OXIDATIONS OF ALKENES AND LIGNIN MODEL COMPOUNDS IN AQUEOUS DISPERSIONS

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CHAPTER I

INTRODUCTION

Transition Metal Catalyzed Oxidation

An oxidation process catalyzed by a transition metal complex can be generalized by the following form:

$$\mathrm{S} + \mathrm{XO} \xrightarrow{\mathrm{MLn}} \mathrm{SO} + \mathrm{X} \qquad (1)$$

where the substrate or oxygen acceptor (S) is oxidized, the oxygen donor (XO) is reduced, and the metal complex (MLn) remains unchanged after the reaction since it acts as a catalyst. In organic chemistry, the scope of the oxidation includes all reactions that either decrease the hydrogen content or increase the oxygen, halogen, or nitrogen content of a molecule. However, the removal of hydrogen and addition of oxygen in organic compounds are still the major types of the oxidation.

The use of transition metal complexes as catalysts for oxidations provides many advantages over non-catalytic oxidations. Catalytic processes are usually carried out under milder conditions, which leads to easy operation and low energy consumption, are generally more selective for preparations of functional compounds with specific structures, and have both biological and industrial importance.

In a catalytic oxidation, the oxygen donor (XO) may first donate oxygen to the transition metal complex to form an oxometal complex (OMLn, eq 2). This OMLn can transfer its oxygen atom to the substrate or abstract hydrogen atom(s) from the substrate to perform the oxidation (eq 3). It also can coordinate with another unit of MLn complex to form a binuclear μ-oxo species (eq 4).

$$XO + MLn \rightleftharpoons OMLn + X \tag{2}$$

$$OMLn + S \longrightarrow SO + MLn \tag{3}$$

$$OMLn + MLn \longrightarrow LnMOMLn \tag{4}$$

The existence of various oxo and μ-oxo metal complexes has been reported by many research groups, and summarized in several reviews.[1-3] The oxo-metal bond (M-O) can be formed with the transition elements from group VB to group VIII. The following canonical forms could characterize the oxo-metal bonds:

$$M^{z}{=}O^{\cdot} \longleftrightarrow M^{z+1}{=}O \longleftrightarrow M^{z+2}{=}O^{+}$$

which show that the central metal is electron-deficient. The basic requirement for a stable M=O bond is that the central metal of OMLn complex must have an oxidation state of no less than 4+ and no more than four d electrons.

On the other hand, the formation of OMLn will depend on the oxygen donor, XO. A weak X-O bond helps the formation of an oxo-metal bond. Many organic and inorganic oxidants can serve as oxygen donors, which are listed in Table I. The oxidizing power of the oxidants is usually estimated by their oxidation potential. However, the true oxidizing ability should depend on the reaction conditions. For example, in the presence of a Mn porphyrin, NaClO can oxidize the double bond of the alkene,[4] but not a C-H bond, while $NaClO_2$ is effective only for the C-H bond oxidation.[5]

Table I. Different Oxidants[a]

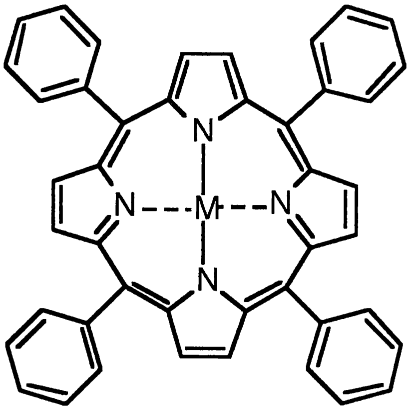
group IIIA	group IVA	group VA	group VIA	group VIIA
$NaBO_3$	$C_2O_6^{2-}$	N_2O, NO_3^-	O_2, O_3	ClO^-
	Na_2CO_4	R_3NO, $ArNO$	H_2O_2	ClO_2^-
	HCO_4^-	$PhN(O)NPh$	R_2SO	ClO_3^-, BrO_3^-
	$ArCO_3H$	H_3PO_5	HSO_5^-	BrO_4^-, IO_4^-
	$ROOH$	Ph_3AsO	$S_2O_8^{2-}$	H_5IO_6
	RCO_3H	Ph_3SbO		Cl_2O, $PhIO$

[a] R = alkyl or aryl (Ar).

Transition metal catalyzed oxidations involve reactant, product(s), and oxo-metal intermediate. The number of such oxidations has been growing rapidly. Therefore, attention will be paid to oxidations catalyzed by iron, manganese, cobalt, and nickel complexes which are related to our research interests. The major emphasis of this chapter is epoxidation.

Oxidation Catalyzed by Manganese Complexes

Manganese porphyrins are important manganese complexes. The structure of typical metal meso-tetraphenylporphyrins (including manganese porphyrin, TPPMn) is shown below. The chemical reactivity and electronic properties of tetraphenylporphyrins can be varied by change of the central metal and substituents of the phenyl rings.

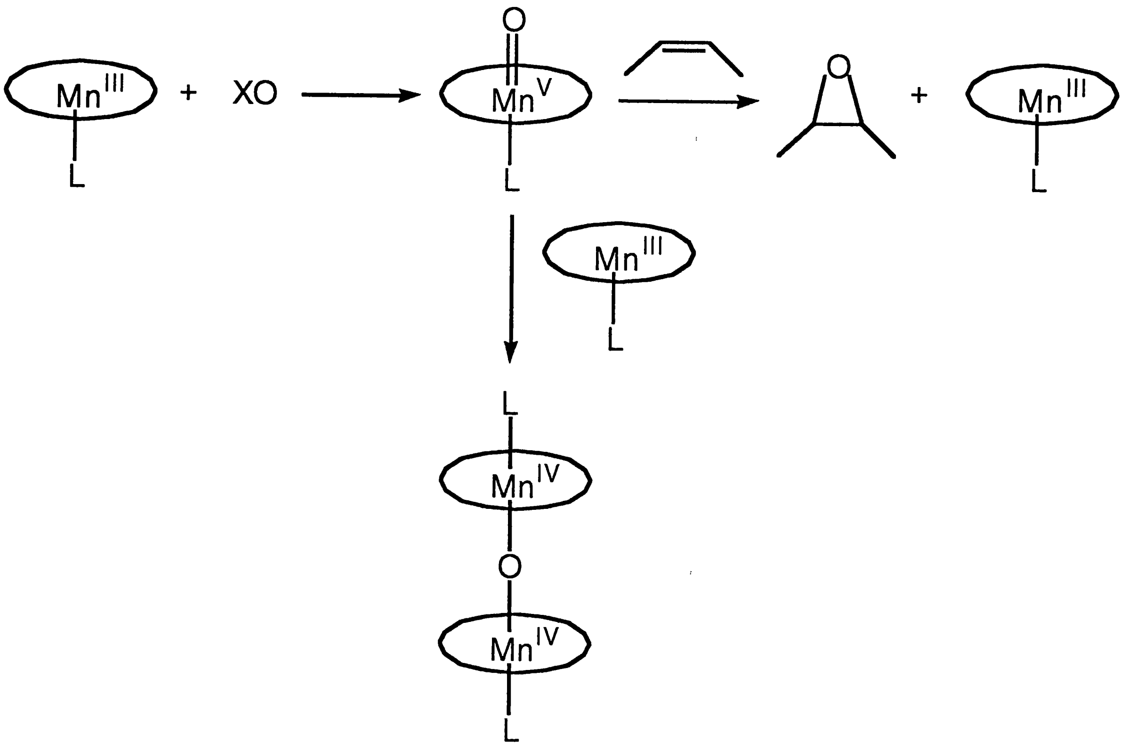


M = Mn: manganese meso-tetraphenylporphyrin (TPPMn)

M = Fe: Iron meso-tetraphenylporphyrin (TPPFe)

The manganese porphyrins can catalyze the oxidations of organic compounds, especially the epoxidations of alkenes, with different oxidants such as iodosylbenzene (PhIO), sodium hypochlorite (NaOCl), alkyl peroxides (ROOH), N-oxides (R_3NO, ArNO), dioxygen (O_2) in the presence of a reducing agent, and potassium peroxymonosulfate ($KHSO_5$).[7] The epoxidation of alkenes is believed to proceed via an oxomanganese porphyrin intermediate. The competing reaction is the formation of dimeric μ-oxo Mn pophyrin.

Scheme I



Both oxo and μ-oxo Mn porphyrins have been experimentally observed,[8-11] but only the μ-oxo complex was isolated in the reaction of manganese meso-tetraphenylporphyrin (TPPMn) with PhIO.[12] It is likely that the μ-oxo species is formed via an irreversible reaction of the oxomanganese (V) complex with another Mn porphyrin, since the only recoverable species is μ-oxo Mn porphyrin. Table II summarizes some oxo and μ-oxo Mn porphyrins.

Table II. Formation of Oxo and μ-Oxo Mn Porphyrins[a]

Mn porphyrin	oxidant	product
Mn(TMP)Cl	KO_2 + *m*-ClC_6H_4COCl	MnO(TMP)Cl
Mn(TMP)Cl	NaOCl	MnO(TMP)Cl
Mn(TMP)Cl	*m*-$ClC_6H_4CO_3H$	MnO(TMP)(OH_2)
Mn(TCPP)	NaOCl	MnO(TCPP)
Mn(TPP)Cl	RCO_3H	MnO(TPP)Cl
Mn(TPP)Cl	ROOH	MnO(TPP)Cl
Mn(TSPP)Cl	NaOCl	MnO(TSPP)Cl
Mn(Cl_8TPP)OAc	NaOCl	MnO(Cl_8TPP)OAc
Mn(Br_8TMP)OAc	O_3	MnO(Br_8TMP)OAc
Mn(TCPP)	OCl^-, BrO_3^-	$[Mn(TCPP)]_2O$
Mn(TPP)Cl	PhIO	$[Mn(TPP)Cl(PhIO)]_2O$
Mn(TPP)N_3(or OCN^-)	PhIO	$[Mn(TPP)N_3]_2O$
Mn(TSPP)Cl	NaOCl	$[Mn(TSPP)L]_2O$

[a] See ref 13.

TMP = meso-tetramesitylporphyrin.

TCPP =meso-tetrakis(*p*-carboxyphenyl)porphyrin, sodium salt.

TPP = meso-tetraphenylporphyrin.

TSPP = meso-tetrakis(*p*-sulfonatophenyl)porphyrin, sodium salt.

Cl_8TPP = meso-tetra(2,6-dichlorophenyl)porphyrin.

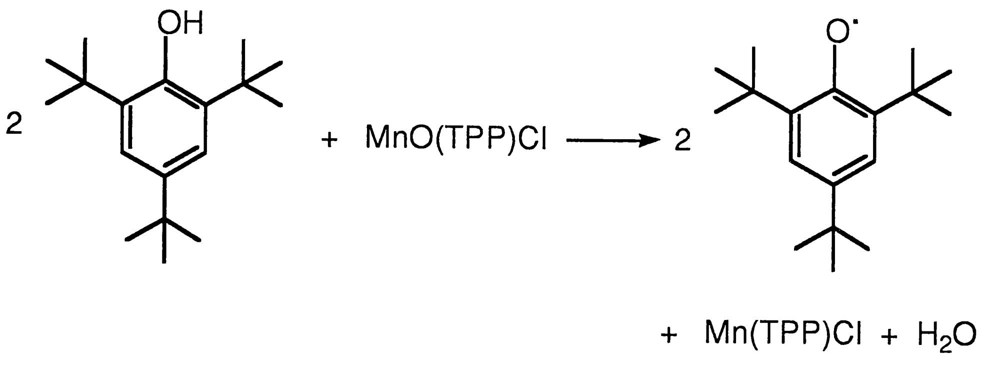
Br_8TMP = meso-tetramesityl-*β*-octabromoporphyrin.

The formation of μ-oxo complex depends on reaction conditions. Harriman and co-workers[10,11] found that μ-oxo dimer is produced from the reaction of Mn(TCPP) with NaOCl through the range $9 < pH < 14$. With excess NaOCl at pH 14 a different species is formed (eq 5), which is believed to be an oxo Mn(V) porphyrin according to its absorption spectrum and magnetic moment.

$$\mathrm{PMn^{IV}{-}O{-}Mn^{IV}P} + \mathrm{OCl^-} \longrightarrow 2\,\mathrm{PMn^{V}{=}O} + \mathrm{Cl^-} \qquad (5)$$

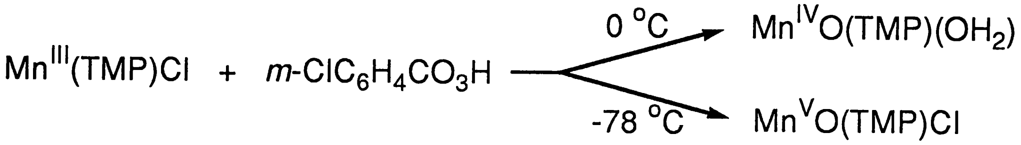
Although both oxo and μ-oxo complexes are able to oxidize organic substrates,[12] the prevailing mechanism proposed so far suggests the oxo Mn porphyrin to be the actual oxidant. The mechanism of the formation of oxo Mn porphyrins has been studied by Bruice and co-workers.[14] In the reaction of Mn(TPP)Cl with different peracids, the following reactivity of the peracids was found: $p\text{-}NO_2C_6H_4CO_3H >$ $m\text{-}ClC_6H_4CO_3H > Cl(CH_2)_2CO_3H > PhCH_2CO_3H > Cl(CH_2)_4CO_3H >$ $CH_3(CH_2)_{10}CO_3H$. The reactions were monitored by the appearance of the 2,4,6-tri-*tert*-butylphenoxy radical (eqs 6). This reactivity order parallels the acidities of the corresponding acids. Bruice and co-workers believe that these results indicate the heterolytic cleavage of peroxy O-O bond.

$$\mathrm{Mn(TPP)Cl} + \mathrm{RCO_3H} \longrightarrow \mathrm{MnO(TPP)Cl} + \mathrm{RCO_2H} \qquad (6a)$$



(6b)

Groves' group observed that the reactions of Mn(TMP)Cl with *m*-$ClC_6H_4CO_3H$ in CH_2Cl_2 in the presence of 2 equiv of methanolic $(Me_4N)OH$ produce the $Mn^{IV}O$ species at 0 °C and the $M^{V}O$ complex at -78 °C (eq 7).[15]



(7)

According to their suggestion, the $M^{V}O$ complex is first formed by oxygen atom transfer from *m*-$ClC_6H_4CO_3H$ and reacts further with hydroxide to form the $Mn^{IV}O$ species. Both oxo complexes epoxidize *cis*-*β*-methylstyrene.

The epoxidations catalyzed by Mn porphyrins are nonstereospecific, because the epoxidation of *cis*-stilbene gives a mixture of *cis*- and *trans*-stilbene oxide and also benzaldehyde.[16] The nonstereospecificity could be explained by a radical process of the oxygen transfer from oxo Mn complex to the alkene. Bortolini and Meunier[16] have shown that the use of bulky groups on the meso-phenyl rings of the porphyrin [e.g. Mn(TMP)Cl in place of Mn(TPP)Cl] increases both the rate of epoxidation and the stereospecificity of the epoxidation of *cis*-stilbene (Table III),[8,17] but the replacement of Mn(TPP)Cl by Mn(TMP)Cl does not eliminate the formation of *trans*-epoxide.

Table III. The Effect of Pyridine and Catalysts on the Epoxidation of *cis*-Stilbene[a]

pyridine	oxidant	Mn porphyrin	% cis-epoxide	% trans-epoxide
0	NaOCl	Mn(TPP)Cl	35	65
0	NaOCl	Mn(TMP)Cl	98	2
0.03 equiv	NaOCl	Mn(TPP)Cl	70	30
0.03 equiv	NaOCl	Mn(TMP)Cl	98	2
0	PhIO	Mn(TPP)Cl	38	62
0	PhIO	Mn(TMP)Cl	90	10
0.15 equiv	PhIO	Mn(TPP)Cl	57	43
0.03 equiv	PhIO	Mn(TMP)Cl	97	3

[a] For reaction conditions see ref. 17.

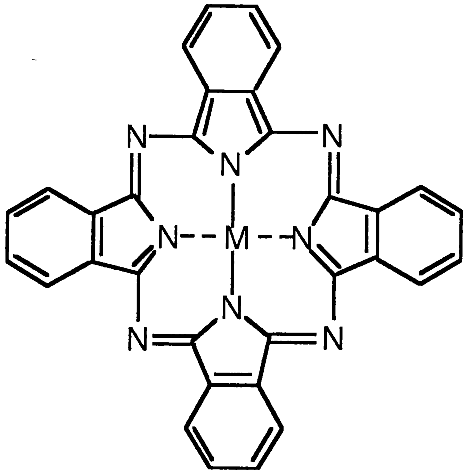
The presence of pyridine also increases the rate of epoxidation and the yield of *cis*-epoxide. Although both $Mn^{IV}O(TMP)(OH_2)$ and $Mn^{V}O(TMP)Cl$ epoxidize *cis-β*-methylstyrene to produce a mixture of *cis*- and *trans-β*-methylstyrene oxides, the $Mn^{V}O(TMP)Cl$ complex gives more *cis*-epoxide than $Mn^{IV}O(TMP)(OH_2)$.[15] The ratio of *cis*- and *trans*- epoxides in the epoxidation of *cis-β*-methylstyrene also depends on the oxidant. The highest yields of *cis*-epoxides are produced with NaOCl in the presence of pyridine as a ligand.[18]

The reactivity of alkenes in the epoxidation by Mn porphyrin/NaOCl was investigated by Meunier and co-workers.[19] Different alkenes show this decreasing order of reactivity: styrene > 2,3-dimethyl-2-butene > 1-methycyclohexene > cyclohexene > 2-methyl-1-heptene. Among styrene derivatives, electron-donating groups slightly increase the rate of epoxidation,[17] with the order of *p*-methoxystyrene > *p*-methylstyrene > styrene > *p*-chlorostyrene.

The axial ligand (L) of Mn(TPP)L plays an important role in the epoxidation reactivity. The ligand cannot be too electron-rich, since it will be easily oxidized by oxo manganese complex. If the ligand is too electron-poor, its coordination becomes insufficient, reducing the overall catalytic cycles. The best ligand for the Mn(TPP)Cl/NaOCl system found by Collman's group is 4'-(imidazol-1-yl)acetophenone.[20]

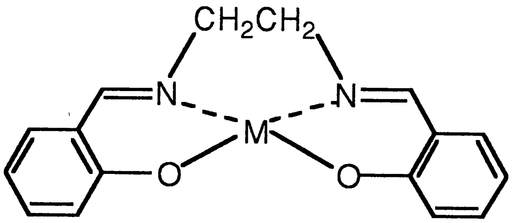
Mn porphyrin and NaOCl or PhIO are capable of hydroxylating some secondary C-H bonds, but yields of the hydroxylation products (usually alcohols) are fairly low.[4,21,22]

Manganese phthalocyanines (MnPcs) are not useful oxidation catalysts, although MnPcs have been prepared.[23] The typical structure of metallophthalocyanines (including MnPc) is shown below:



Metallophthalocyanine (MPc)

Another important macrocyclic ligand for manganese is salen [salen = bis(salicylaldehyde)ethylenediamine]. The following represents the structure of metallosalens.



Metallosalen (Msalen)

Mn(III) salen complexes are also effective catalysts for the epoxidation of alkenes.[24,25] The epoxidation catalyzed by Mn salen complexes is believed to proceed via the similar pathway to that catalyzed by Mn porphyrin, i.e., the key species is the oxo Mn(V) (salen) complex. The presence of donor ligands such as pyridine increases the yield of epoxide.

The major problem encountered in Mn porphyrin or salen oxidation is the instability of the complex under the oxidative conditions. The cause of deactivation of Mn porphyrins has not been studied and understood, although some research groups suggest that the deactivation is due to the formation of μ-oxo dimers or oxidative demolition of the porphyrin ring or both. The reported methods for the epoxidations with metalloporphyrins (including Mn porphyrins) or metallosalens are impractical, since they employ a large excess of substrate with relatively a small amount of oxidant.

Oxidation Catalyzed by Iron Complexes

The simplest transition metal system for oxidation is Fenton's reagent which consists of ferrous salts and H_2O_2.[26] The iron(II) catalyzed oxidation of organic substrates by hydrogen peroxide is believed to proceed via a free radical chain process as shown below.

$$Fe^{II} + H_2O_2 \longrightarrow Fe^{III} + OH^- + HO^\bullet \qquad (8)$$

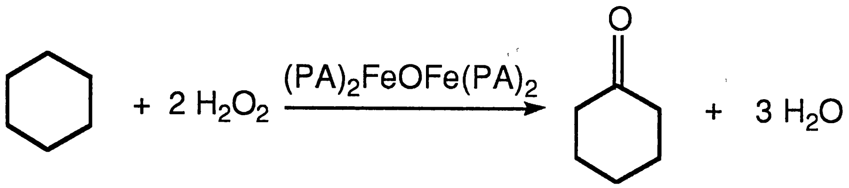
$$RH + HO^\bullet \longrightarrow R^\bullet + H_2O \qquad (9)$$

$$R^\bullet + Fe^{III} \longrightarrow R^+ + Fe^{II} \longrightarrow \text{products} \qquad (10)$$

$$R^\bullet + Fe^{II} \longrightarrow R^- + Fe^{III} \xrightarrow{H_2O} RH \qquad (11)$$

This mechanism has been challenged recently by several research groups. Sawyer and co-workers[27] found that in the case of phenylselenization of hydrocarbons the Fenton chemistry exists only with 1:1 molar ratio of $H_2O_2/Fe^{II}(PA)_2$ (PA = picolinate). If the molar ratio is $\geq$ 10:1, the major part of the chemistry does not involve HO·, and the following pathway leading to cyclohexanone should be considered.

