibition of 19 chlorophenol congeners on the growth rate of an aerobic bacteria culture[122]. The rate is expressed as IC$_{50}$; the effective chlorophenol concentration causing 50% growth inhibition of the bacteria. There are some similarities between chlorophenol oxidation by metalloporphyrin and chlorophenol inhibition of bacterial growth. For example 2,3,4,5-tetrachlorophenol (IC$_{50}$=0.030 mmol/L) inhibits bacterial growth much more than 2,3,4,6-tetrachlorophenol (IC$_{50}$=0.354 mmol/L) or
2,3,5,6-tetrachlorophenol (IC$_{50}$=0.319 mmol/L). Also 3,5-dichlorophenol (IC$_{50}$=0.80 mmol/L) is one of the most toxic of the tested chlorophenols. This parallels the observation that 2,3,4,5-tetrachlorophenol and 3,5-dichlorophenol were the most resistant to oxidation in the study presented here.

Developing methods for assessing potential impact on organisms and the environment of a vast array of chemicals of concern is an important pursuit. The use of a simple chemical oxidation could be a relevant part of an assay to evaluate the potential toxicity of particular substrates to aerobic organisms. Much more research would be required to evaluate this possibility.
3.3 Conclusions and Suggestions for Further Studies

These studies demonstrate that the use of metalloporphyrins for the catalyzed oxidation of chlorophenols is, in principle, a useful technique for the remediation of aqueous chlorophenol waste.

To further evaluate the catalysts for industrial applications, future studies should involve oxidation of more complex chlorophenol containing wastes. Chemical characterization of the waste and oxidation products may be too tedious, but an investigation of the effect of this type of oxidation on the toxicity of the waste would be interesting.

The products from the oxidation of chlorophenols are not necessarily more benign, but this treatment may make the waste more treatable by other methods. The use of this technique as one part of a multiple step treatment of waste could be assessed. For example, oxidation followed by microbial treatment may be more effective than microbial treatment alone.

The chlorinated metalloporphyrins have recently been immobilized onto water insoluble silica supports. Preliminary work suggests that the supported catalysts retain their catalytic activity. The fixed catalysts may have significant advantages over homogeneous catalysts. Solid phase catalysts are easier to remove from reaction mixtures and immobilization might extend catalyst lifetime. In terms of practical application, immobilized catalysts may facilitate design of a flow through bed type reactor. The uses and chemistry of these supported
catalysts should be studied.

It has been suggested that dioxins are produced during horseradish peroxidase oxidation of chlorophenols\textsuperscript{[62]}. The formation of dioxins by porphyrin oxidation was not evaluated in this study but, due to the toxicity of dioxins, this possibility would be an important concern for application of this technique.

As with all other potential methods of pollution remediation, this method has disadvantages. Of primary concern is the cost of the metalloporphyrin catalysts. Research towards cheaper synthesis of these metalloporphyrins is recommended. Use of oxygen or air as the oxidant rather than the more costly hydrogen peroxide would be a relevant investigation.
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