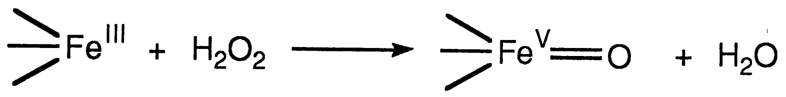
$$2\,Fe(PA)_2 + HOOH \longrightarrow (PA)_2FeOFe(PA)_2 + H_2O \qquad (12a)$$



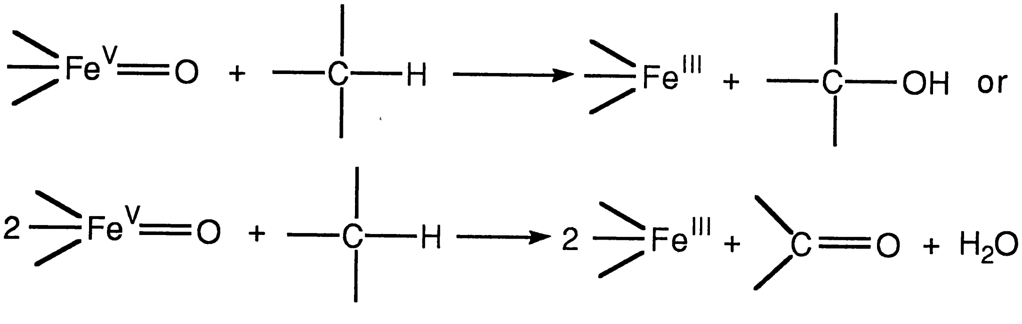
(12b)

The species $(PA)_2FeOFe(PA)_2$ activates H_2O_2 for the ketonization of cyclohexane.

Another observation made by Larpent's group[28] indicated that $FeSO_4/H_2O_2$ in a reverse microemulsion can oxidize a number of secondary C-H bonds. The mechanism for the oxidation seems to involve a pentavalent oxo iron complex, because none of the usual Fenton reaction coupling products were produced.



(13)

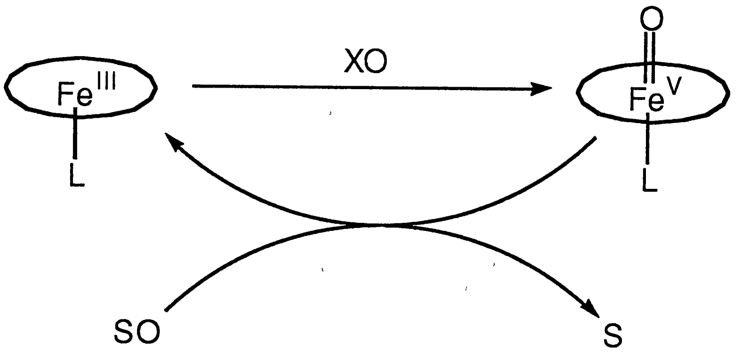


(14)

Fenton's reagents are not synthetically useful, since the yields of oxidized substrates are very low.

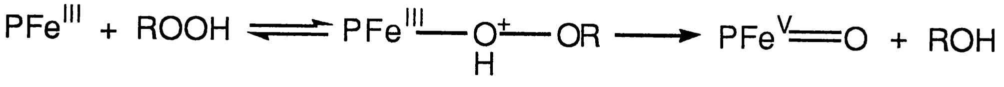
The important iron complexes as catalysts for oxidations are iron porphyrins. The interest in iron porphyrins arises from their structural resemblance to heme groups in cytochrome P-450 monooxygenases, for these enzymes show unique oxidation properties. The oxidation catalyzed by Fe pophyrin is believed to involve an oxo iron complex, similar to that observed in Mn porphyrin catalyzed oxidation (Scheme II).

Scheme II



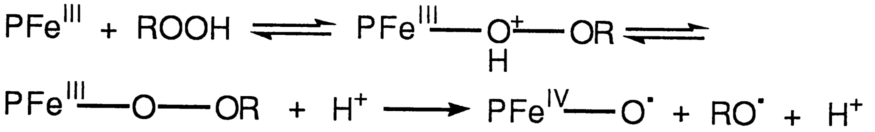
As with Mn porphyrins, the oxo iron porphyrin is formed through transfer of oxygen atom to Fe metal. Kinetics and mechanism of the oxygen transfer reaction have been studied by Bruice's group.[29] In the reaction of Fe(TPP)Cl with different peracids and hydroperoxides, the reactivity of these oxidants is found to be *m*-$ClC_6H_4CO_3H$ >

$PhCH_2CO_3H > CH_3(CH_2)_{10}CO_3H \approx Cl(CH_2)_4CO_3H > Ph_2C(CN)COOH >$ $Ph_3COOH > Ph_2C(CO_2Me)OOH \approx PhC(CH_3)_2OOH > H_2O_2 > t\text{-}BuOOH$. There is a big difference in reaction kinetics between peracids and hydroperoxides. The oxygen transfer reaction with peracids and the more acidic hydroperoxides [e.g., $Ph_2C(CN)COOH$] involves heterolytic cleavage of peroxy O-O bond (eq 15, P = TPP).



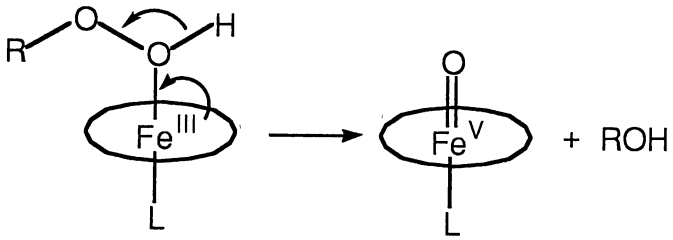
$$PFe^{III} + ROOH \rightleftharpoons PFe^{III}-\underset{H}{O^{+}}-OR \longrightarrow PFe^{V}{=}O + ROH \qquad (15)$$

The less acidic hydroperoxides undergo homolytic cleavage of O-O bond, and have small dependence on leaving group acidity (eq 16, P = TPP).



$$PFe^{III} + ROOH \rightleftharpoons PFe^{III}-\underset{H}{O^{+}}-OR \rightleftharpoons PFe^{III}-O-OR + H^{+} \longrightarrow PFe^{IV}-O^{\bullet} + RO^{\bullet} + H^{+} \qquad (16)$$

In the homolytic cleavage, the deprotonation occurs before O-O bond scission. In the heterolytic pathway, the proton can be transferred directly to the oxygen atom of the leaving group as shown below:



(17)

Bruice and co-workers[30,31] also investigated the pH effect on the reaction of a water-soluble Fe porphyrin with H_2O_2. The reaction at pH 2.8-9.15 is monitored by the observation of $ABTS^{+\cdot}$ [2,2'-azinobis(3-ethylbenzthiazoline) sulfonic acid radical cation] which is formed after trapping the oxo iron porphyrin complex. The reaction occurs faster in base than in acid. The highest reaction rate is observed at pH 8.09 with

4-methoxy-2,6-dimethylpyridine as a buffer. This buffer acts as a strong donor which assists the homolytic cleavage of HO-OH bond to form the oxoiron species.

The oxo Fe porphyrin can undergo dimerization to form μ-oxo Fe porphyrin as expected. The dimerization can take place even in the absence of the oxidant. Fleischer and co-workers[32] report that the water-soluble tetra(*p*-sulfophenyl)porphyrinatoiron ($Fe^{III}TSPP$) exists in a monomeric form in acidic solutions and a dimeric form in basic solutions (pH>9). The dimeric species $(Fe^{II}TSPP)_2O$ was isolated and characterized. Table IV lists some oxo and μ-oxo iron porphyrins.

Table IV. Formation of Oxo and μ-Oxo Iron Porphyrins[a]

Fe porphyrin	oxidant	product
Fe(TMP)Cl	PhIO	FeO(TMP)Cl
Fe(TMP)OH	PhIO	FeO(TMP)
Fe(TMP)OH	$PhCH_2CO_3H$	FeO(TMP)
Fe(TMP)Cl	*m*-$ClC_6H_4CO_3H$	FeO(TMP)Cl
$Fe(TMP)ClO_4$	*m*-$ClC_6H_4CO_3H$	$FeO(TMP)ClO_4$
Fe(TPP)Cl	*p*-$NCC_6H_4NMe_2O$	FeO(TPP)Cl
Fe(TPP)Cl	$PhI(OAc)_2$	FeO(TPP)Cl
$Fe(Cl_8TPP)Cl$	*p*-$NCC_6H_4NMe_2O$	$FeO(Cl_8TPP)Cl$
$Fe(Me_8TPP)Cl$[b]	*p*-$NCC_6H_4NMe_2O$	$FeO(Me_8TPP)Cl$
$Fe(Br_8TMP)OAc$[c]	O_3	$FeO(Br_8TMP)OAc$
$Fe(Br_8TPP)Cl$[d]	C_6F_5IO	$FeO(Br_8TPP)Cl$
Fe(TPP)	$PhNMe_2O$	$[Fe(TPP)]_2O$

[a] See ref 13.

[b] Me_8TPP = meso-tetra(2,6-dimethylphenyl)porphyrin.

[c] Br_8TMP = meso-tetramesityl-*β*-octabromoporphyrin.

[d] Br_8TPP = meso-tetra(2,6-dibromophenyl)porphyrin.

The oxidation with Fe porphyrin-oxidant systems resembles that by manganese complexes in many aspects. One major difference is that the epoxidation by Fe porphyrins is stereospecific.[16,33-36] *cis*-Alkenes are epoxidized to *cis*-epoxides by $Fe(TPP)Cl/C_6H_5IO$ [16,33,34] or $Fe(Br_8TPP)Cl/C_6F_5IO$.[35] *trans*-Alkenes are epoxidized much slower than *cis* isomers. Control experiments made by Meunier and co-workers[37,38] show that Fe porphyrins have lower catalytic activity than Mn porphyrins in alkene epoxidation. Highly steric hindered porphyrins are more stable under oxidative conditions,[39] but usually give lower oxidation yield.

There are relatively few reports on epoxidation catalyzed by Fe phthalocyanines (FePc). Rohde and co-workers[40] found that FePc can catalyze the epoxidation of 5(10),9(11)-estradienes in the presence of PhIO as the oxidant, while O_2, metal peroxides, pyridine-N-oxide, and N-methylmorpholine-N-oxide are inactive oxidants. Hydrogen peroxide and *tert*-butylhydroperoxide decompose very rapidly, giving only small quantities of the epoxide and a large amount of starting material and byproducts. FePc is found to be the best among CuPc, NiPc, CoPc, MnPc, and FePc.

Using $KHSO_5$ as an oxidant, Meunier's group epoxidized styrene and cyclohexene.[41] In these oxidations, the catalytic activity of FePc is lower than that of corresponding Fe porphyrins. The oxidation is suggested to proceed via an oxo-FePc intermediate by comparing the similarities of the oxidation with Fe porphyrins.[41]

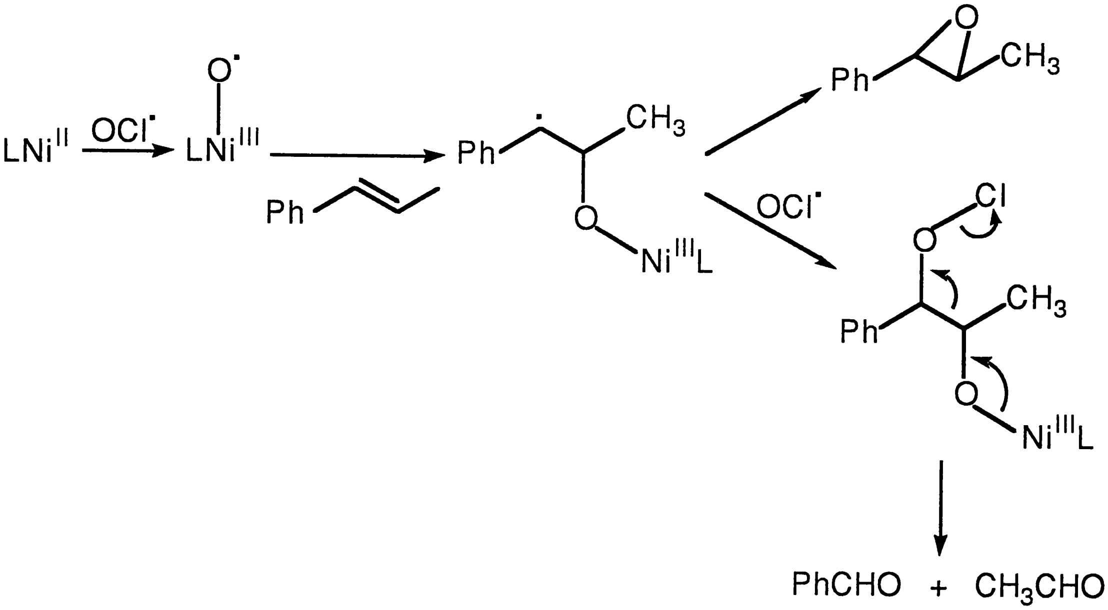
Oxidation Catalyzed by Cobalt and Nickel Complexes

In a biphasic system containing CH_2Cl_2, water, and a PTC agent, Co(TPP)Br catalyzes slowly the epoxidation of styrene with NaOCl as the oxidant.[37] A preliminary comparison among Mn, Fe, Co porphyrins, and Schiff base complexes shows the following catalytic activity for epoxidation: Mn(TPP)OAc > Co(TPP)Br > Fe(TPP)Cl > Schiff base complexes. The actual oxidant of Co porphyrin catalyzed oxidation has not been identified. In the reaction of Co(TPP)Cl with peracids and alkyl hydroperoxides, no oxocobalt complex can be detected.[42]

Co phthalocyanines seem inactive for epoxidations except autoxidation in which CoPcs catalyze the oxidations of phenols and thiols with O_2 via a completely different mechanism.

Relatively little research has been performed on the catalytic oxidation with Ni porphyrins and Ni phthalocyanines. The Ni tetraazamacrocycles (cyclam and dioxocyclam) catalyzed the alkene epoxidation using NaCl and PhIO.[43-46] The epoxidation is nonstereospecific. *cis*-β-Methylstyrene is epoxidized to a mixture of *cis*- and *trans*-epoxides. In the case of NaOCl epoxidation at pH 12-13, benzaldehyde is also formed as byproduct.[45] A mechanism is proposed as follows:

Scheme III



Autoxidation

An autoxidation is a reaction in which the substrate is oxidized by molecular oxygen. Because molecular oxygen in its triplet ground state cannot react with organic substrates, the initiators or transition metal catalysts have to be used to activate the dioxygen. Such autoxidations usually proceed via a free radical mechanism, and result in a mixture of several products.

Autoxidation in Neutral Media

This type of autoxidation has been investigated extensively and is believed to occur via a pathway as shown below:

Initiation:

$$In_2 \xrightarrow{k_I} 2\,In^\bullet \qquad (18)$$

$$In^\bullet + RH \longrightarrow InH + R^\bullet \qquad (19)$$

Propagation:

$$R^\bullet + O_2 \longrightarrow ROO^\bullet \qquad (20)$$

$$ROO^\bullet + RH \longrightarrow ROOH + R^\bullet \qquad (21)$$

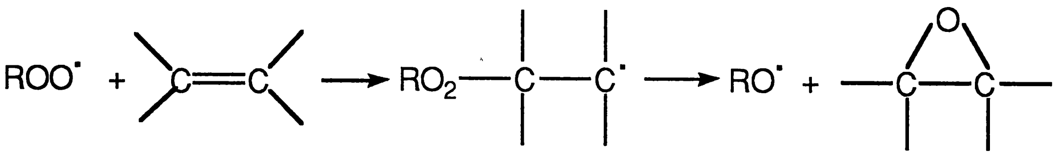
Termination:

$$R^\bullet + ROO^\bullet \longrightarrow ROOR \qquad (22)$$

$$2\,ROO^\bullet \longrightarrow RO_4R \longrightarrow \text{nonradical products} + O_2 \qquad (23)$$

$$2\,R^\bullet \longrightarrow \text{nonradical products} \qquad (24)$$

Hydroperoxides RO_2H are usually the primary products and may be isolated in some cases. In the presence of alkenes, the peroxy radical may react with the alkene by addition rather than by abstraction.



(25)

The chain initiation is accomplished by the deliberate addition of initiators that produce free radicals on thermal decomposition. Practical initiators should decompose at a substantial rate in the temperature range between 50 ° and 150 °C. The rate of chain initiation R_I is given by

$$R_i = 2fk_i[In_2]$$

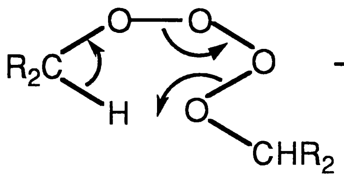
where f is the efficiency of radical production and k_1 is the unimolecular rate constant for decomposition of the initiator In_2.

Since the addition of the alkyl radical to oxygen is very rapid, the rate-determining step in autoxidations might be the hydrogen transfer from substrate to the alkylperoxy radical in propagation stage. The propagation rate depends on the nature of both the attacking alkylperoxy radical (RO_2) and the organic substrate (RH). Relative reactivities of substrates are determined by the dissociation energy of R-H bond. Some of R-H dissociation energies are available in the reference.[47] Polar and steric effects may also play important roles in the propagation rate. In the transition state of hydrogen abstraction, $RO_2^{-}\cdots\cdots H\cdots\cdots R^{+}$, the rate will be increased by the presence of electron withdrawing groups in RO_2 and the presence of electron donating groups in RH.

The termination step usually occurs by the self-coupling of two alkylperoxy radicals under appreciable pressure of oxygen.

$$2\,ROO^{\bullet} \rightleftharpoons RO_4R \qquad (26)$$

The further decomposition of tetroxide is proposed via a cyclic mechanism:[48]



$$\longrightarrow R_2C{=}O + R_2CHOH + O_2 \qquad (27)$$

In the case of R = *tert*-alkyl, the tetroxide may decompose to dialkylperoxides and molecular oxygen.

Autoxidation in Alkaline Media

Alkaline autoxidations are less well understood in many aspects than those in neutral media. A possible mechanism is suggested, in which the initiation step involves electron transfer from a carbanion (R^-) to an acceptor molecule, A, which could be the solvent or a small amount of cosolvent.

Initiation:

$$B^- + RH \longrightarrow BH + R^- \tag{28}$$

$$R^- + A \longrightarrow R^\cdot + A^{-\cdot} \tag{29}$$

Propagation:

$$R^\cdot + O_2 \longrightarrow ROO^\cdot \tag{30}$$

$$ROO^\cdot + R^- \longrightarrow ROO^- + R^\cdot \tag{31}$$

Termination:

$$ROO^\cdot + A^{-\cdot} \longrightarrow ROO^- + A \tag{32}$$

The oxidation of hindered phenols is believed to proceed via the above mechanism in the presence of the catalytic amount of quinone as an electron acceptor.[49] In this case, R^- represents a phenoxy anion, and A is quinone.

Metal Catalyzed Autoxidation

Without added initiator, molecular oxygen can be activated by transition metals such as Cr, Mn, Fe, Co, Ni, Pd, and Cu to initiate autoxidations. The metal catalyzed autoxidation is generally considered to be a free radical reaction. One of the possible mechanisms is the metal assisted generation of organic radicals, which react with dioxygen to form hydroperoxides.

Initiation:

$$RH + M^{n+1} \longrightarrow (RH^{\bullet})^{+} + M^{n+} \quad (33)$$

$$(RH^{\bullet})^{+} \longrightarrow R^{\bullet} + H^{+} \quad (34)$$

Propagation:

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet} \quad (35)$$

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet} \quad (36)$$

Termination:

$$ROO^{\bullet} + ROO^{\bullet} \longrightarrow \text{nonradical products} \quad (37)$$

This mechanism requires low oxidation potentials of R-H bonds to insure the initiation step to take place. The autoxidation of toluene with cobaltic acetate is believed to follow this mechanism.[50]

A second possible mechanism involves the activation of dioxygen by metal in the initiation step.

Initiation:

$$M^{n+} + O_2 \longrightarrow M^{n+1}OO^{\bullet} \quad (38)$$

$$M^{n+1}OO^{\bullet} + RH \longrightarrow M^{n+1}OOH + R^{\bullet} \quad (39)$$

Propagation:

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet} \quad (40)$$

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet} \quad (41)$$

The termination is the same as that in the first mechanism. The autoxidation of different phenols with macrocyclic metal complexes may proceed via this mechanism.[51]

Many metallosalens, metalloporphyrins, and metallophthalocyanines can catalyze autoxidations.[51,52] The formation of metal dioxygen complexes is presumably the key step. The metal dioxygen complexes are experimentally observed with UV-visible and ESR spectroscopy, but the exact structures of these species have not been fully identified.

Kothari and Tazuma[52] investigated the autoxidation of substituted phenols with different metallosalens and metallophthalocyanines. The reactions are carried out under 50-60 psig pressure of O_2 gas at 20-100 ^oC. The most active Pc is CoPc, followed by MnPc, FePc, and CuPc. CuPc is the least active and requires higher temperature to complete the reaction. The MnPc catalyzed reaction produces nearly all diphenoquinone from 2,6-di-*tert*-butylphenol. CoPc can catalyze the oxidation of nearly all substituted phenols except phenol, which suggests that phenol has higher oxidation potential than CoPc. The study of solvent effect on the oxidation reveals that DMF is the best solvent. The addition of pyridine accelerates the oxidation, which is probably due to the enhancement of the formation of metal dioxygen complex by pyridine. In their research Co(salen) seems to be more active than CoPc and FePc. However the results from Tada and Katsu's[53] research indicate that FePc has higher catalytic activity than Co(salen).

Martell and co-workers[54] report the autoxidation of 2,6-di-*tert*-butylphenol with different metallotetraphenylporphyrins. The activities of the catalysts decrease in the order of CoTPP >> Fe(TPP)Cl > Mn(TPP)Cl > VO(TPP), while Cu(TPP) is inactive. The autoxidation leads to two major products, 2,6-di-*tert*-butyl-*p*-benzoquinone (BQ) and 3,3',5,5'-tetra-*tert*-butyldiphenoquinone (DPQ). The distribution of these two products in the reaction mixture depends on catalysts. CoTPP reaction gives BQ the main product, while DPQ is the major product of the oxidation with Fe(TPP)Cl, Mn(TPP)Cl, or VO(TPP). The use of DMF and pyridine has the same effect on the autoxidation as observed in the autoxidation with metallophthalocyanines.

An Fe pophyrin with O_2 can catalyze the hydroxylation of secondary and tertiary alkanes.[55] The yield of hydroxylation is very low, and depends on the stability of porphyrins. The reaction also needs high pressure (100 psig) of O_2 or air (1000 psig). The dioxygen and cobalt Schiff base have been used to oxidize terminal alkenes, but this method is not synthetically useful because it leads to a mixture of several oxidation products in low yields.[56,57]

At present, most autoxidations are performed with substituted phenols which are easily oxidized. No method has been reported to oxidize alcohols or other nonphenol compounds under one atmosphere pressure of O_2 with metalloporphyrins or metallophthalocyanines. There is also no report on the effect of pH on the autoxidation, which is an important factor in many organic reactions.

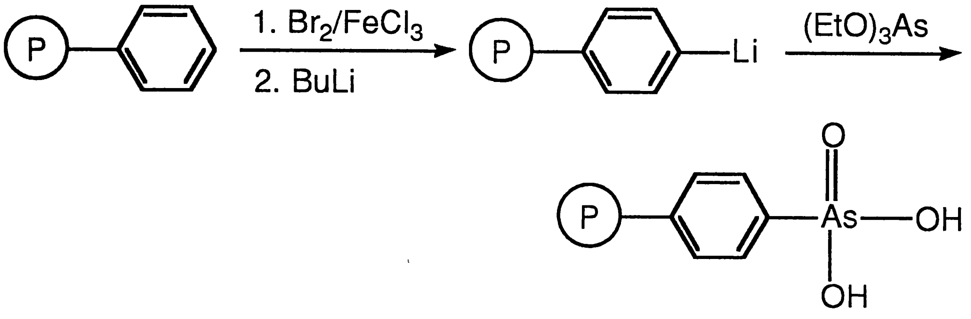
Polymer-Supported Oxidation

Oxidation with Polymer Resin Catalysts

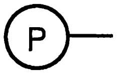
In a polymer-supported reaction, at least one species, a reagent, a catalyst, or a substrate is bound to a polymer. The polymers employed are usually crosslinked polymers which are insoluble in solvents. Organic reactions supported on insoluble polymers have several practical advantages:[58,59] (1) The separation procedure is simple because the supported species can be easily removed from the reaction mixture. (2) The supported species can be reused. This is particularly important when the supported species is precious. (3) The chemical process can be automated, which is of industrial interest. (4) The toxicity and odor of reagents and catalysts are reduced since crosslinked polymers are insoluble and non-volatile. (5) The unique selectivity for the products can be achieved since the catalyst is bound to a restricted matrix.

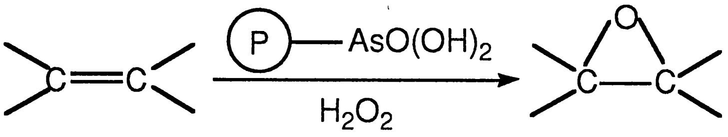
Crosslinked polystyrene resins are often used as polymer supports. These resins can be functionalized by organic reactions, and catalysts or reagents can be anchored to the funtional sites.

Jacobson and co-workers[60] synthesized arsonated polystyrene resins as catalysts for alkene epoxidation. The polymer bound catalysts were prepared via the following procedure:



(42)

where  is polystyrene. The epoxidations were carried out at 70-80 °C in solvents miscible with aqueous H_2O_2 (biphase) and in solvents immiscible with H_2O_2 (triphase). In the biphase reaction, 90% H_2O_2 was used to avoid the hydrolysis of the epoxide to diol. A cheaper, safer oxidant (30% H_2O_2) can be used in the triphase oxidation, since in this case the aqueous phase is separated from organic layer which contains alkene and epoxide.



(43)

The choice of arylarsonic acid is due to its same pK_a (3.82) as that of *m*-chlorobenzoic acid, the peroxy form of which is the most common oxidant. The oxidation of cyclohexene leads to a mixture of epoxide and diol. No attempt was made to avoid acidic hydrolyses by adjusting the pH of the reaction mixture to neutral or basic. The oxidizing power of peroxy acids usually decreases with the increase of pH of the reaction medium. The arsonated polystyrenes also catalyzed the Baeyer-Villiger oxidation of ketones by aqueous H_2O_2. Although these arsonated polystyrene catalysts offer many promising advantages such as facile separation and recycle of the catalysts, their catalytic activity is relatively low. The oxidation of cyclooctene which is fairly reactive produces 69% epoxide in 21 h at 70 °C. With $4\text{-}CH_3C_6H_4AsO(OH)_2$ as the catalyst, 91% epoxide is formed in 29 h at 70 °C.

Metalloporphyrins (especially Fe and Mn porphyrins) are capable of binding to the polymer supports.[61-69] Wohrle's group reported some polymers containing porphyrins or phthalocyanines.[61] In their research, zinc 5,10,15,20-tetrakis(4-aminophenyl)-porphyrin or zinc 2,9,16,23-tetrakis(4-hydroxyphenyl)phthalocyanine was covalently bound to poly(methacrylic acid), poly(N-vinylpyrrolidone-co-methacrylic acid), and poly(chloromethylstyrene). The above porphyrin polymers catalyzed the oxidation of 2,5-dihydrofuran by NaOCl to form 3,4-epoxytetrahydrofuran and 3,4-dihydroxytetrahydrofuran.[62]

In another route to porphyrin-containing polymers, Kamogawa and co-workers[63] first prepared the *p*-vinylbenzyl monomer bearing the moiety of a Mg meso-tetrakis(*p*-carboxyphenyl)porphyrin. This monomer was copolymerized with N-vinyl-2-pyrrolidone in the presence of AIBN. Copolymers with less than 1 mol % of porphyrin moiety were soluble in aqueous solvents.

Similarly, polyacrylates and polymethacrylates containing porphyrins were prepared by the free radical polymerization of porphyrin-acrylate or porphyrin-methacrylate monomers synthesized from acryloyl or methacryloyl chloride and copper or vanadyl 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin.[64]

In a study of polymeric environment on the epoxidation, Drenth and co-workers[65] observed enhancement of the rate of cyclohexene epoxidation by binding Mn(TPP)OAc to an isocyanide polymer. They attributed this enhancement to the site isolation of Mn porphyrin on the polymer, which prevents the formation of μ-oxo dimer. However, this explanation seems vague since catalysts bound on the polymer support usually tend to aggregate rather than separate. The method reported by Drenth's group is impractical because the Mn porphyrin decomposed fast and an excess amount of substrate was used with relatively small amount of oxidant.

Tabushi and Morimitsu[66] reported a catalytic system of MnTPP and colloidal Pt supported on a synthetic polymer. The supporting polymer could be poly(vinyl alcohol) (PVA) or polyvinylpyrrolidone (PVP), both of which have strong affinity for colloidal Pt and solvents such as ethanol (for PVA) and benzene (for PVP). This system is active for epoxidations of polyolefins in the presence of H_2 and O_2. The method offers some advantages of high recycling numbers, monoepoxidation of the polyolefins, and regioselectivity and stereospecificity of the epoxide formation.

Manganese and cobalt complexes of tetrakis(sulfophenyl)porphyrins bound on anion exchange resins (Amberlite IRA 900, 24-42 mesh) catalyzed the decomposition of H_2O_2 to water and oxygen in aqueous phase.[67] These supported catalysts were active for H_2O_2 decomposition even after ten cycles.

Cobalt tetrasulfophthalocyanine bound to a polystyrene resin catalyzed the autoxidation of 2-mercaptoethanol.[68] The presence of a poly(quaternary ammonium) salt, 2,4-ionene, increased the autoxidation rate. However, this polymeric catalyst had lower activity than the homogeneous catalyst. An enhancement of the autoxidation rate was achieved using a cationic latex containing N-methylpyridium salt to replace the polystyrene resin.[70]

Oxidation with Latex Bound Catalysts

As indicated before, polymer supported catalysts usually have lower activity than soluble catalysts, mainly due to chemical or diffusional restrictions. When the reaction is controlled by external mass transfer or intraparticle diffusion of reactants to the active sites, the activity of polymer catalyst increases with the decrease of catalyst particle size. Therefore, colloidal polymer catalysts could be useful catalysts, because their small particle size (10 nm to 1 μm) may overcome the disadvantage of low activity of the conventional polymer catalysts while retaining many features of polymer catalysts. A colloidal polymer, also known as polymer colloid or polymer latex, is a stable dispersion of polymer particles in a liquid (aqueous or non-aqueous). A charged colloidal polymer can be prepared by emulsion polymerization, and can be modified by chemical reactions. Colloidal polymer catalysts may be conveniently obtained by binding metal complexes to the charged colloidal polymer. The charged sites in the colloidal polymer serve as linkages to metal complexes. Because the colloidal polymer has such small particle sizes, we expect that the colloidal polymer catalysts could overcome the diffusional and mass transfer limitations in the catalysis and enhance the reaction rate. In one example a colloidal polymer catalyst tremendously increased the rate of nucleophilic substitution of alkyl bromide by cyanide ion, compared with the solution catalyst and a polymer resin catalyst (particle size >10 μm).[71] Since then a number of colloidal polymer catalysts have been prepared by Ford's group and other groups.[72-84] These catalysts show relatively high activities to catalyze various chemical reactions.

Oxidations catalyzed by metalloporphyrins bound to vesicles and membranes were reported.[72,73] Vesicles are association colloids which form readily in aqueous solution by the spontaneous self-association of amphiphilic molecules. Unlike polymer colloids, vesicles are soft and flexible, because the forces that hold amphiphilic molecules together are weak van der Vaals forces.

A synthetic mimic of cytochrome P-450 consisted of Mn 5,10,15,20-tetra[4-(hexadecyloxy)phenyl]porphyrin and colloidal Pt incorporated into the vesicles of the isocyano surfactant.[72] With O_2, this vesicle bound porphyrin catalyzed the oxidation of styrene to form 1,2-dihydroxy-1-phenylethane, and of 2,5-dihydrofuran to form 3,4-epoxytetrahydrofuran and 3,4-dihydroxytetrafydrofuran.

Regioselective epoxidations of polyunsaturated sterols and fatty acids were conducted with a membrane-spanning iron tetra(o-cholenylamidophenyl)porphyrin and

PhIO as an oxidant.[73] All the sterols were epoxidized exclusively on the side chain, while the epoxidations of fatty acids showed less regioselectivity.

The autoxidation of 1-decanethiol was achieved with cationic latex bound Co tetra(sulfophenyl)phthalocyanine (CoPcTS), and the latex bound CoPcTS had 14 times higher activity than soluble CoPcTs.[74] The cationic latexes were prepared from the emulsion polymerization of 2% of quaternary ammonium ion surfactant monomers, 1-5% of divinylbenzene (DVB), and styrene.

In the epoxidation of styrene by Mn porphyrin and NaOCl, the reaction rate increases by binding Mn porphyrin to the cationic polymer latex.[79] This supported catalyst also showed higher activity than soluble Mn porphyrin. The cationic latexes used in this research were prepared by emulsion polumerization of vinylbenzyl chloride and DVB, and subsequent quaternization of CH_2Cl groups.

Other examples of using colloidal catalysts are autoxidations of 2,6-di-*tert*-butylphenol[75,76] and tetralin[76-78] by latex bound cobalt catalysts, and the oxidation of ascorbic acid by a latex bound histamine-Cu(II) complex.[81]

Although the mechanism of colloidal catalysis is not well understood so far, high activities of colloidal catalysts might be due to their very small particle sizes (<1 μm) and high surface areas which can adsorb the substrates around particles efficiently and hence increase the chance of the collisions between substrates and reagents. On the other hand, colloidal particles may be able to entrap substrates into particles - a hypothetical solvation process which also helps the catalysis.

In this research, three types of cationic polymer colloids have been prepared by batch and semicontinuous emulsion polymerization, and subsequent quaternization. These cationic latexes are bound with a water-soluble manganese porphyrin to form latex bound porphyrin catalysts which are used to catalyze the oxidation of alkenes.

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CHAPTER II

OXIDATIONS OF ALKENES CATALYZED BY A MN (III) PORPHYRIN BOUND TO CATIONIC POLYMER LATEXES

Introduction

Catalysis by transition metal ions has aroused increasing interests in today's science, because it is important for both biological and industrial applications. Transition metal catalysts can be used for carbon-metal bond formation, C-C bond formation (alkylation, acylation, olefination, polymerization, etc.), reduction (hydrogenation, hydrogenolysis), and oxidation (epoxidation and hydrocarbon activation). Many macrocyclic metal complexes are able to catalyze the oxidation effectively in the presence of oxygen donors.[1] Among the most common complexes are metallocyclam and dioxocyclam,[2,3] metallosalen,[3-5] metallophthalocyanine[6] and metalloporphyrin.[7-12] These complexes have been intensively studied, including their syntheses, structures and catalytic activities, for two reasons: to develop efficient catalysts for both laboratory and industrial use, and to mimic the unique properties of natural enzymes. Many research groups report a number of catalytic systems of these metal complexes. The catalytic activities vary with the reaction type and metal complexes. Metalloporphyrins usually show high activity in alkene epoxidations[2-12] and alkane hydroxylations.[13-18] Cobalt phthalocyanine is effective for autoxidation of some organic phenols. However, all reported metal complexes suffer from the same problem--deactivation under oxidative conditions.

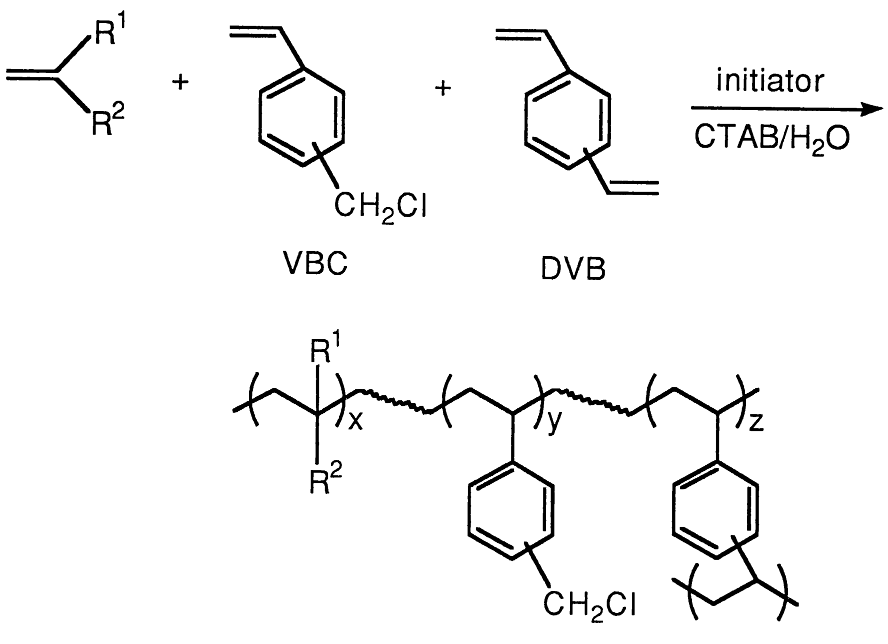
Alkene epoxidation catalyzed by metalloporphyrins has both chemical and biological importance. Epoxides are intermediates which can be converted to many products for various purposes. Metalloporphyrins serve the models of the cytochrome P-450 family of natural monooxygenase enzymes. These models are used to study biomimetic mechanisms. The model usually consists of a synthetic metalloporphyrin and an oxidant (PhIO, NaOCl, $KHSO_5$, ROOH, H_2O_2, or O_2 and an electron source). The key species in these systems is the high valent oxometalloporphyrin which is formed by transfer of an oxygen atom from the oxidant to metalloporphyrin,[10,11] and then this active oxometalloporphyrin donates the oxygen to substrates to perform oxidations (such as epoxidations). However, along with the oxidations is the rapid deactivation of the metalloporphyrin, mainly due to the formation of μ-oxometal porphyrin dimers which are incapable of transferring the oxygen atom. In the absence of substrates, this suicidal process takes place even faster. Many methods to retard the deactivation of metalloporphyrins have been proposed, including introduction of bulky groups and electron-withdrawing substituents in the meso positions,[12,13,14,19] using silica[17] or zeolite[4,20] as supports which allow porphyrin molecules to stay in the pores to prevent the dimerize, and binding porphyrins onto polymers.[21,22] The latter two cases are actually the methods to isolate the active sites of oxo-intermediates, so that the oxometalloporphyrins can perform the oxygen transfer efficiently rather than dimerization. Although these methods partly improve the stability of porphyrins, they cannot stabilize porphyrins throughout the oxidations.

At present, nearly all porphyrin-catalyzed oxidations are carried out in biphasic media with phase transfer catalysts. The typical medium which includes the oxdant-containing aqueous phase and porphyrin-containing organic layer (usually CH_2Cl_2) is biologically not a good model of the environment of monooxygenase enzymes. The oxidations are even chemically impractical. Most experiments use a large excess ratio of substrate to oxidant (e.g., NaOCl) to delay the decomposition of porphyrin and to get the best calculation of turnover numbers based on the amount of oxidant. Previous work in this group found that the reactivity of the water-soluble manganese porphyrin increased after being bound to a colloidal polymer. The supported porphyrin catalyzed the epoxidation of styrene and its derivatives even in the absence of organic solvent.[23] In this research, several cationic latexes were prepared and were used to bind a water soluble Mn porphyrin. The oxidation of alkenes was carried out in the presence of latex bound porphyrin, and the influence of polymer latexes and different oxidants on the oxidation were investigated.

Results

Preparation of Latexes. Cationic latexes were prepared via two steps: (1) emulsion copolymerization of vinylbenzyl chloride (VBC), divinylbenzene (DVB), and a third monomer (vinyl octadecyl ether, styrene, or n-decyl methacrylate) with 2,2'-azobis(N, N-dimethyleneisobutyramidine)dihydrochloride as the initiator and cetyltrimethylammonium chloride as a surfactant; (2) quaternization of the resulting colloidal copolymers with 25 wt % aqueous trimethylamine (Scheme 1). The emulsion polymerization was performed by either batch or semicontinuous polymerization (Table I). The quaternization was carried out in the ordinary round bottom flask with a condenser or in a stainless steel pressure vessel. The pressure quaternization gave higher conversion of chloromethylene groups in VBC to quaternized sites (e.g.: L-3 and L-4), since trimethylamine has a low boiling point, 2.9 °C. The conversion did not increase noticeably after 4 days in the pressure reaction.

Scheme I



1

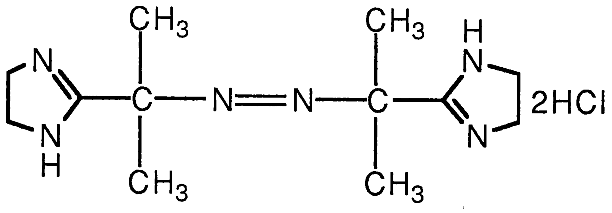
1a: R^1= H, R^2= $-OC_{18}H_{37}$ (VODE)

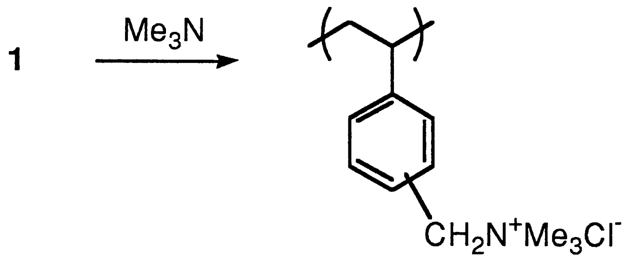
1b: R^1= H, R^2= $-C_6H_5$ (St)

1c: R^1= H, R^2= $-CO_2C_{10}H_{21}$ (DMA)

CTAB: $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$

Initiator:





2

These charged latexes were purified by ultrafiltration to remove unbound surfactant. The quaternized sites were characterized by Cl^- content in the latex which was determined by chloride-selective electrode titration. These latexes had the quaternized sites of 1.72-4.09 mequiv. of Cl^-/g of the dried latex, which corresponds to 52.8-89.4 % conversion of original VBC units (Table II). The quaternized sites obtained by titration might be underestimated by 2-3% because Br^- could exchange with Cl^- in the latex. The titration result was consistent with the elemental analysis. For example, quaternized site of L-4 was 4.09 mmol/g by titration and 3.94 by elemental analysis. The chloride selective electrode titration accounted for as high as 89 % of VBC units converted. The rest of VBC units could remain unreacted, though IR analyses of the dried latexes did not evidence the benzylic chloromethyl group (-$C_6H_4CH_2Cl$) at 1266 cm^{-1} which was detected in these colloidal copolymers, or could be converted to benzylic alcohol groups, since the acidity (pH 1.5) of the colloidal polymer was observed after emulsion polymerization, possibly due to the partial hydrolysis of chloromethylene groups.

Table I. Preparations of Colloidal Copolymers

copolymer	monomers[a], g (mol %)				polymn method	solids wt %	yield %	latex viscosity
	VBC	VODE	St	DMA				
C-1	1.94 (93.2)	0.20 (5.0)	-	-	Batch	6.04	79	High
C-2	1.74 (83.2)	0.61 (15.0)	-	-	Batch	5.45	71	High
C-3	1.53 (73.2)	1.01 (25.0)	-	-	Batch	5.12	64	High
C-4	3.06 (73.2)	2.02 (25.0)	-	-	Batch	5.51	70	High
C-5	1.01 (48.2)	-	-	1.55 (50.0)	Batch	9.50	70	Low
C-6	7.63 (25.0)	-	15.25 (73.2)	-	Semicontinuous	12.75	85	Low

[a] 1.8 mol % of commercial DVB was used in each copolymer, which contains 1.0 mol % of DVB and 0.8 mol % of ethylvinylbenzene.

Table II. Properties of Quaternized Latexes and Microemulsions

sample	N^+Cl^- site		conv of VBC	solid content	D_n[a], nm	D_w/D_n[b]	viscosity
	mmol/g	mol %	%	wt % solids	std dev		
L-1	3.42	65.3	66.5	1.28	70.8(10.5)	1.08	High
L-2	3.17	59.4	60.7	2.45	50.4 (7.4)	1.08	High
L-3	2.82	51.5	52.8	2.70	53.7 (7.3)	1.07	High
L-4	4.09	82.0	84.1	3.46	50.0 (7.2)	1.09	High
L-5	1.90	40.6	84.3	4.28	44.4 (7.9)	1.06	Low
L-6	1.72	22.4	89.4	4.41	47.3 (6.5)	1.07	Low
L-7	1.72	22.4	89.4	4.03	47.7 (7.7)	1.10	Low
L-8[c]	1.36	-	-	5.54	58.0 (8.1)	1.07	High
μE-1[d]	0.57[f]	-	-	-	-	-	Low
μE-2[e]	0.79[f]	-	-	-	-	-	High

[a] Number average diameter and standard deviation of 50 particles in transmission electron micrographs.

[b] Polydispersity = D_w/D_n, D_w = weight average diameter.

[c] L-8 was prepared by mixing 98.8 wt % of L-6 with 1.2 wt % of 1-octadecanol.

[d] μE-1 was prepared by mixing 215.5 mg of 1-octadecanol with 56.9 mg of cetyltrimethylammonium bromide (CTAB) in 45 mL of H_2O at 65 °C with stirring.

[e] μE-2 was prepared by mixing 270.5 mg of 1-octadecanol with 109.6 mg of CTAB in 10 mL H_2O at 65 °C with stirring.

[f] N^+Br^- sites were calculated from the compositions of microemulsions.

Some unusual phenomena of VODE latexes (L-1 to L-4 in Table I) were observed. First, 1-octadecanol was recovered after extracting the latex with CH_2Cl_2 and evaporating CH_2Cl_2. Second, the latex did not contain long chain aliphatic units, which was confirmed by ^{13}C solid state NMR spectra. Third, these latexes were highly viscous, while the other latexes were fluid-like as indicated in Tables I and II. In a control experiment, polymerization of VODE alone in dioxane with AIBN as an initiator at 70 °C gave about 4 % yield of a white polymer after 3 days stirring. This suggested that the reactivity of VODE in the free radical polymerization was low.

The number average diameters (D_n) of latexes, which represent the particle sizes of the latexes, are from 44 nm to 71 nm. Both batch and semicontinuous polymerizations gave small particle sizes. Except L-1 and L-8, these latexes had nearly the same particle sizes and size distributions. L-8 had almost the same particle size as L-6 after mixing with 1-octadecanol.

Figures 1-8 are transmission electron micrographs (TEM) of L-1 to L-8, which show that the dry cationic latex particles are polydisperse. Although the particles appear aggregated in some of the micrographs, particles did not precipitate from any of the samples over periods of two years. This indicates that large (> 1 μm) aggregates were not present. The aggregates in the micrographs could be an artifact of preparation of TEM samples. The diameters of 50 non-aggregated particles from the TEM negative were used to determined the particle sizes.

Attempts to Prepare Latexes with Other Monomers. Emulsion polymerizations of N-methyl-N-octadecyl methacrylamide (MODMA) and trimethylvinyl-benzylammonium chloride (TVBA), of hexadecyl methacrylate (HDMA) and TVBA, of TVBA and N,N-dioctyl methacrylamide (DOMA) and N,N'-dimethylethylene bismethacrylamide (DMBMA), of vinylbenzyl octadecyl ether (VBODE) and TVBA and DVB produced latexes precipitated after the polymerization.

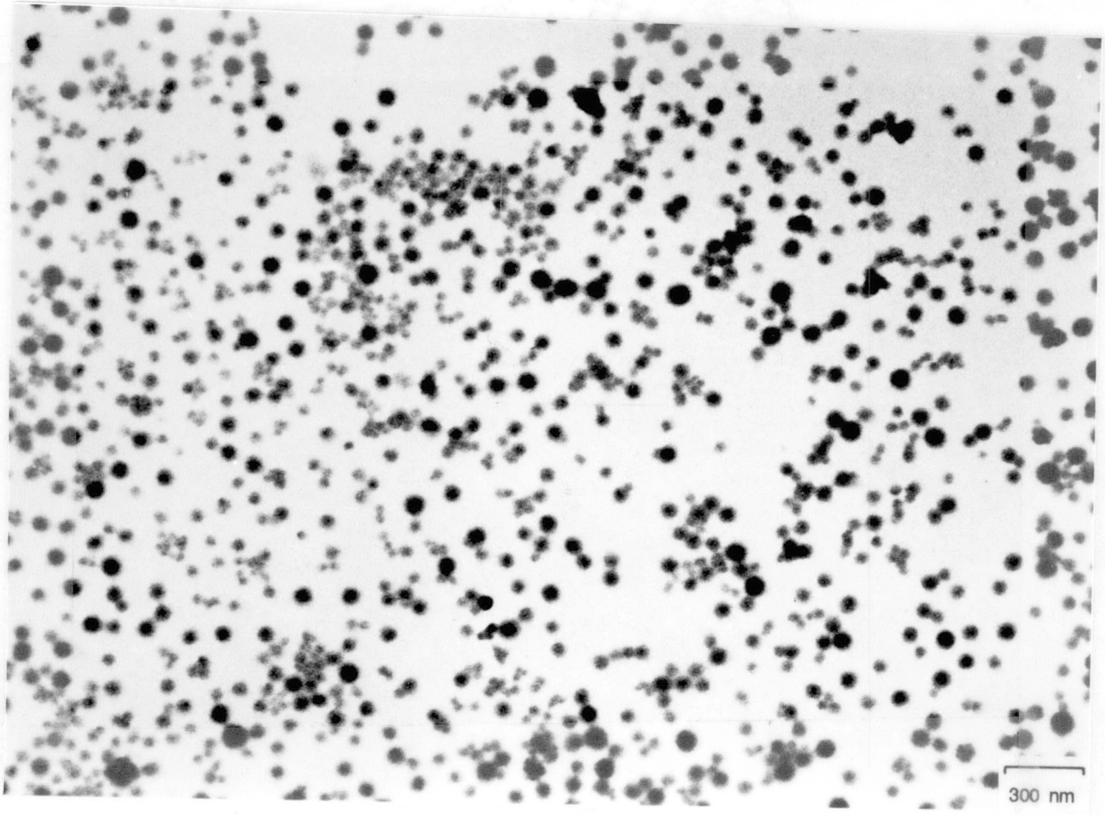


Figure 1. Transmission electron micrograph of latex L-1, 7200 magnification

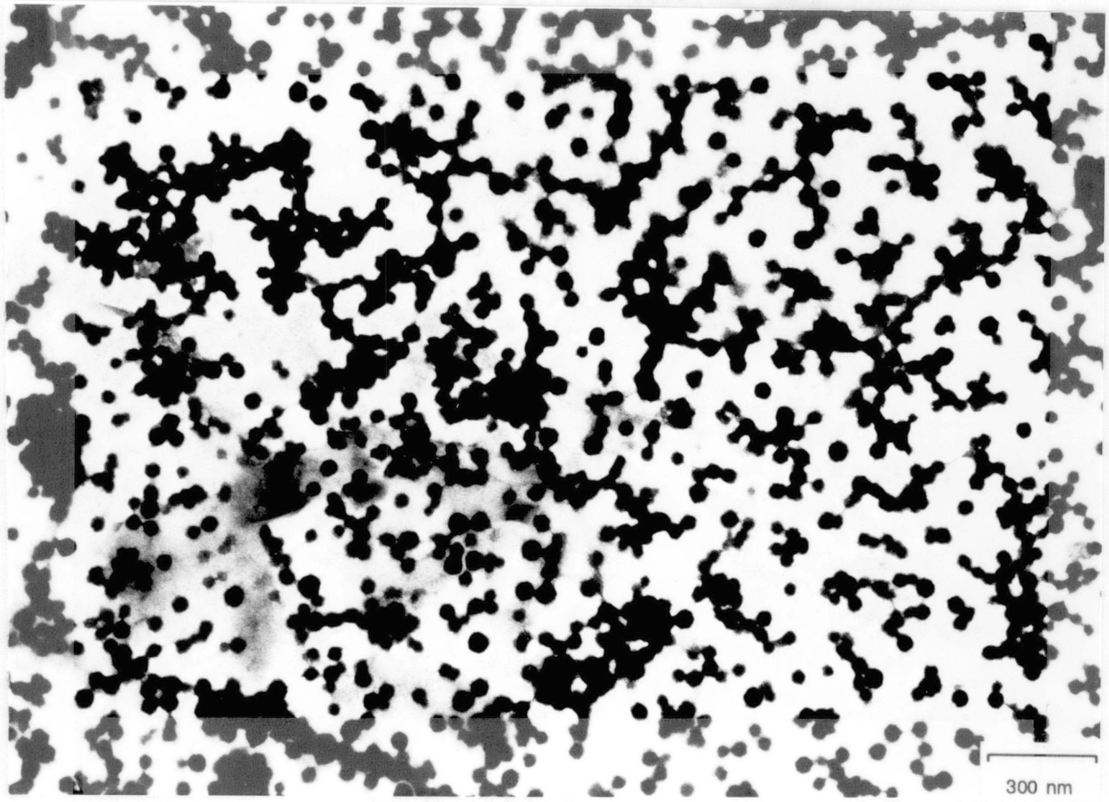


Figure 2. Transmission electron micrograph of latex L-2, 10000 magnification

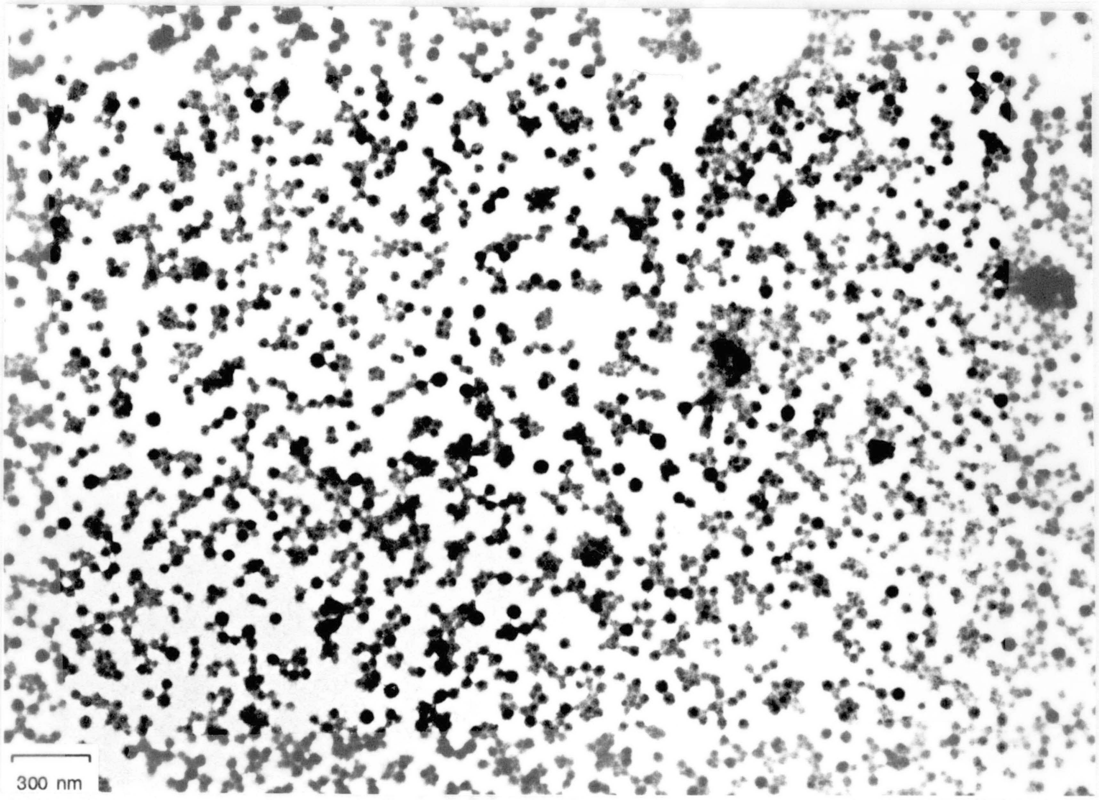


Figure 3. Transmission electron micrograph of latex L-3, 7200 magnification

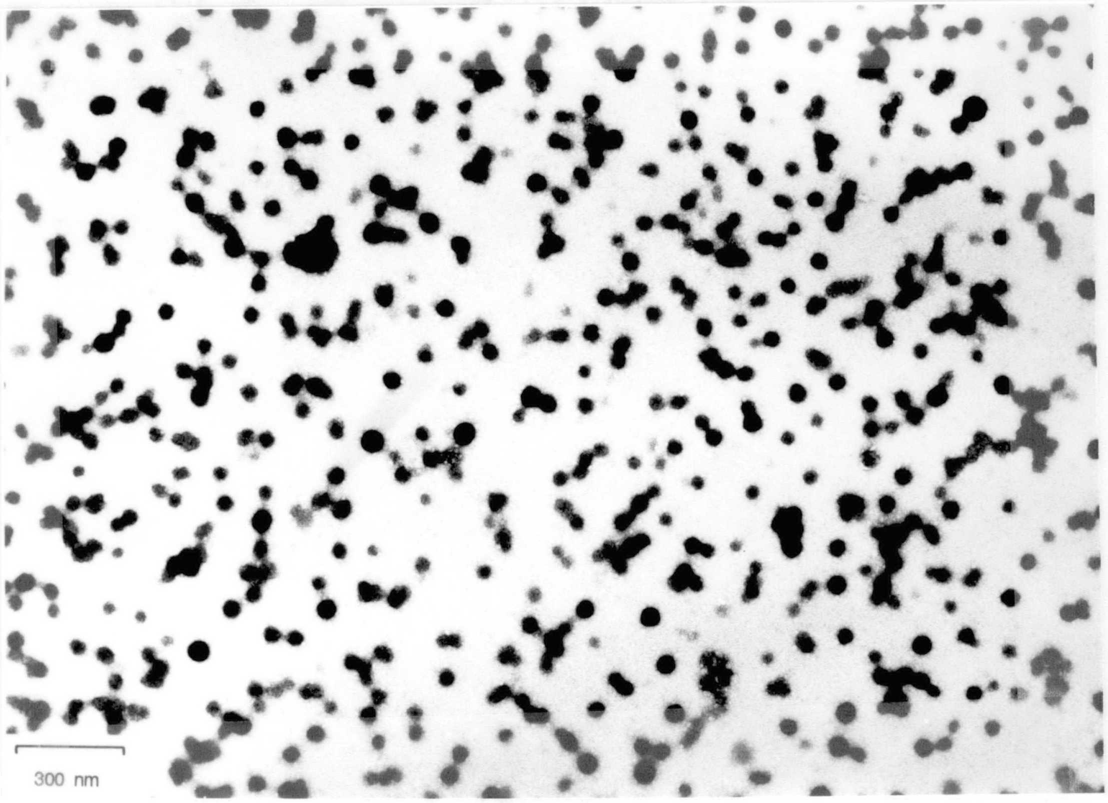


Figure 4. Transmission electron micrograph of latex L-4, 10000 magnification

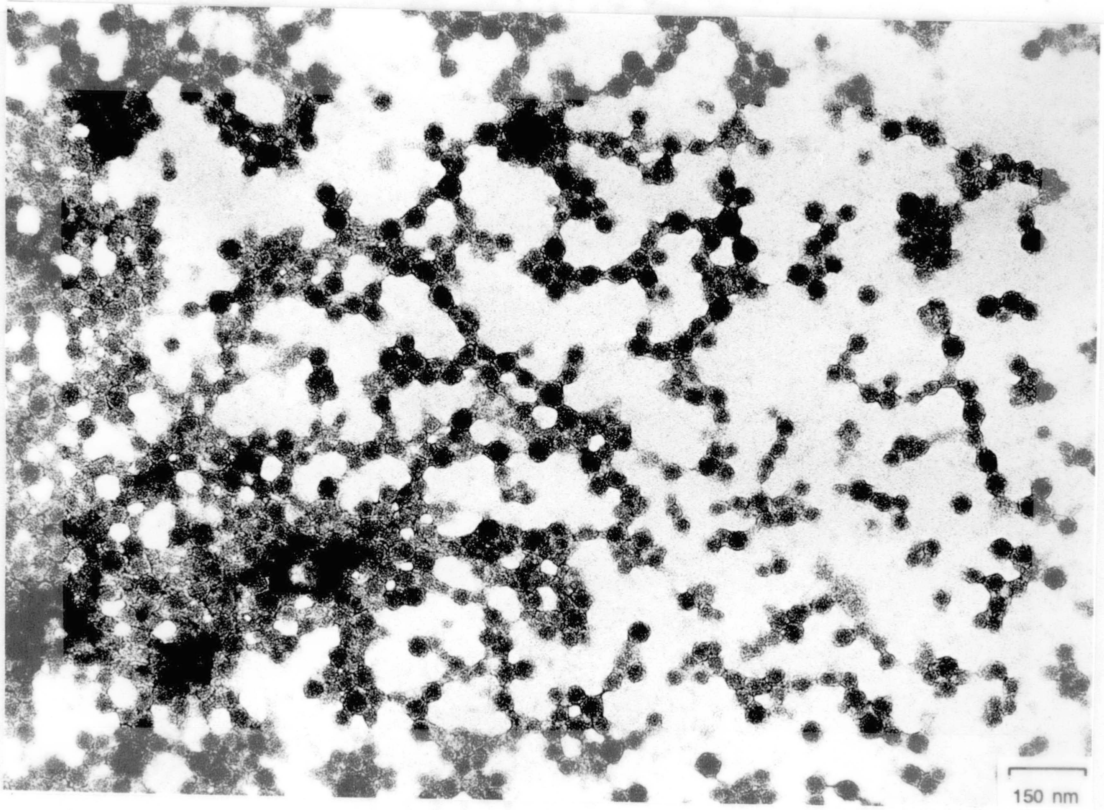


Figure 5. Transmission electron micrograph of latex L-5, 14000 magnification

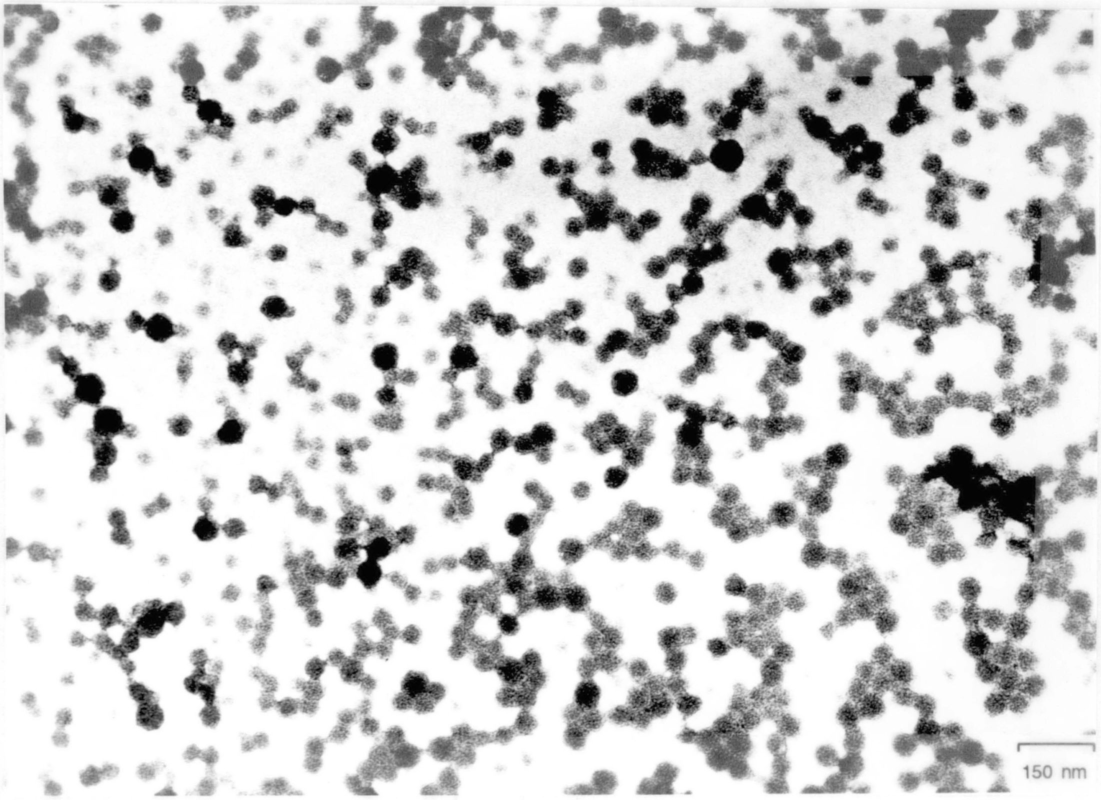


Figure 6. Transmission electron micrograph of latex L-6, 14000 magnification

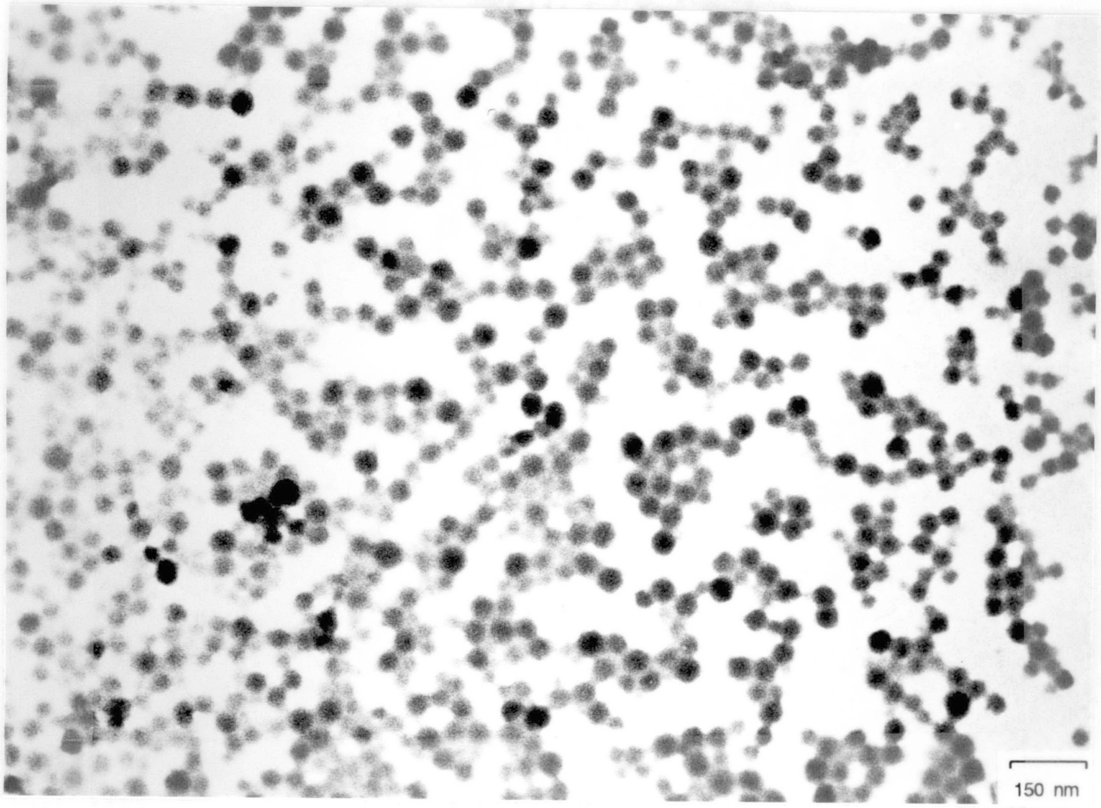


Figure 7. Transmission electron micrograph of latex L-7, 14000 magnification

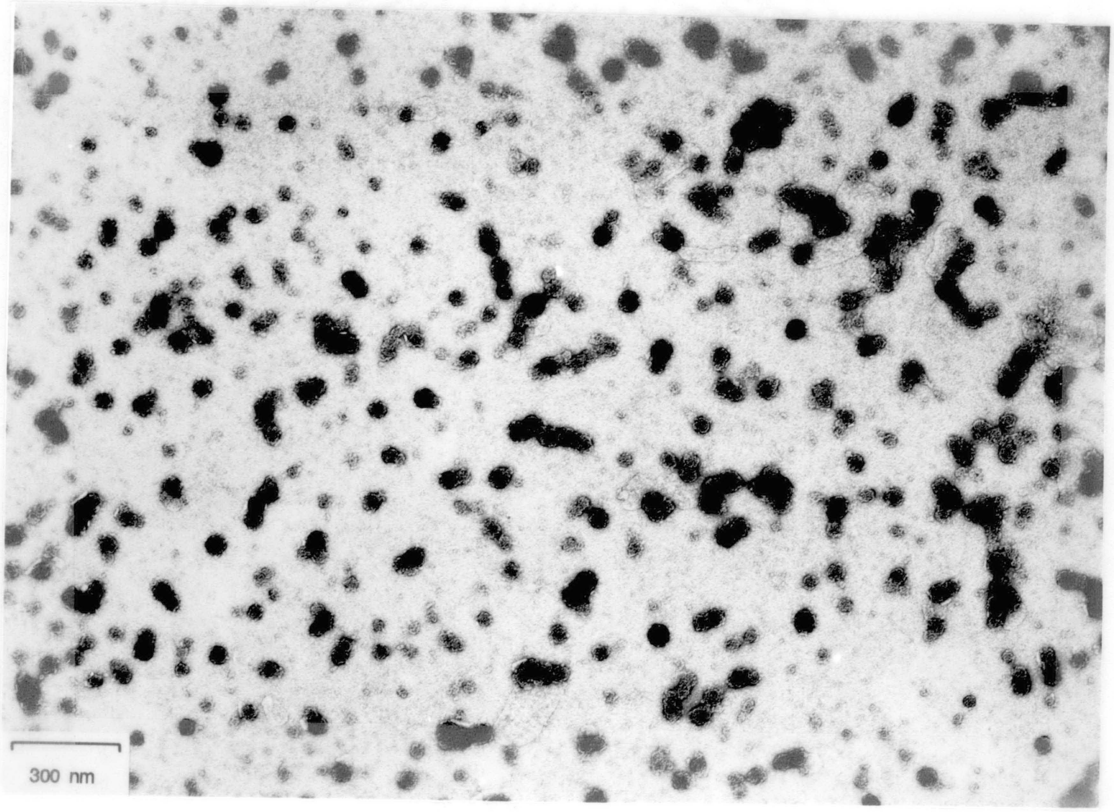
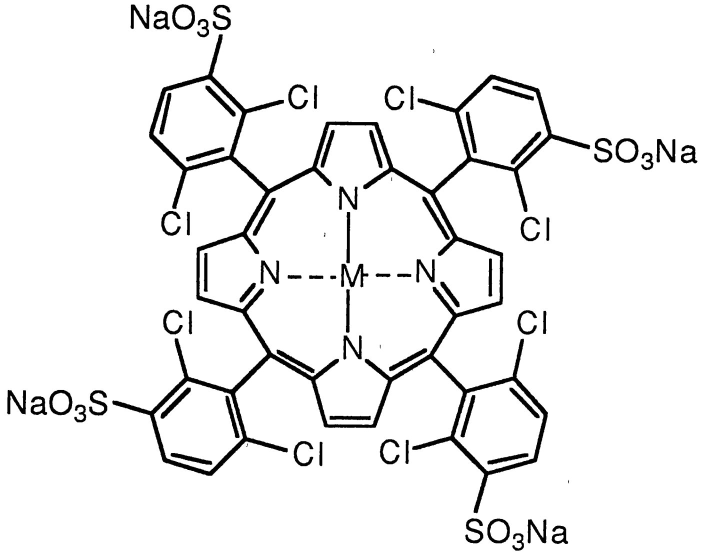


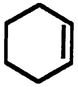
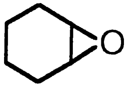
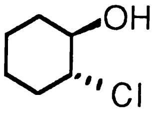
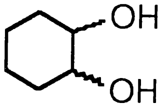
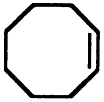
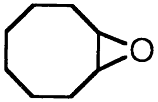
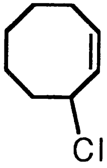
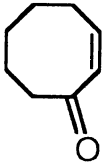
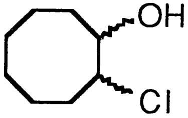
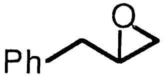
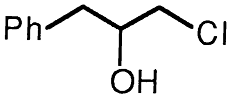
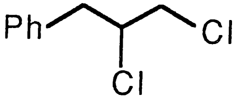
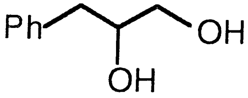
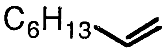
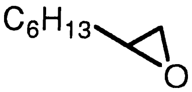
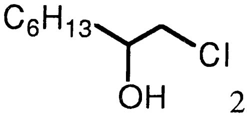
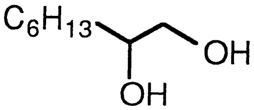
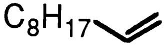
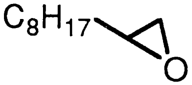
Figure 8. Transmission electron micrograph of latex L-8, 10000 magnification

Oxidation with NaOCl. The oxidations with NaOCl catalyzed by latex bound Mn porphyrin were carried out with cyclooctene, cyclohexene, 1-octene, allylbenzene and 1-decene at 40 °C for 5 h (Table III). The anionic Mn porphyrin (MnTSPP) was first ionically bound to the cationic latexes,[23] and then the resulting red colloidal catalyst was used to perform the reactions. The reaction mixtures had three phases, aqueous, colloidal particles, and organic liquid. Cyclohexene reacted fastest, giving 97% conversion, while only 10% 1-decene was converted after 5 h. Solubilities of alkenes in the dispersion phase might be one of the reasons for the differences in reactivity. The solubility of cyclohexene in water at 25 °C is 2.6×10^{-3} M,[24] while that of 1-decene is estimated to be 1.5×10^{-6} M.[25]



MnTSPP

Table III. Oxidation of Alkenes with NaOCl[a]

alkene	conv (%)	products, mol %			
	97	 55	 10	 32	
	47	 16	 13	 4	 14
	39	 25	 6	 4	 4
	39	 7	 25	 7	
	10	 4			

[a] All experiments were carried out at 40 °C for 5 h by using 0.35 mmol of alkene, 0.52 mmol of NaOCl, 6.91 x 10^{-4} mmol of MnTSPP, and 13.5 mg of L-3 containing 0.038 mmol N^+Cl^- sites in 1.64 mL of aqueous mixture. The ratio N^+/MnTSPP was 55.

In the oxidations of cyclohexene and cyclooctene, both reaction conversion and epoxide yield increased with the increase of NaOCl concentration (Table IV). Under the same conditions, oxidation of cyclohexene showed higher reactivity and selectivity than that of cyclooctene.

Table IV. Effect of NaOCl Concentration on the Oxidation[a]

alkene	NaOCl, M	alkene, mol %	epoxide, mol %
cyclohexene	0.24	33	49
cyclohexene	0.27	22	55
cyclohexene	0.32	3	55
cyclooctene	0.27	64	11
cyclooctene	0.32	53	16

[a] All experiments were carried out under conditions reported in Table III unless noted otherwise.

Latex compositions did not have much influence on the oxidation of cyclooctene (Table V). The conversions were 49-54% with 1.5 equiv of NaOCl (0.52 mmol) and 33-41% with 1.25 equiv of NaOCl (0.44 mmol). Latex bound porphyrin showed higher activity than porphyrin in solution (37-54% vs. 15%).

Table V. Oxidation of Cyclooctene with Different Latexes[a]

latex mg	N^+Cl^- site mmol	mol ratio of N^+/MnTSPP	NaOCl M	conversion %
L-1 (9.6)	0.034	49	0.32	53
L-3 (13.5)	0.038	55	0.32	54
L-5 (17.1)[b]	0.033	48	0.21	49
L-2 (12.3)	0.039	56	0.27	41
L-3 (13.5)	0.038	55	0.27	38
L-3 (13.5)[c]	0.038	110	0.27	33
L-8 (17.7)	0.031	45	0.27	37
L-3 (13.5)[d]	0.038	55	0.27	15
none	-	-	0.27	15

[a] Reactions were carried out at 40 °C for 5 h as reported in Table III except for variations in amounts of latex and in NaOCl.

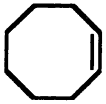
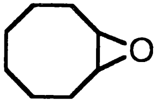
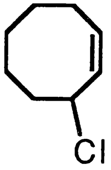
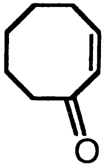
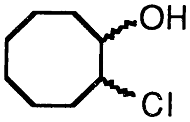
[b] This reaction was done in 2.5 mL of aqueous mixture.

[c] 3.46×10 mmol^{-4} of MnTSPP was used.

[d] Reaction time was 1 h.

The oxidation of cyclooctene by NaOCl resulted in a mixture of several products. In addition to cyclooctene oxide, 3-chlorocyclooctene, 3-cyclooctenone and 2-chlorocyclooctanol (*cis* and *trans* isomers) were found. The distribution of these products depends depends on the reaction conditions (Table VI). In the absence of Mn porphyrin, the oxidation produced a mixture of several products of which cyclooctene oxide is negligible (2 mol %, Run 1). The presence of MnTSPP raised the yield of the epoxide, but did not raise the yield of other products (Run 2). Lower concentration of NaOCl gave slightly less epoxide (Run 3), and one hour reaction produced lower yields of these four products than five hour reaction. Highly basic media ($pH \geq 13$) resulted in selective epoxidation. Therefore, the presence of latex bound porphyrin is necessary to form the epoxide. Without Mn porphyrin, oxidative destruction of cyclooctene takes place.

Table VI. Product Distribution from the Oxidation of Cyclooctene[a]

expt	MnTSPP µM	NaOCl M	pH	 mol %	 mol %	 mol %	 mol %	 mol %
1	-	0.32	10.3	68	2	13	2	15
2	0.42	0.32	10.3	53	16	13	4	14
3	0.42	0.27	10.3	64	11	13	2	10
4[b]	0.42	0.27	10.3	87	3	4	1	5
5[c]	0.34	0.22	≥13	75	25	-	-	-

[a] Experiments were done under conditions reported in Table III unless noted otherwise.

[b] This experiment was performed for 1 h.

[c] pH was adjusted by addition of 0.2 mL of 1 N NaOH.

Oxidation with Potassium Peroxymonosulfate ($KHSO_5$). $KHSO_5$ oxidation of cyclooctene leads to high conversion and high selectivity (Table VII). Commercial OXONE contained $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ in molar ratio of 1.73:1.0:1.34. The active species is $KHSO_5$. The oxidations were done at room temperature with latex bound Mn porphyrin at pH 1.5. In more acidic solution (pH = 0.3), diol rather than epoxide was produced due to the ring opening of cyclooctene oxide. Higher temperature (40 ^oC) reaction gave slightly higher conversion with lower selectivity than room temperature reactions as expected.

The latex particles coagulated during $KHSO_5$ reactions. In the case of L-7, the emulsion looked stable at the beginning of the reaction, but coagulated after 5 h. In the other cases, latexes coagulated immediately after $KHSO_5$ was added. Although every possible combination of $KHSO_5$ reagent, substrate, latex quantity and water, and even addition of CTAB (surfactant) was tried, it failed to give the stable latex throughout the reaction. It should be noted that the addition of the solution of 0.31 M $KHSO_4$ and 0.10 M K_2SO_4 (ionic strength = 0.61 M, the same as that in the oxidation mixture) into the aqueous latex under the same epoxidation condition did not coagulate the latex particles. Thus we suggest that the active species $KHSO_5$ is responsible for the coagulation.

Like NaOCl, $KHSO_5$ can also oxidize Mn porphyrin to oxoporphyrin, which is a key intermediate for the epoxidation.[37,38] The high activity of $KHSO_5$ could be attributed to easy breakage of the HO-OSO_3 bond, for SO_4^{-2} is a good leaving group in water. Since the $KHSO_5$ solution is acidic (pH 1.5) due to the accompanying $KHSO_4$, small amount of trans-1,2-cyclooctanediol was also formed because of the acid catalyzed ring opening of the epoxide.

Table VII. Oxidation of Cyclooctene with $KHSO_5$[a]

latex mg	aq vol. mL	Mn por mM	$KHSO_5$ M	temp °C	pH	alkene mol %	epoxide mol %	diol mol %
L-3 (13.5)	2.65	0.32	0.17	40	1.5	31	56	13
L-3 (13.5)	2.65	0.32	0.17	23	1.5	37	57	6
L-3 (13.5)	3.65	0.23	0.12	23	0.3	5	-	95
L-7 (20.2)	2.85	0.30	0.15	23	1.5	43	46	11

[a] Experiments were carried out for 5 h using 0.35 mmol of cyclooctene, 6.91×10^{-4} mmol of MnTSPP and 0.44 mmol of $KHSO_5$.

Oxidation of Cyclooctene with Hydrogen Peroxide, Sodium Perborate and Sodium Periodate. A number of oxidations with H_2O_2, $NaBO_3$ and $NaIO_4$ were carried out under the standard conditions for NaOCl epoxidations except that stock solutions of 30% H_2O_2, 0.16 M of $NaBO_3 \cdot 4H_2O$ and 0.349 M of $NaIO_4$ were used. Since the solubility of $NaBO_3 \cdot 4H_2O$ in water is low (2.55g/100g water), mixture is relatively diluted. These oxidants were less reactive than NaOCl. Epoxidation by H_2O_2 produced only 2% epoxide, while $NaBO_3$ and $NaIO_4$ did not oxidize the substrate. The addition of $NaIO_4$ solution to the reaction media coagulated the latex particles.

Discussion

Emulsion Polymerization. Results in Tables I and II indicate that the emulsion polymerization initiated by an amidine initiator and subsequent quaternization with trimethylamine are the effective route to prepare cationic latexes. These latexes have been colloidally stable 2 years. In the case of latexes prepared with VODE monomer, three unexpected results suggested that vinyl octadecyl ether did not copolymerize with other monomers. It hydrolyzed to form acetaldehyde and 1-octadecanol in the presence of HCl which was generated from the partial hydrolysis of chloromethyl groups in VBC.

$$CH_2{=}CHO(CH_2)_{17}CH_3 \xrightarrow[H_2O]{H^+} CH_3CHO + CH_3(CH_2)_{17}OH$$

It has been pointed out that in the emulsion polymerization initiated by a water-soluble initiator, the charged radical must overcome a Coulombic repulsive energy barrier to reach the identically charged micelle. The radical may have to react with monomer first in aqueous phase to form an oligomer radical until the van der Waals attractive force between the oligomer radical and the micelle is sufficiently high to overcome the Coulombic repulsion.[29] Therefore, highly water-insoluble monomers (e.g., *p-tert*-butylstyrene, octadecyl methacrylate) do not easily undergo emulsion polymerization with a water-soluble initiator. Satpathy and Dunn found that these monomers could be polymerized in an emulsion only using high emulsifier-monomer ratio (1:1 or 1:2).[30] The high concentration of the emulsifier generated a large amount of mini-emulsion droplets which were significant reaction loci. The addition of methanol to the emulsion increased the polymerization rate. Even the trace amount of methyl methacrylate accelerated the polymerization of octadecyl methacrylate.

The solubility of VODE in water should be very low due to its long aliphatic chain, and is expected to increase in the presence of surfactant. In the aqueous emulsion polymerization, low solubility usually results from low polarity of the monomer. Thus the water-soluble amidine radical may not effectively initiate the VODE polymerization, and growing radical chains may not have sufficient hydrophobic attraction to react with VODE.

Reportedly, VODE monomer can copolymerize in bulk with vinyl acetate, acrylonitrile, vinyl chloride, vinylidene chloride and styrene at 70 °C in the presence of organic peroxide,[31] but its reactivity ratio of copolymerization with styrene is relatively low, $r_1 = 0.0027$ for VODE and $r_2 = 102.9$ for styrene.[32] Our control polymerization of VODE alone also shows its low reactivity. The presence of emulsion may increase its reactivity, because the VODE in a growing latex particle may have its polymerizable double bonds concentrated near the particle surface. Therefore, in the emulsion copolymerization of VODE, VBC, and DVB, the hydrolysis of VODE takes place because of its low reactivity towards free radical polymerization. The possible concentration of VODE on the particle surface may help the hydrolysis.

The high viscosity of L-1 to L-4 is presumably due to the presence of 1-octadecanol, since non-VODE containing latexes (L-5 to L-7) are normal fluids. Schulman and Cockbain[33] studied the behavior of some emulsions prepared with NUJOL, sodium hexadecyl sulfate (sodium cetyl sulfate) and different alcohols, and found that emulsions prepared with cholesterol, *trans*-9,10-octadecen-1-ol (elaidyl alcohol), and hexadecyl alcohol (cetyl alcohol) were liquid, viscous and grease emulsions respectively. They concluded that the viscosity of the emulsion ranging from grease to low viscosity depends on the state of the interfacial film at the air-water interface, solid, viscous or liquid. Cetyl alcohol forms a solid interfacial film penetrated by cetyl sulfate at the air/water interface. It is also known that cetyl alcohol and many long chain polar compounds form solid films at an air/water interface. 1-Octadecanol could behave the same as cetyl alcohol, since they are all solid fatty alcohols at room temperature. Thus, cationic colloidal particles and 1-octadecanol form solid molecular complexes at the oil/water interface which give a grease-like emulsion, and octadecanol may serve as a cosurfactant to stabilize the latex particles. Some previous work showed that alcohols could disperse and stabilize oil-in-water emulsions.[33-35]

To support this explanation, L-8 was prepared by mixing 98.8 wt % of L-6 with 1.2 wt % of 1-octadecanol, and two octadecanol-CTAB microemulsions were also prepared (µE-1 and µE-2). L-8 and µE-2 were highly viscous as were the VODE latexes, while µE-1 did not appear highly viscous due to low content of alcohol and CTAB. The octadecanol (as a cosurfactant) may form a condensed layer on the surface of the latex particles or swell the latex particles.

Vinyl octadecyl ether and/or its hydrolyzed product, 1-octadecanol, may act as coemulsifiers to stabilize the monomers and polymer emulsions. Previous research showed that the the addition of non-volatile paraffin or long chain fatty alcohol could help the formation of both stable monomer and polymer emulsions.[36,37] Ugelstad and co-workers[38] prepared dispersed styrene microemulsions and polystyrene latexes stabilized by a combination of sodium lauryl sulfate and cetyl alcohol (SLS-CA). They found that the emulsion of styrene monomer with SLS-CA combination was more stable than that with SLS alone, and the particle size of the latex produced decreased with the increasing concentration of the combination emulsifier, but was larger than that with SLS alone. Another finding made by Chou and co-worker[39] was that the styrene emulsion droplets could be stabilized by an adsorbed CTAB-cetyl alcohol complex. These observation might be applicable to our results. Therefore, I conclude that: (1).finely dispersed and narrowly distributed cationic latexes could be prepared with or without VODE in the presence of cetyltrimethylammonium bromide (CTAB); (2). the presence of 1-octadecanol may stabilize the latex particles; and (3). addition of octadecanol to a cationic latex will produce a viscous latex.

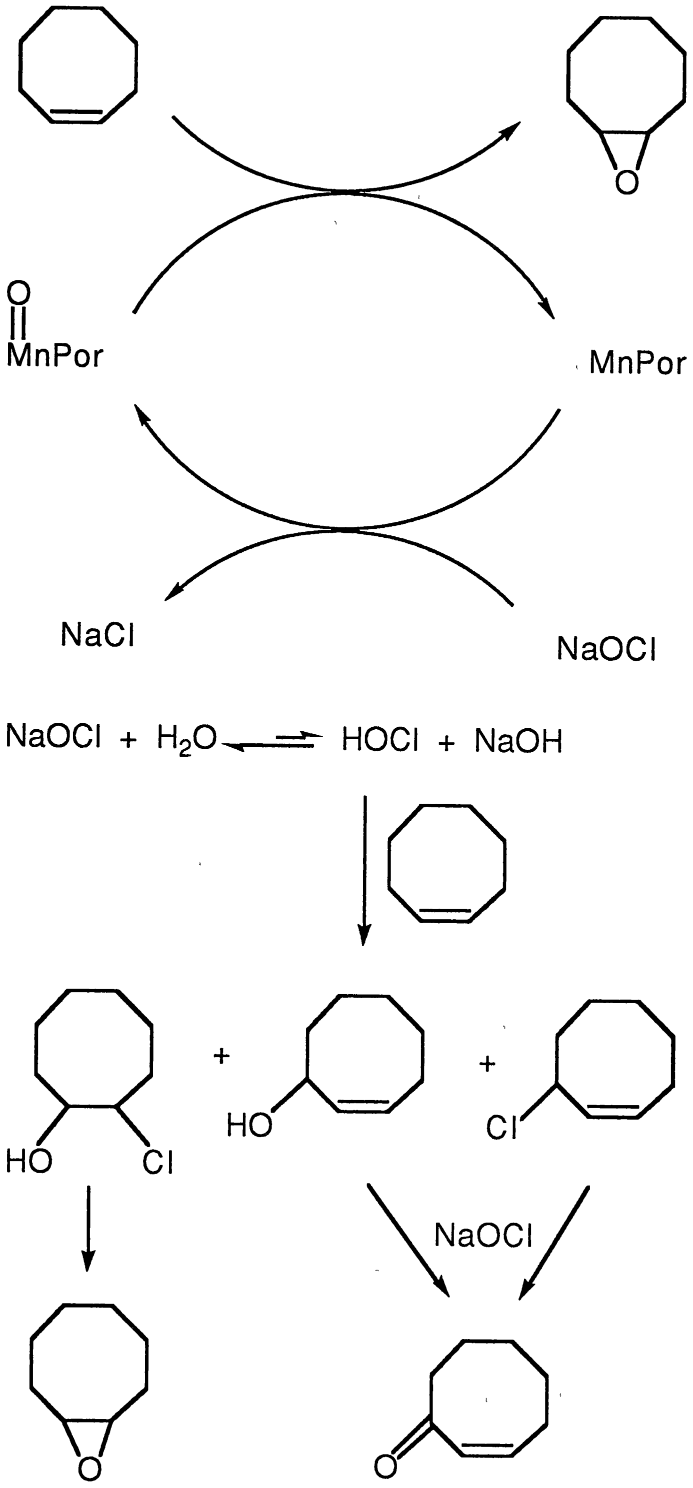
Mechanism of Oxidation by NaOCl and Mn Porphyrin. The oxidation with latex bound Mn porphyrin (MnTSPP) is a triphase reaction: aqueous, latex, and organic phases. The latex phase is likely the reaction site, because all Mn porphyrin is bound to the latex. In the absence of the latex, the oxidation probably occurs in the aqueous phase, and proceeds slowly due to the low solubility of alkenes in water. Meanwhile, the deactivation of porphyrin predominates, since it always competes with the oxidation of the alkene in the aqueous phase. The cationic latex binds ClO^- and MnTSPP, transfers the alkene to the reaction site, and hence accelerates the oxidation.

The reactivity of the oxidation in the presence of latex particles may be related to the effective concentration of reactants in the colloidal particles. This effective concentration could be characterized by the mean volume of emulsion droplets. All of dry latexes in Table II have nearly the same particle diameters and consequently have nearly the same total volumes of the latex phase. Thus, the effective concentration of reactants in the droplets might be the same no matter what latex is used in the oxidation. On the other hand, the particle sizes of these latexes are relatively small, which would have large surface sites to effectively absorb the catalyst and substrate. Therefore, these latexes exhibit almost the same reactivity towards the oxidation.

According to the results on the oxidation of cyclooctene by NaOCl, a possible pathway is suggested to account for these findings (Scheme II). Mn porphyrin coordinates with NaOCl to form an oxo-Mn porphyrin in the presence of latex particles[23] or in the absence of the latex,[10] as shown in Scheme 2. The oxo-Mn porphyrin, the existence of which has been proved by UV spectroscopy in the previous research,[10,23] transfer its oxygen atom to the cyclooctene to form epoxide. On the other hand, aqueous NaOCl is in equilibrium with HOCl in the reaction media (pH 10.3). Because HOCl is more reactive than NaOCl in the organic phase,[5] it can react with cyclooctene, although the concentration of HOCl in the aqueous phase is only 1.7×10^{-3} of that of NaOCl, based on pH 10.3 and pK_a 7.53 for HOCl. This reaction produces 3-cyclooctenone, 3-chlorocyclooctene, and cyclooctene chlorohydrin which may further dehydrochlorinate to form a small amount of cyclooctene oxide as shown in Scheme 3. In the absence of MnTSPP, the aqueous HOCl oxidation is almost the only reaction (Run 1 in Table VI).

With MnTSPP, both epoxidation by NaOCl/Mn porphyrin and HOCl oxidation take place, which results in the epoxide and other oxidation products. Highly basic condition (pH ≥ 13) stops the reactions of HOCl, and hence produce the epoxide only (Run 5).

Scheme II


O
MnPor
MnPor
NaCl
NaOCl
NaOCl + H2O ⇌ HOCl + NaOH
HO
Cl
+
HO
+
Cl
NaOCl
O
O

Conclusion

Finely dispersed cationic polymer latexes can be prepared by emulsion polymerization of vinylbenzyl chloride, divinylbenzene and vinyl octadecyl ether, styrene or *n*-decyl methacrylate in the presence of amidine initiator and CTAB as surfactant, and subsequent quaternization with trimethylamine. These cationic polymer latexes had 44 nm to 71 nm in diameters, with the polydispersity from 1.06 to 1.10. The latexes prepared with vinyl octadecyl ether showed unusually high viscosity due to the presence of octadecanol as a cosurfactant which was generated through the acidic hydrolysis of vinyl octadecyl ether. The polymer latex bound Mn(III) porphyrin system was formed by incorporation of above latexes with tetrasodium 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl) porphinatomanganese (III) chloride. This latex bound porphyrin catalyzed the oxidation of cyclohexene, cyclooctene, allylbenzene, and 1-octene by sodium hypochlorite and potassium peroxymonosulfate. The colloid bound porphyrin catalysts showed higher activity than solution porphyrin. The order of the oxidation power of different oxidants tested is $KHSO_5$ > NaOCl > H_2O_2. Sodium perborate ($NaBO_3$) and sodium periodate ($NaIO_4$) are inactive for the oxidation.

Future work may focus on the investigation of actual reaction sites in the oxidation catalyzed by the latex bound Mn porphyrin. Since the latex bound Mn porphyrin has higher catalytic activity than the Mn porphyrin in solution, it might be worth while to study the interactions between the substrate and the colloidal polymer. It would be of interest to investigate the oxidations catalyzed by other latex bound catalysts, such as metallophthalocyanines, metallosalens, and metallodioxocyclams.

Experimental Section

Instruments. IR spectra were recorded on a Perkin-Elmer 681 instrument. ^{1}H NMR spectra at 300 MHz and ^{13}C NMR spectra at 75.4 MHz were obtained on a Varian XL-300 instrument. GLC analyses were performed on a Hewlett-Packard 5890A gas chromatograph equipped with a DB-1 capillary column from J & W Scientific and a Hewlett-Packard 5840A gas chromatograph equipped with a thermal conductivity detector and a Tenax column from Supelco. The conductivities of aqueous solution were measured with a YSI Model 31 conductivity meter having a cell constant of 1.00 cm^{-1}.

Materials. Styrene (Aldrich), divinylbenzene (DVB, 55% of active DVB, Aldrich) and vinylbenzylchloride (VBC, Scientific Polymer Product, m/p:70/30 based on NMR spectra) were distilled under vacuum and stored under Ar at -17 ^{o}C. *n*-Decyl methacrylate (DMA, Scientific Polymer Product) was passed through an anionic exchange resin column supplied by Scientific Polymer Product to remove the inhibitor. 2,2'-Azobis(N,N'-dimethyleneisobutyramidine)dihydrochloride (Wako), hexadecyltrimethylammonium bromide (CTAB, Fisher), vinyl octadecyl ether (VODE, Polysciences), allylbenzene (Aldrich), cyclooctene (Fluka), cyclohexene (Aldrich), 1-octene (Aldrich), 1-decene (Aldrich), and $KHSO_5$ (Aldrich, available in OXONE form) were used without purification. Clorox bleach was obtained from a local supermarket. The active $KHSO_5$ in OXONE and NaOCl in Clorox bleach were determined by iodometric titration^{40} as 0.739 M of NaOCl and 2.75 mmol of $KHSO_5$ ($KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ = 1.73:1.0:1.34) per gram of OXONE. Tetrasodium manganese tetra(3-sulfonato-2,6-dichlorophenyl)porphyrin chloride (MnTSPP) was kindly supplied by Dr. H. Turk.^{23} The sample had composition of $C_{44}H_{16.9}N_4Cl_{8.85}Mn_{0.85}(SO_3Na)_{3.4}(H_2O)_{12}(NaCl)$, corresponding to 85 % metalation of porphyrin. Glass-distilled water (pH 5.9, conductivity 9.4 x 10^{-7} $ohm^{-1}cm^{-1}$) was used throughout all experiments.

Emulsion Polymerization. Copolymer-1. Into a three neck flask were charged CTAB (0.15 g, 3.0 mol %), deionized water (20 mL), VBC (1.94 g, 12.74 mmol, 93.2 mol %), and DVB (33 mg, 0.25 mmol, 1.8 mol %, 55% active) and VODE (0.20 g, 0.68 mmol, 5.0 mol %). The mixture was heated to 70 °C under Ar before addition of initiator (22 mg, 68.0 mmol, 0.5 mol %), and then mechanically stirred for 20 h at 70 °C under slightly positive pressure of Ar. After polymerization, the white latex was diluted with 20 mL of deionized water, and filtered through cotton to remove some coagulum (< 1.0 g) while the latex was hot. The aqueous dispersion was extracted with methylene chloride (3 x 80 mL) and hexane (3 x 80 mL) to remove possible unreacted monomers, and remaining organic solvents entrapped in the copolymer, along with a small amount of water, were evaporated by a rotary evaporator. The latex is a white, slightly viscous emulsion at room temperature. Total latex volume: 31 mL. Solid content: 6.04%. Yield: 79%.

Copolymer-2. The procedure for copolymer 1 was used except that VBC (1.74 g, 11.34 mmol, 83.2 mol %) and VODE (0.61 g, 2.03 mmol, 15.0 mol %) were used, and polymerization was carried out at 65 °C. The dried organic extract (0.1 g) was 1-octadecanol according to ^{1}H NMR analysis. This latex is a viscous emulsion. Total latex volume: 33 mL. Solid content: 5.45%. Yield: 71%.

Copolymer-3. The procedure for copolymer 2 was used except VBC (1.53 g, 10.0 mmol, 73.2 mol %) and VODE (1.01 g, 3.42 mmol, 25.0 mol %). The dried organic extract (0.41 g) was 1-octadecanol. The latex is white, viscous emulsion. Total latex volume: 34 mL. Solid content: 5.12%. Yield: 64%.

Copolymer-4. The procedure for copolymer 3 was employed except that the quantities of all reagents (monomers, water, surfactant and initiator) were doubled. The dried organic extract was 1.06 g of 1-octadecanol. This latex is also a white, viscous emulsion. Total latex volume: 70 mL. Solid content: 5.51%. Yield: 70%.

Copolymer-5. A mixture of CTAB (0.15 g, 3.0 mol %), deionized water (20 mL), VBC (1.01 g, 6.59 mmol, 48.2 mol %), DVB (32 mg, 0.25 mmol, 1.8 mol %, 55% active) and DMA (1.55 g, 6.84 mmol, 50.0 mol %) was heated to 65 °C under Ar. Upon addition of initiator (22 mg, 68.0 mmol, 0.5 mol %), the mixture was mechanically stirred at 65 °C under the slightly positive pressure of Ar. After 12 h, more initiator (11 mg, 34.0 mmol) was added into the mixture, and the mixture was stirred for another 36 h. Upon cooling to room temperature, the white colloidal copolymer was filtered through cotton to remove coagulum (0.97 g). The resulting latex is a white liquid. Total latex volume: 20 mL. Solid content: 9.50%. Yield: 70%.

Copolymer-6. Solution A: Into a four neck flask were charged CTAB (0.51 g, 1.4 mmol) and deionized water (120 mL), and the solution was heated to 65 °C under Ar. Solution B: A mixture of CTAB (1.31 g, 3.6 mmol), deionized water (30 mL), styrene (15.25 g, 0.15 mol, 73.2 mol %), VBC (7.63 g, 0.05 mol, 25.0 mol %) and DVB (0.47 g, 3.6 mmol, 1.8 mol %, 55% active) was stirred to form a milky white emulsion before transferring into the additional funnel, and the emulsion was stirred by an overhead stirrer during the polymerization. After adding initiator (ADMIBADH, 0.39 g, 1.2 mmol) to solution A, solution B was added dropwise to solution A over 40 min with mechanical stirring under the slightly positive pressure of Ar. The polymerization was continued for 1 h 20 min at 65 °C. Upon cooling to room temperature, the emulsion was filtered through cotton to remove coagulum (< 1 g). This latex is a white fluid. Total latex volume: 170 mL. Solid content: 12.75%. Yield: 85%.

Quaternization of Chloromethyl Sites in the Latexes. L-1. A mixture of deionized water (10 mL), copolymer-1 (10 g, 3.27 mmol of VBC) and 25 wt % aqueous trimethylamine (2.0 mL, 7.87 mmol) was stirred at 40 ^{o}C for 16 h and at 60 ^{o}C for 4 h in a round bottom flask at atomspheric pressure. The latex was purified by ultrafiltration through a 0.1 mm cellulose acetate/nitrate membrane (Millipore) under pressure of 60 psig of nitrogen, rinsing with deionized water (1000 mL in 30 mL portions) for about 5 days. The conductivity decreased from 820 x 10^{-6} ohm^{-1}cm^{-1} of the initial filtrate to 18 x 10^{-6} ohm^{-1}cm^{-1} of the final filtrate. The cationic latex produced is a cream colored emulsion. Total volume of the cationic latex: 42 mL. Solid content: 1.28%.

L-2. The procedure for L-1 was used except for the amount of deionized water (25 mL), copolymer-2 (22 g, 5.54 mmol of VBC) and 25 wt % aqueous trimethylamine (4.8 mL, 18.81 mmol, 3 equiv of VBC content in the copolymer). The same procedure of purification as for L-1 was used. The conductivity of the filtrate decreased from 1200 x 10^{-6} ohm^{-1}cm^{-1} to 32 x 10^{-6} ohm^{-1}cm^{-1}. This cream color latex is viscous. Total volume of the cationic latex: 45 mL. Solid content: 2.45%.

L-3. The procedure for L-1 was used except deionized water (25 mL), copolymer-2 (20 g, 4.40 mmol of VBC) and 25 wt % aqueous trimethylamine (4 mL, 15.78 mmol). The mixture was stirred at 40 ^{o}C for 18 h and at 60 ^{o}C for 6 h. The same procedure of purification as for L-1 was used. The conductivity of the filtrate decreased from 670 x 10^{-6} ohm^{-1}cm^{-1} to 48 x 10^{-6} ohm^{-1}cm^{-1}. The cationic latex is a viscous emulsion. Total volume of the cationic latex: 35 mL. Solid content: 2.70%.

L-4. A mixture of copolymer-4 (35 g, 8.71 mmol of VBC) and 25 wt % trimethylamine (30 mL, 0.12 mol) was stirred in a stainless steel pressure vessel at 60 ^oC (oil bath temperature) for 8 days. Three-forth of the pressure vessel was immersed into the oil bath. The same procedure of purification as for L-1 was used. The conductivity of the filtrate decreased from 1200 x 10^{-1} $ohm^{-1}cm^{-1}$ to a final value of 57 x 10^{-6} $ohm^{-1}cm^{-1}$ (58 x 10^{-6} and 57 x 10^{-6} $ohm^{-1}cm^{-1}$ in the final two collections of the filtrates). The latex is also a viscous emulsion. Total volume of the cationic latex: 47 mL. Solid content: 3.46%.

L-5. The method for L-4 was used except copolymer-5 (20.5 g, 4.62 mmol of VBC) and 25 wt % trimethylamine (17.0 mL, 65.9 mmol). The quaternization was carried out for 4 days at 60 ^oC (oil bath temperature). The 3 day ultrafiltration brought the conductivity of the filtrate from 800 x 10^{-6} to 20 x 10^{-6} $ohm^{-1}cm^{-1}$. This latex is a white liquid. Total volume of the cationic latex: 42 mL. Solid content: 4.28%.

L-6. The method for L-4 was employed except copolymer-6 (34.0 g, 8.48 mmol of VBC) and 25 wt % trimethylamine (13.0 mL, 51.0 mmol). The conductivity of the filtrate decreased from 1100 x 10^{-6} to 30 x 10^{-6} $ohm^{-1}cm^{-1}$ after 3 days. The latex is a pale liquid. Total volume of the cationic latex: 99 mL. Solid content: 4.41%.

L-7. The method for L-6 was used except that the reaction time was extended to 8 days. The conductivity of the filtrate decreased from 1000 x 10^{-6} to 25 x 10^{-6} $ohm^{-1}cm^{-1}$. The appearance of the resultant latex is the same as of L-6. Total volume of the cationic latex: 107 mL. Solid content: 4.03%.

L-8. This latex was prepared by mixing 10.0720 g of L-6 with 0.1208 g of 1-octadecanol at 65 ^oC with stirring. The resulting latex is a white viscous emulsion.

μE-1. This white liquid microemulsion was prepared by mixing of 0.2155 g of 1-octadecanol, 0.0569 g of CTAB and 45 mL deionized water at 65 °C with stirring.

μE-2. This white, viscous microemulsion was prepared by mixing of 0.2705 g of 1-octadecanol, 0.1096 g of CTAB and 9.63 g of deionized water at 65 °C with stirring.

Determination of Particle Sizes of Latexes. TEM micrographs were used to determine the particle sizes of latexes. The samples for TEM were prepared by placing a drop of a diluted latex on a Formvar®-coated Cu grid, and drying in air. Subsequently a drop of 5% solution of uranyl acetate was added on the grid, and the grid was dried in air again. The filament current and accelerating voltage of TEM were 100 mamp and 80 KV respectively. Particles were photographed at 7200-14000 magnification. The diameters of 50 non-aggregated particles from the TEM negative were measured by using an optical microscope equipped with a movable calibrated stage and a 10-fold magnification lens. The number average diameters D_n are reported in Table II.

$D_n = \frac{\Sigma D_i}{50}$, $D_w = \left(\frac{\Sigma D_i^6}{\Sigma D_i^3}\right)^{1/3}$, polydispersity $= \frac{D_w}{D_n}$, D_i is the diameter of each particle, i = 1, 2, 3, ···, 50.

Analysis of L-4. L-4 (30.63 g) was freeze-dried, followed by drying in vacuo at room temperature for 12 h and at 80 °C for 24 h at 10 mmHg, to give 1.0598 g dried solid (solid content of L-4: 3.46 %). The solid was extracted with $CHCl_3$ in a Soxhlet extractor for 2 days, and with acetone for 1 day. After evaporation of the organic solvents of the extract, 0.2724 g of pale solids was obtained which was dried again in vacuo at 40 °C for 24 h, and was analyzed by ^1H NMR to contain 1-octadecanol (0.2155 g, 0.779 mmol, 84 mol %) and CTAB (0.0569 g, 0.156 mmol, 16 mol %). ^1H NMR of 1-octadecanol: δ 3.62 (t, J = 6.8 Hz, 2H), 2.0 (broad, 1H), 1.55 (m, 2H), 1.30 (m, 30H), 0.89 (t, J = 6.5 Hz, 3H, CH_3). ^1H NMR of 1-octadecanol: δ 3.38 (s, 9H), 1.74 (m, 2H), 1.30 (m, 28H), 0.89 (t, J = 6.5Hz, 3H, CH_3). The solid state ^{13}C CP-MAS NMR spectrum of the extracted L-4 showed no peaks for long aliphatic chain. ^{13}C CP-MS NMR (122.8 mg of sample, 9.86 mg of Delrin): δ 42 ($-\underline{C}H_2\underline{C}H-$), 46 ($-\underline{C}H_2Cl$), 55 ($-N^+\underline{C}H_3$), 68 ($-N^+\underline{C}H_2^-$), 132 and 148 (aromatic carbons). ^1H NMR ($CDCl_3$, TMS, the latex particles were partly swollen in $CDCl_3$): δ2.55 ($-C\underline{H}_2C\underline{H}-$, $\Delta\nu_{1/2}$ = 105 Hz), 3.15 ($-N^+C\underline{H}_3$, $-C\underline{H}_2Cl$), 5.80 ($-N^+C\underline{H}_2^-$, $\Delta\nu_{1/2}$=135 Hz), 7.82 (aromatic protons, $\Delta\nu_{1/2}$=190 Hz), 8.46 (aromatic protons, $\Delta\nu_{1/2}$=150 Hz). The proton integration could not be measured accurately because of the breadth of the peaks.

Elemental analysis of the extracted L-4 gave the following result: C: 64.1 %; H: 8.62 %; N: 5.52 %; Cl: 14.82 %, corresponding to the latex composition of $(VTAC)_{78}(VBC)_{20}(DVB)_2$ (VTAC: quaternized site in the latex). The Cl^- selective electrode titration gave 4.09 mequiv/g which corresponds to the structure of $(VTAC)_{82}(VBC)_{16}(DVB)_2$.

Titration of Chloride Ions in the Latexes. The quaternized sites, namely N^+Cl^- units, were determined by titration of the content of chloride ions in the latex with a combination chloride selective electrode (Model 96-17B, Orion) connected to a Zeromatic IV pH/mV meter (Altex).

A sample of latex (1.0 mL) was diluted to a volume of 30 mL with deionized water in a 50 mL beaker. After addition of 0.5 mL of 5 M $NaNO_3$ (as ion strength adjustor) and immersion of the electrode, the aqueous latex was titrated with 0.02010 N standard $AgNO_3$ solution, recording the electrode potential in millivolts. A standard 0.10 N NaCl solution was also titrated for calibration. A plot of the measured potential vs. consumed volume (mL) gave a nearly symmetrical curve in which the end point volume (mL) was taken as the midpoint of the steep increase in potential. The quaternized sites were calculated by the following equation:

$$\text{mmol of } N^+Cl^- \text{ per gram of dried latex} = \frac{0.02010 \text{ x volume of } AgNO_3 \text{ (mL)}}{\text{latex weight x solid content}}$$

The relative error of the titration was 2% (e.g., L-6 had an average value of 1.72 from 1.70 and 1.74 mmol Cl^-/g).

Calculation of Composition of Cationic Latexes. The quaternized site of L-5: Y = 1.90 mmol/g.

Total VBC in the monomer mixture: VBC = 6.59 mmol/2.59 g = 2.54 mmol/g.

Let X be the conversion of VBC units, and W_N be the amount (g) of NMe_3 in the latex after quaternization. Thus, 1 g of dried solids of copolymer-5 will have 1 + W_N (g) after the quaternization. $W_N = \frac{59.11 \text{ x VBC}\cdot\text{X}}{1000}$. Thus,

$1 + W_N = 1 + \frac{59.11 \text{ x VBC}\cdot\text{X}}{1000} = 1 + 0.150X$, where 59.11 is molecular weight of trimethylamine.

$$Y = \frac{\text{VBC.X}}{1 + (59.11 \text{ x VBC}\cdot\text{X}/1000)} = \frac{2.54\cdot X}{1 + 0.150\cdot X}$$

$$X = \frac{Y}{2.54 - 0.150Y}$$

If Y = 1.90 mmol/g, then X = 84.3%; i.e., the conversion of quaternization is 84.3%.

Oxidation of Alkene. Typical Procedure for Oxidation by NaOCl. A mixture of L-3 (0.5 g, 13.5 mg solid, 0.038 mmol N^+ sites) and an aqueous stock solution of 1.607 x 10^{-3} M (MnTSPP, 0.43 mL, 6.91 x 10^{-4} mmol) was stirred for several minutes at room temperature (23 °C). After addition of cyclooctene (46 μL, 0.35 mmol) and argon-purged Clorox bleach solution (0.71 mL, 0.52 mmol of NaOCl), the mixture was magnetically stirred at 40 °C for 5 h. Upon cooling to room temperature, the mixture was extracted with ethyl ether for 5-7 times (total ether volume: 8-10 mL), and the ether extract was analyzed by GLC with octane as an internal standard. Response factors for cyclooctene and cyclooctene oxide were 1.031 and 1.125 respectively. Recoveries were from 75% to 95%.

Typical Procedure for Oxidation by $KHSO_5$. A mixture of 0.5 g of L-3 (13.5 mg solid, 0.038 mmol N^+ sites), 0.43 mL of 1.607×10^{-3} M of MnTSPP solution (6.91×10^{-4} mmol) and 1 mL of water was stirred for several minutes at 23 °C. After addition of cyclooctene (46 μL, 0.35 mmol) and $KHSO_5$ solution (0.72 mL, 0.44 mmol), the mixture was stirred at 23 °C for 5 h. The procedures to separate and analyze products were the same as those for NaOCl epoxidations.

Th oxidation products were identified by GC-MS, and compared with authentic samples and standard spectra. The GC conditions for alkenes and oxidation products are in Table VIII.

GC-MS results are listed below.

Cyclohexene oxide: m/e 98 (7), 97 (13, -H), 83 (100, -H, $-CH_2$), 69 (44), 54 (82, $-CH_2CH_2CO$).

trans-2-Chlorocyclohexanol: m/e 134 (3), 98 (6, -HCl), 81 (19), 80 (20, -HCl, $-H_2O$), 57 (100, -HCl, $-H_2O$, $-CHCH_2$).

1,2-Cyclohexanediol: m/e 116 (4), 98(12, $-H_2O$), 83 (22), 70 (100, $-H_2O$, -CO), 57 (68, $-CH_2CH_2CH_2OH$).

Cyclooctene oxide: m/e 126 (7), 98 (28, $-CH_2CH_2$), 97 (33, -CHO), 83 (42, $-CH_2CHO$), 67 (68), 55 [100, -H, $-(CH_2)_5$].

3-Chlorocyclooctene: m/e 144 (12), 116 (23, $-CH_2CH_2$), 109 (22, -Cl), 81 (36), 80 (37), 79 (43), 67 (100, -Cl, $-CH_2CH_2CH_2$), 54 [39, -HCl, $-(CH_2)_4$].

3-Cyclooctenone: m/e 124 (64), 95 (37, -CHO), 81 (44, -CHO, $-CH_2$), 80 (100, -CHCHCO), 67 (64), 55 (62).

2-Chlorocyclooctanol: m/e 144 (6, -H_2O), 126 (6, -HCl), 116 (21, -H_2O, -CH_2CH_2), 109 (23, -OH, -HCl), 98 (33, -HCl, -CH_2CH_2), 81 (47), 82 (100), 67 (84), 57 (92). The molecular ion (M^+) could be detected due to the loss of water.

1,2-Epoxy-3-phenylpropane: m/e 134 (17), 104 (52, -H_2CO), 91 (100, -$CHCH_2O$), 78 (46), 65 (29), 51 (50).

1-Chloro-3-phenylpropan-2-ol: m/e 170 (4), 121 (8, -CH_2Cl), 103 (14, -CH_2Cl, -H_2O), 92 (59, -$ClCH_2CHO$), 91 (100, -$CHOHClCH_2$), 65 (34).

1,2-Dichloro-3-phenylpropane: m/e 188 (3), 115 (13, -2HCl, -H), 91 (100, -$CHClCH_2Cl$), 77 (12), 65 (22), 51 (21).

3-Phenyl-1,2-propanediol: m/e 134 (18, -H_2O), 117 (25, -H_2O, -OH), 103 (31, -H_2O, -CH_2OH), 91 (100, -$CHOHCH_2OH$), 77 (39, -$CH_2CHOHCH_2OH$), 65 (23), 51 (32). The molecular ion (M^+) could be detected due to the loss of water.

1,2-Epoxyoctane: m/e 110 (47, -H_2O), 81 (70, -CH_2CH_3), 70 (73, -$CH_2CH_2CH_2CH_2$), 67 (88, -H_2O, -$CH_2CH_2CH_3$), 54 (100, -O, -$CH_2CH_2CH_2CH_2$). The molecular ion (M^+) could be detected due to the loss of water.

1-Chloro-2-octanol: m/e 128 (2, -HCl), 115 (30, -CH_2Cl), 97 (100, -CH_2Cl, -H_2O), 69 (26), 55 (77). The molecular ion (M^+) could be detected due to the loss of HCl.

1,2-Octanediol: m/e 110 (22, -H_2O), 95 (45, -H_2O, -CH_3), 81 (100, -H_2O, -CH_2CH_3), 70 (69), 55 (93). The molecular ion (M^+) could be detected due to the loss of water.

Table VIII. GC Conditions for Alkenes and Oxidation Products[a]

GC conditions	cyclohexene oxidation	cyclooctene oxidation	allylbenzene oxidation	1-octene oxidation
initial, temp, °C	35	60	100	60
time 1, min	3	1.5	3	3
rate, °C/min	5	20	5	10
final temp, °C	90	100	250	250
time 2, min	1	1	1	1
rate A, °C/min	1	5	-	-
final temp A, °C	100	250	-	-
time A, min	1	1	-	-

[a] Injection temperature: 250 °C, TCD temperature: 300 °C, helium gas flow rate: 40 mL/min.

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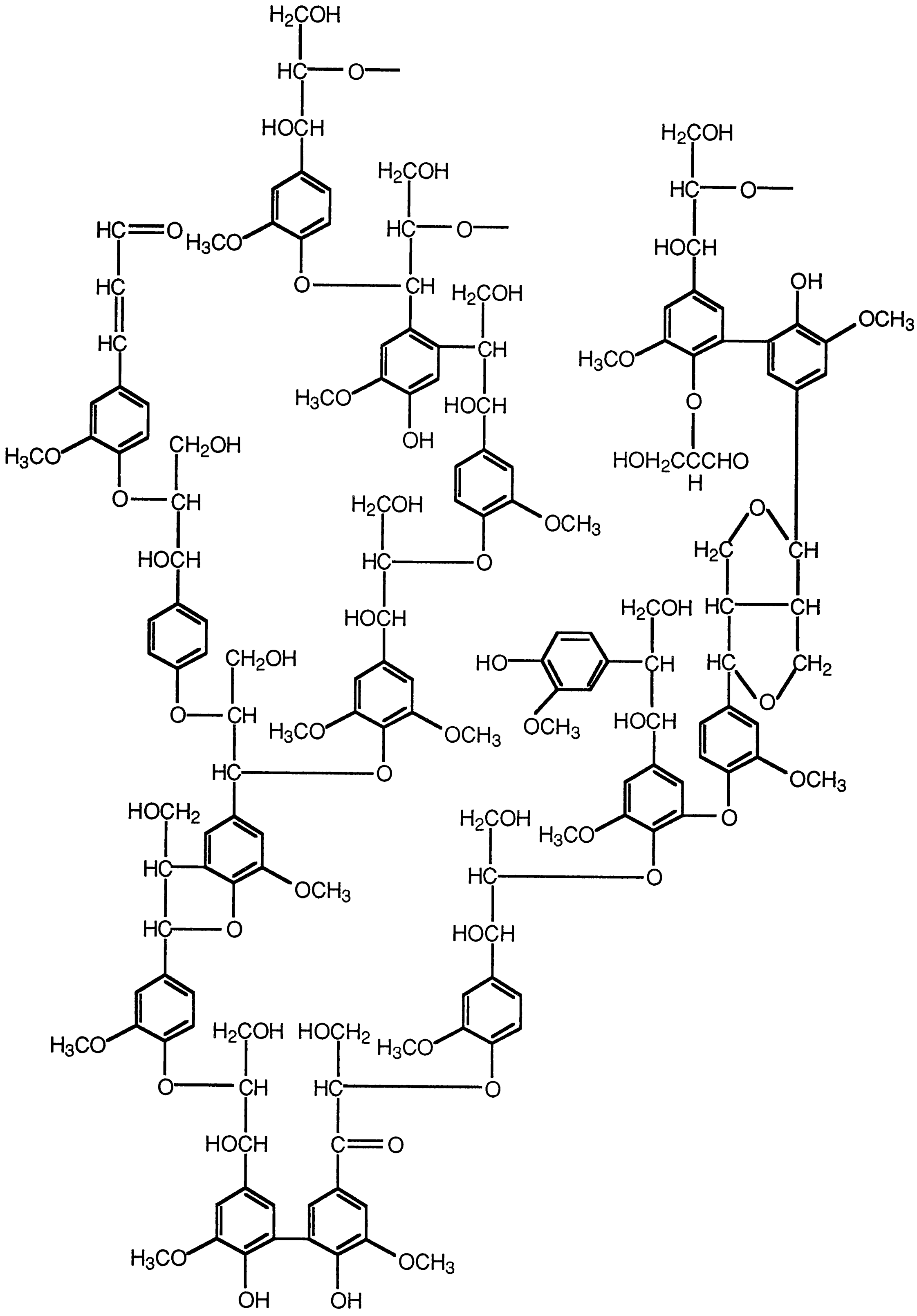
CHAPTER III

OXIDATION OF LIGNIN MODEL COMPOUNDS WITH METALLOPORPHYRINS AND METALLOPHTHALOCYANINES AND CATIONIC LATEXES

Introduction

Paper is formed as a felted sheet of fibers on a fine screen from a water suspension. In the papermaking industry, wood is by far the most important source of fibers. Wood usually consists of cellulose (45%), hemicellulose (25-35%), lignin (21-25%), and extractives (fatty acids, resin acids, etc, 2-8%).[1] Cellulose determines the character of the fiber and permits its use in papermaking. Cellulosic fibers have high tensile strength, flexibility, conformability, resistance to plastic deformation, water insolubility, hydrophilicity, wide range of dimensions, inherent bonding ability, ability to absorb modifying additives, chemical stability, and white color, which are needed for paper. In general, the best papermaking properties can be reached when the lignin is removed from the fibers while retaining substantial amounts of hemicellulose.

Lignin is an amorphous, crosslinked biopolymer. Its principal role is to form the middle lamella which links the fibers together. The structure of lignin is very complex, and has not been determined, because the native (or unaltered) lignin has not been isolated. This means that the lignin structure changes easily during the isolation from wood. The structure of lignin also depends on the type of wood. The following is a structural illustration of the lignin in spruce wood:[2,3]

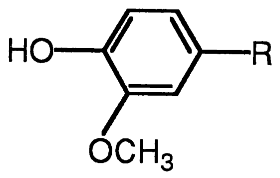

H₂COH
HC—O—
HOCH
H₃CO
HC=O
HC
HC
OH
OCH₃
H₃CO
HOH₂CCCHO
H
CH₂OH
O—CH
HOCH
H₂C
CH
HC—CH
HC
CH₂
HO
OCH₃
O
HOCH₂
HC
C=O

The structure consists primarily of phenyl propane units linked together in three dimensions. The linkages between the propane side chains and the benzene rings are broken during chemical pulping processes that liberate the cellulosic fibers.

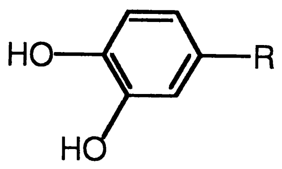
Pulping is the process by which wood (or wood chips) is transformed to a fibrous mass. This process can be accomplished mechanically, thermally, chemically, or by combinations of these treatments.[1] Chemical pulping is a major process used worldwide, and it uses chemical reactions to delignify wood. The objective of chemical pulping is to degrade and dissolve away the lignin and leave behind most of the cellulose and hemicellulose, since the properties of fibers will be improved after removal of the lignin. Chemical pulping processes can remove most of the lignin in wood, but also degrade a certain amount of the cellulose and hemicellulose so that the yield of pulp is low relative to mechanical pulping.

There are two major chemical pulping methods: the kraft process and the sulfite process. The kraft process involves cooking the wood chips in a solution of NaOH and Na_2S. This process produces strong paper product, but also leaves dark-brown unbleached pulp. The kraft process is also associated with the formation of organic sulfides which cause environmental concern. The residual lignin can be removed from the pulp through further reaction using chlorine bleach, and of course this reaction generates pollutants too. The sulfite process uses a mixture of sulfurous acid and bisulfite ion to attack and solublilize the lignin under acidic conditions (pH 1-2). This process removes the lignin more efficiently than the kraft process. However the sulfite process randomly hydrolyzes the cellulose and hemicellulose due to its high acidity, so that the paper strength is relatively low.

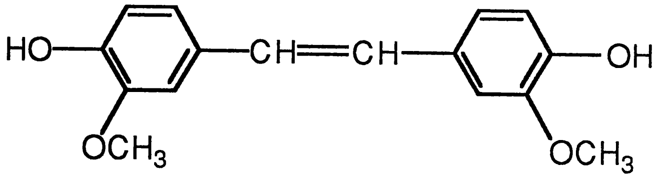
The mechanisms of chemical pulping process are not fully understood. In the sulfite pulping, one possible mechanism is the initial sulfonation of the α-C atom of phenolic and nonphenolic units, followed by cleavage of β-aryl ether bonds through elimination of the α-sulfonic acid group.[2,3] The kraft pulping might involve the alkaline cleavage of α-aryl ether bond in phenolic arylpropane units and cleavage of β-aryl ether bonds in nonphenolic lignin units.[2,3] Chemical pulping processes lead to several small molecules, including those shown below:



R = $COCH_2CH_3$, CHO, $COCH_3$, COOH,
CH_2COOH, CH_2CH_2OH, $CH_2CH_2CH_2OH$



R = CHO, $COCH_3$



Although chemical pulping is the most useful process currently, it still has some practical disadvantages as mentioned above. Therefore, the ideal chemical pulping and subsequent bleaching processes will be sulfur free, effective to remove the lignin to zero or very low content, neither strongly acidic nor strongly basic (pH 3-9), autoxidative (oxygen as the oxidant), and effective in water.

Many efforts have been made to develop an efficient pulping process. To achieve this purpose, powerful lignin degraders must be obtained. In nature, white rot fungi are found to be among the best lignin degraders.[4-8] Studies indicate that two types of extracellular heme-containing enzymes in fungi are responsible for lignin degradation.[9-13] These enzymes include a group of lignin peroxidases and a group of manganese peroxidases. However, the practical use of lignin peroxidases for the pulping process is unlikely because biosynthesis of lignin peroxidases has been be achieved only under certain conditions and the peroxidases are difficult to obtain in large quantity. Thus, scientists turn to synthesize chemical models of these lignin peroxidases.[14-18] Many of the lignin peroxidase models are metalloporphyrins and oxygen donors.[17-19] There are reports of using metallophthalocyanines (Pcs) as lignin peroxidase models, but Pcs are usually less active than porphyrins.[11] Our objective of this research is to test the oxidative catalytic activity of metalloporphyrins and metallophthalocyanines, to explore cheap oxidants (ideally dioxygen as an oxidant), and finally to develop efficient catalysts for the practical delignification of wood chips.

In order to understand the chemistry of both lignin and delignification, lignin model compounds have been used.[14-23] Model compounds are usually phenolic derivatives, substituted benzyl alcohols, and substituted benzenes or biphenyls. In this research, three model compounds, 3,4-dimethoxybenzyl alcohol (veratryl alcohol, **1**), 4-hydroxy-3-methoxytoluene (**3**), and 3,4-dimethoxytoluene (**8**) were used, because their structures resemble those repeating units of spruce lignin. The oxidations of these three model compounds with metalloporphyrins and metallophthalocyanines as catalysts were investigated under different conditions.

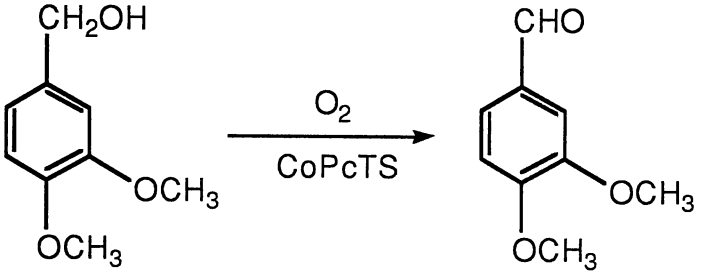
Results

Oxidation of Model Compounds by Dioxygen (O_2).

Oxidation by dioxygen was conducted in a three neck flask with a condenser to which the oxygen inlet was connected, water-soluble metallophthalocyanines, and fast stirring (1800 rpm) in place of the gas buret system. The oxygen gas pressure was kept slightly positive in the system so that the amount of oxygen was constant throughout the reaction. Several factors controlling the autoxidation were investigated: (1) catalyst structure, (2) pH, (3) temperature and time, (4) reactivity of different substrates.

Most experiments were performed using **1**, since this compound has been used before as a lignin model compound to investigate the effectiveness of oxidation methods with transition metal catalysts.[14,18,19]

Autoxidation of DMBA (1) with Different Catalysts. Autoxidations were carried out with different metalloporphyrins and metallophthalocyanines to test their catalytic activities. The reaction proceeded as shown in eq 1. Results in Table I showed that the only oxidation product was 3,4-dimethoxybenzaldehyde (**2**). Only CoPcTS is active for the autoxidation of **1**, and other Pcs and porphyrins are inactive. At pH 11 and 85°C, 76% of the aldehyde was formed in 5 h. No reaction occurred in the absence of CoPcTS or in the absence of both latex and CoPcTS (runs 9 and 10). Thus, the CoPcTS is essential to the autoxidation.



1 **2** (1)

Most of the oxidations were carried out in the presence of the cationic latex. Previous research in our group showed that the cationic latex could accelerate CoPc autoxidations of thiol and phenol derivatives.[24,25] In this research, however, the presence of cationic latex particles failed to increase the reaction rate.

All metal catalysts appeared to be stable during the autoxidation, since the colors of the catalysts remained unchanged after the reaction. With stronger oxidants such as NaOCl, the color of Mn porphyrin often is bleached during the oxidation.[26]

Table I. Autoxidation Activity of Different Catalysts[a]

run	catalyst	latex	**2**, %
1	CoPcTS	L-4	76
2	CoPcTS	-	78
3[b]	FePcTS	L-4	1
4	FePcTS	L-4	< 1
5	CuPcTS	L-4	< 1
6	NiPcTS	L-4	< 1
7	FeTCPP	L-4	< 1
8	MnTSPP	L-4	< 1
9	-	L-4	0
10	-	-	0

[a] Experiments were carried out using 14 mg of L-4, 0.35 mmol of **1**, 10.5 μmol of catalyst, and oxygen gas in 4.25 mL of aqueous phase at 85 °C for 5 h. The aqueous phase was buffered to pH 11 with 0.39 M carbonate/bicarbonate buffer.

[b] This reaction was performed without control of pH which decreased from 6.65 to 6.02.

The Effect of pH on the Autoxidation of 1. The success of using CoPsTS to catalyze the autoxidation of **1** led us to examine the effect of pH on the reaction, since in the absence of the buffer solution, a decrease of pH was observed during the autoxidation by CoPcTS/O_2. Data in Table II indicated that pH had significant influence on the autoxidation. Under slightly basic conditions (pH 11), all starting alcohol was converted to aldehyde after stirring for 12 h at 85°C. At pH 8.0, the reaction rate decreased drastically, and at pH ≤ 5.0, no autoxidation took place.

Table II. The Effect of pH on the Autoxidation[a]

run	buffer	pH	**2**, %
1	0.29 M citrate	3.0	< 1
2	0.31 M citrate	5.0	< 1
3	0.12 M phosphate	8.0	18
4	0.31 M carbonate/bicarbonate	10.0	84
5	0.39 M carbonate/bicarbonate	11.0	100
6[b]	0.39 M carbonate/bicarbonate	11.0	76

[a] Reactions were carried out using 14 mg of L-4, 0.35 mmol of **1**, and 10.5 μmol of CoPcTS (3 mol % of the substrate), and oxygen gas in 4.25 mL of aqueous phase at 85 °C for 12 h. pH was measured at 23 °C.

[b] 5 h reaction time.

Several reactions were performed using CoPcTS as the catalyst. The increase of reaction time from 16 h to 48 h had little effect on the yield (Table III). However, the pH of the system decreased gradually during the reaction, which may be responsible for the low yield of the product.

Table III. The Effect of Reaction Time on the Autoxidation of 1[a]

time, h	initial pH	final pH	**2**, %
16	9.60	7.40	15
30	9.60	6.62	17
48	9.60	6.62	18

[a] Reactions were carried out using 20 mg of L-7, 0.35 mmol of **1**, 0.0035 mmol of CoPcTS (1 mol % of the substrate), and oxygen gas in 4.25 mL of aqueous phase at 70 ^oC.

As shown in Table IV, the yield of 3,4-dimethoxybenzaldehyde almost doubled with an increase of 15 ^oC in reaction temperature. On the other hand, higher concentration of CoPcTS did not appreciably raise the product yield. Without control of pH of the reaction, 29% of **1** was converted by using CoPcTS/O_2, while the reaction buffered at pH 11 gave 100% conversion of **1**.

Table IV. Autoxidation of 1 in Unbuffered Media[a]

run	CoPcTS µmol	temperature °C	time h	initial pH	final pH	**2** %
1	3.5	70	16	9.60	7.40	15
2[b]	10.5	70	12	9.80	8.22	16
3[b]	10.5	85	12	9.80	8.12	29
4[c]	0	70	16	5.50	5.70	0

[a] Reactions were performed using 20 mg of L-7, 0.35 mmol of **1**, and oxygen gas in 4.25 mL of aqueous phase.

[b] 14 mg of L-4 was used in place of L-7.

[c] No latex was used.

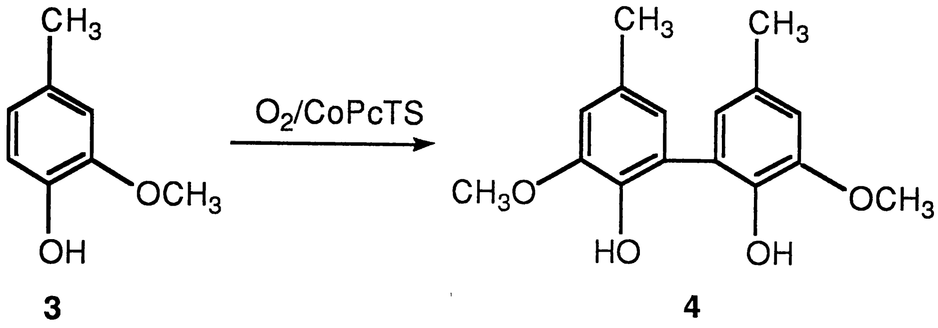
At pH 11, the addition of H_2O_2 into the reaction system decreased the autoxidation rate, but in the absence of O_2, H_2O_2 also oxidized **1** to produce **2** in the lower yield than the autoxidation (Table V). Upon addition of H_2O_2, the formation of bubbles (presumably O_2) was observed.

Table V. The Effect of the Addition of H_2O_2 on the Autoxidation[a]

run	H_2O_2, mmol	O_2	**2**, %
1	0.39	no	49
2	0.39	yes	70
3	no	yes	76

[a] Reactions were carried out using 14 mg of L-4, 0.35 mmol of **1**, and 10.5 µmol of CoPcTS (3 mol % of the substrate) in 4.25 mL of aqueous phase at 85 °C for 5 h. The aqueous phase was buffered to pH 11 with 0.39 M carbonate/bicarbonate buffer.

The Reactivity of Different Model Compounds Towards Autoxidation. The same conditions used for autoxidation of **1** were employed to oxidize 4-hydroxy-3-methoxytoluene (**3**) and 3,4-dimethoxytoluene (**8**) (Table VI). The autoxidation of **3** produced one major product, 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl (**4**, 32%), at 100% conversion (eq 2). Bisphenol **4** was identified by both ^1H and ^{13}C NMR. The other products could not be identified because ^1H NMR results of these products were fairly complicated and hence not informative. Compound **8** failed to react under both acidic and basic conditions (pH 3.0 and 11.0). Autoxidation of three model compounds with CoPcTS showed the following reactivity order: **3** > **1** > **8**. Without control of pH, 48% of **3** was converted after stirring for 12h at 70 °C (run 5). This conversion is higher than that of **1** autoxidation (15%, Table III). At 85 °C **1** and **3** are soluble in water, but **8** is not completely soluble in water.



(2)

Table VI. Autoxidation of 3 and 8[a]

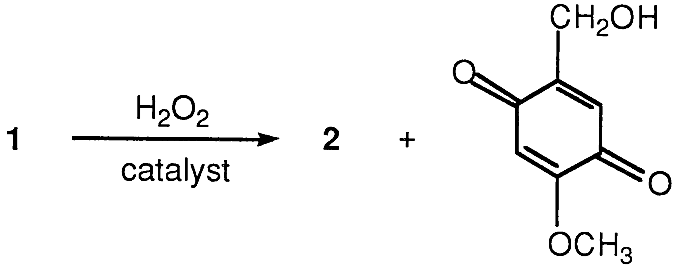
substrate	initial pH	final pH	conversion, %
3	11.0	10.9	100
3[b]	9.60	3.93	48
1	11.0	11.0	76
8	11.0	11.0	0
8	3.0	3.0	0

[a] Reaction conditions were the same as in Table I except that 10.5 μmol of CoPcTS was used.

[b] The reaction was done at 70 °C for 12 h.

Oxidation of Model Compounds by H_2O_2

Oxidation of 1 with Different Metalloporphyrins and Metallophthalocyanines. A number of oxidations to examine the catalytic activity were carried out at room temperature and at 70 °C (Tables VII and VIII). Both low and high temperature reactions showed that the iron phthalocyanine (FePcTS) has the highest catalytic activity. Iron porphyrin was more active than manganese porphyrin, which is predictable according to the literature report.[19] High temperature reactions gave higher conversion of the oxidation than room temperature reactions. However, the reaction temperature (25-70 °C) and the catalyst concentration (0.1-1.0%) did not affect the catalytic activity of MnTSPP towards the oxidation. Without the catalyst, < 1% of **1** was converted in 24 h at 25 °C. Therefore, a metal complex catalyst is essential for the oxidation. H_2O_2 oxidation of **1** resulted in two major products (**2** and **5**) as indicated in eq 3.



5

(3)

FePcTS appeared to be stable at 25 °C but unstable at 70 °C by monitoring the color change of the catalyst. H_2O_2 oxidized the substrate but also underwent decomposition during the reaction. In the case of the oxidation with FePcTS, 75.1% of the original amount of H_2O_2 was detected by iodometric titration after 1 h with 9% conversion of the substrate, corresponding to 22.3% of H_2O_2 decomposed.

Table VII. Oxidation of 1 with H_2O_2 at 25 °C[a]

catalyst	mol % of catalyst vs. substrate	initial pH	final pH	**1** mol %	**2** mol %	**5** mol %
MnTSPP	0.1	5.35	4.12	99	1	
CoPcTS	1.0	7.27	5.05	98	2	
FePcTS	1.0	4.75	3.30	92	5	3
-	-	5.15	5.15	100		
-	-	5.15	5.17	> 99[b]	< 1	

[a] Reactions were carried out using 20 mg of L-7, 0.35 mmol of **1** and 1.74 mmol of H_2O_2 in 4.25 mL of aqueous phase at 25 °C for 1 h.

[b] 24 h reaction time.

Table VIII. Oxidation of 1 with H_2O_2 at 70 °C[a]

catalyst	initial pH	final pH	**1** mol %	**2** mol %	**5** mol %
MnTSPP	5.35	4.11	99	1	
FeTCPP	7.50	4.70	96	2	2
NiPcTS[b]	4.70	3.75	99	1	
CoPcTS	7.27	4.15	96	2	2
CuPcTS[b]	5.70	3.15	94	3	3
FePcTS[c]	4.75	2.69	73	11	12

[a] Reactions were carried out using 0.35 mmol of **1**, 1.74 mmol of H_2O_2, and 3.5 μmol of catalyst in 4.25 mL of aqueous phase at 70 °C for 1 h.

[b] 3.5 mmol of **1**, 17.4 mmol of H_2O_2, and 0.035 mmol of catalyst were used.

[c] 15 min reaction time.

The Effect of Time and Temperature on the Oxidation. Since FePcTS has the highest activity, the factors of time and temperature were examined with FePcTS catalyzed oxidation. Data in Fig 1 indicated that 59% of the conversion took place in the first 5 h. More aldehyde **2** and quinone **5** were produced as the reaction proceeded, while the yield of **5** increased faster than that of **2**.

Temperature also affected the conversion of the reaction (Table IX). The oxidation at room temperature was relatively slow. The reaction rate increased more than 3.4 times with the increase of the temperature from 25 °C to 40 °C.

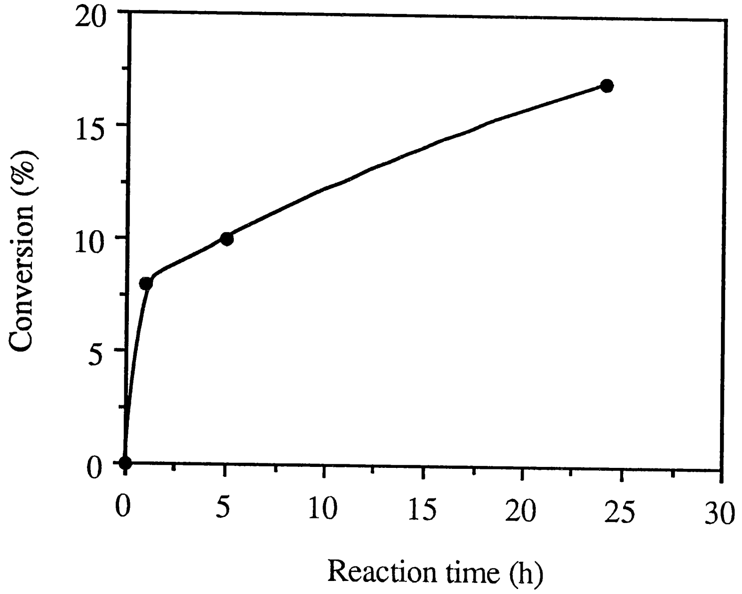


Figure 1. Influence of reaction time on the conversion of the oxidation. Conditions were the same as in Table VII.

Table IX. The Effect of Temperature on the Oxidation of 1[a]

latex (mg)	temp °C	initial pH	final pH	conv %	**2**, %	**5**, %
L-7 (20)	21	4.75	3.30	8	5	3
-	25	4.75	3.45	9	5	4
L-7 (20)	40	4.75	3.30	31	4	3
-	70[b]	4.75	2.69	27	11	12
-	85[b]	4.75	2.61	69	5	12

[a] For conditions see Table VII unless noted otherwise.

[b] 15 min reaction time.

pH Influence on the Oxidation. In the absence of buffer solution, we found a decrease of pH during the H_2O_2 oxidations no matter what catalyst was used. Investigation of pH influence was performed on the oxidation catalyzed by FePcTS at 4 different pH values (3.0, 5.0, 7.0, and 9.1), and results are reported in Table X. Low pH gave the highest conversion. Under the neutral or basic condition, no quinone product was formed. By comparison with unbuffered oxidations, buffers seemed to have little effect on the conversion of the oxidations.

Cationic latex had little influence on the oxidation. Potassium hydrogen phthalate buffer solutions coagulated the cationic latex, while citrate buffer did not.

Table X. pH Influence on the Oxidation of 1 Catalyzed by FePcTS[a]

buffer	pH	conv %	**2**, %	**5**, %
0.60 M citrate	3.0	13	2	11
0.31 M hydrogen phthalate	3.0[b]	7	4	3
0.60 M citrate	5.0	2	2	
0.32 M hydrogen phthalate	5.0[b]	5	4	1
0.20 M phosphate	7.0	3	3	
0.40 M bicarbonate	9.1	2	2	

[a] Reaction conditions were the same as in Table VII unless noted otherwise.

[b] The experiment was done for 5 h in the absence of latex.

The Effect of FePcTS Concentration on the Oxidation. The above results indicated that FePcTS catalyzed both oxidation and decomposition of H_2O_2. FePcTS could be deactivated by forming μ-oxodimer or by oxidative degradation with H_2O_2. Since the FePcTS color faded during the reactions, there must be degradation of the Pc ring. Results in Table XI show that the concentration of the catalyst from 3.5 μmol (1 mol %) to 17.5 μmol (5 mol %) had nearly no effect on the oxidation. The oxidations of **1** gave **2**, **5**, and other unidentified products that had complicated and uninformative ^{1}H NMR spectra.

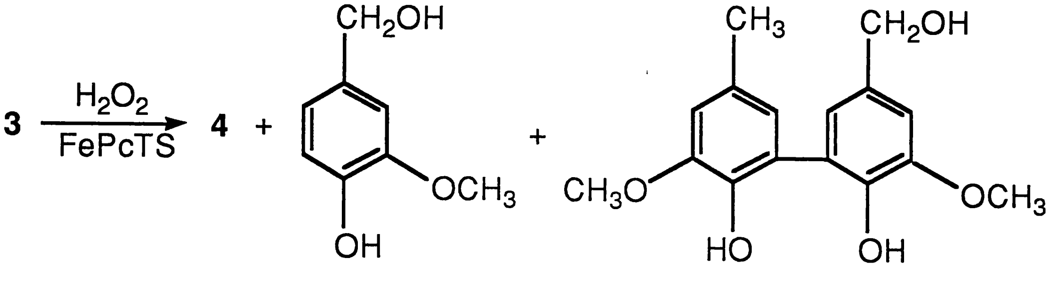
At 85 ^oC, H_2O_2 did not decompose in the absence of FePcTS, while 42% of the original amount of H_2O_2 decomposed in 15 minutes in the presence of 3.5 μmol of FePcTS.

Table XI. The Effect of FePcTS Concentration on the Oxidation of 1[a]

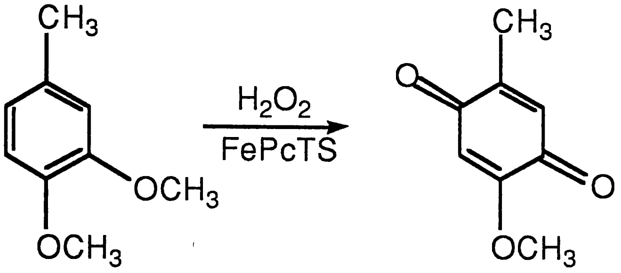
FePcTS, μmol	initial pH	final pH	conv, %	**2**, %	**5**, %
none	5.05	3.92	0		
3.5 (1)	4.75	2.61	69	5	12
10.5 (3)	4.82	2.70	70	6	9
17.5 (5)	4.95	2.81	71	6	9

[a] Reactions were carried out using 0.35 mmol of **1** and 2.8 mmol of H_2O_2 in 4.25 mL of aqueous phase at 85 ^oC for 15 min.

H_2O_2 Oxidation of 3 and 8. Catalytic oxidation of 4-hydroxy-3-methoxytoluene (**3**) and 3, 4-dimethoxytoluene (**8**) was carried out under the conditions used for DMBA oxidation (eqs 4 and 5). Compound **3** was oxidized easily to three major products, 4-hydroxy-3-methoxy-benzyl alcohol (**6**, 19%), 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl (**4**, 69%), and 4-hydroxy-3-[2-hydroxy-3-methoxy-5-methylphenyl]-5-methoxybenzyl alcohol (**7**, 12%). Oxidation of **8** gave only one major product, 2-methoxy-5-methyl-1,4-benzequinone (**9**, 4%) (Table XII). A decrease of pH during both oxidations was also observed. In contrast to autoxidation, reactivities under FePcTS/H_2O_2 oxidative conditions were: **3** > **1** > **8**.



6 **7** (4)



8 **9** (5)

Table XII. Oxidations with FePcTS/H_2O_2[a]

run	substrate	initial pH	final pH	conv %
1	**3**	4.75	3.80	96
2	**1**	4.75	2.69	27
3	**8**	4.75	2.88	10

[a] Experiments were carried out using 0.35 mmol of substrate and 3.5 μmol of FePcTS (1 mol % based on the substrate) in 4.25 mL of aqueous phase at 70 °C for 15 min.

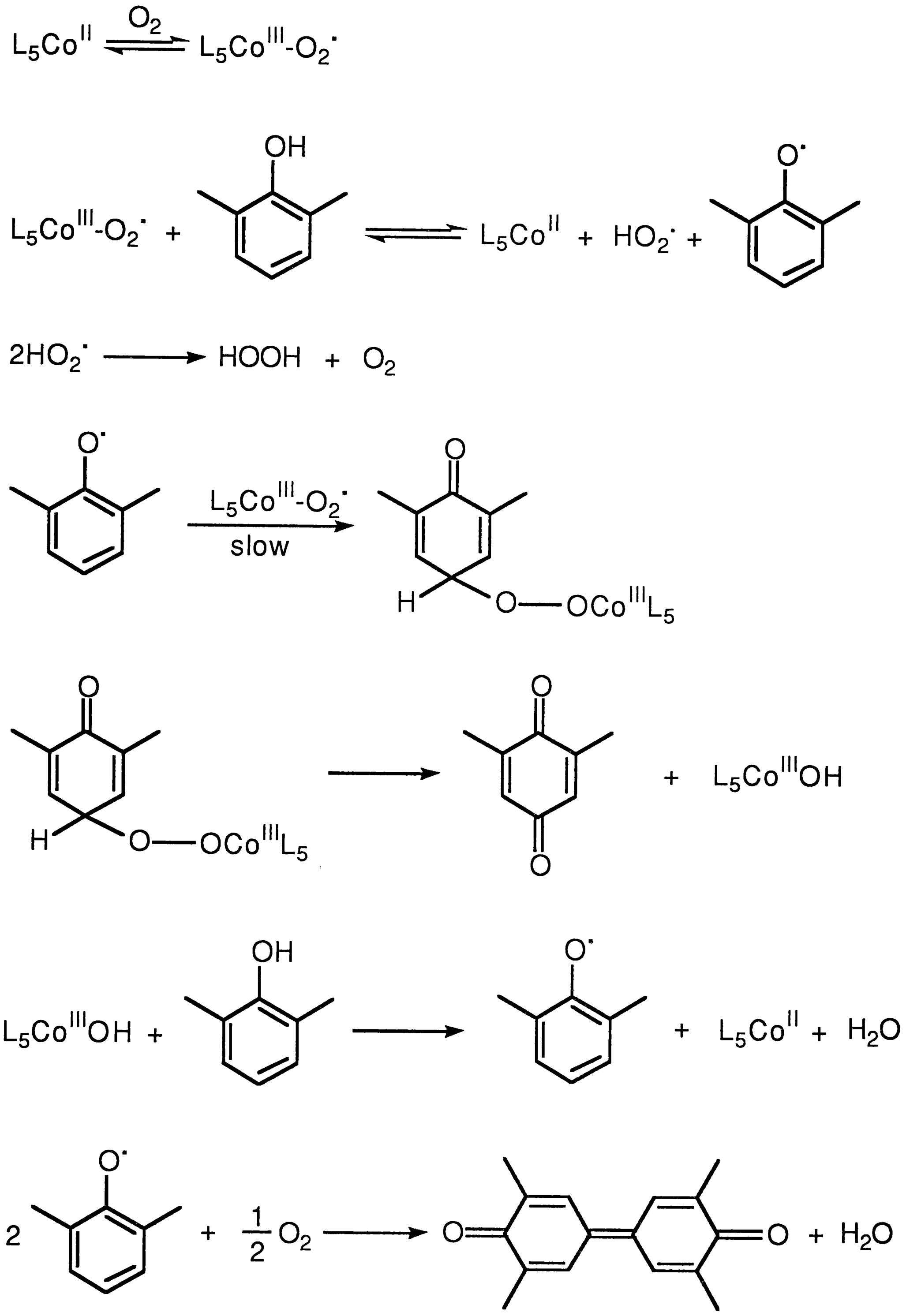
Discussion

Autoxidation of Lignin Model Compounds. The CoPcTS/O_2 system is active for autoxidations of **1** and **3** in basic solutions. Cationic latex particles failed to increase the rate of the oxidation of **1**. One possible explanation is that the autoxidation in aqueous phase might be sufficiently fast since **1** is soluble in water, and the enhancement of the reaction rate by latex particles could be achieved. The role of latex particles in a reaction is to concentrate the reactant and the catalyst, and hence to accelerate the reaction, provided that the reactant has low reactivity in the reaction media without the latex.

Autoxidation of **1** catalyzed by Co(II) complexes has not been reported, while that of phenols has been studied for many years.[27-38] The Co(II)-catalyzed autoxidations of phenols have several characteristics: (1) The two most common products are alkylbenzoquinone and alkyldiphenoquinone, and high temperature favors the formation of diphenoquinone. (2) A solvent having good coordinating ability helps the autoxidation. (3) Electron donating groups on the phenol accelerate the reaction. (4) Steric effects of substituents on the phenol are insignificant. (5) The rate of oxidation is first order in the concentration of the substrate. Thus, mechanisms for the autoxidation were proposed by several groups.[31-34]

The mechanism of Drago and co-workers,[34] based on their experimental observations and the modification of previous mechanisms is shown in Scheme I.

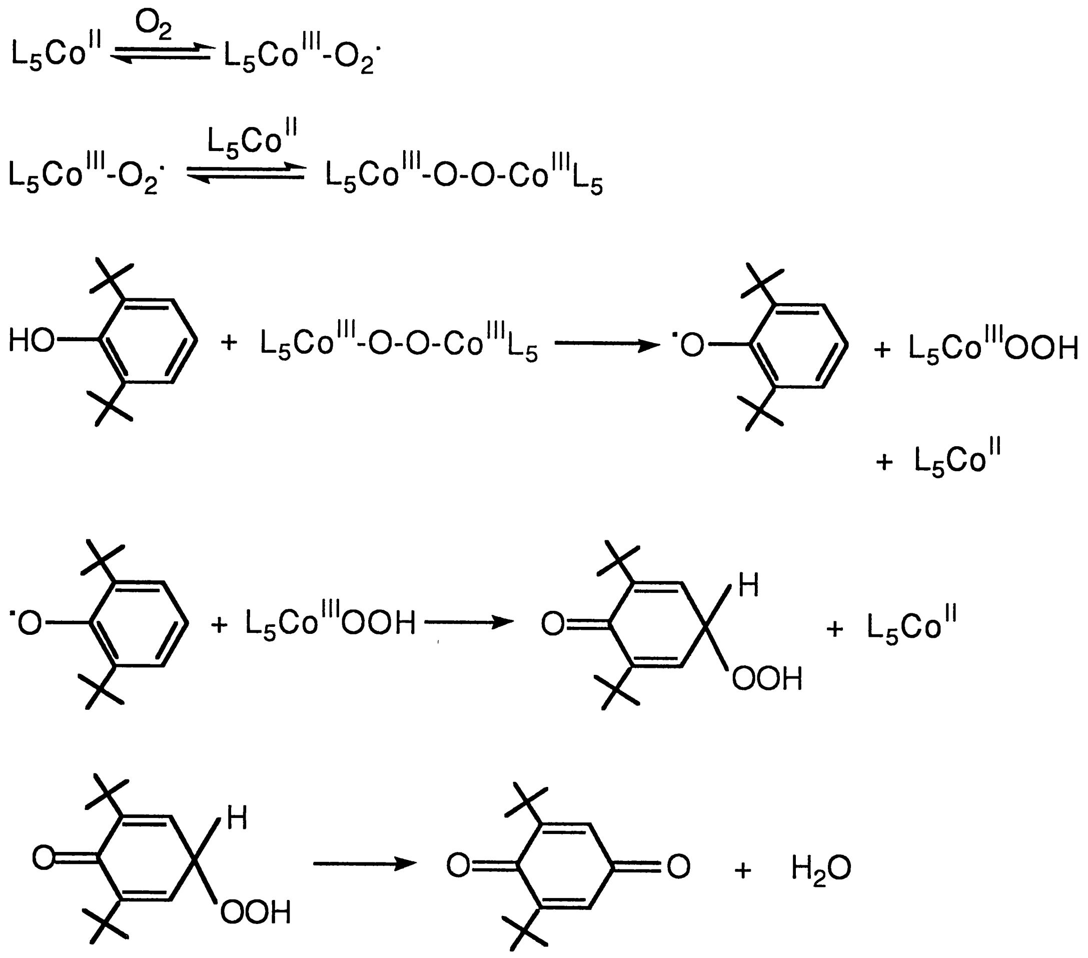
Scheme I


L5CoII ⇌ (O2) L5CoIII-O2•
L5CoIII-O2• + OH ⇌ L5CoII + HO2• + O•
2HO2• → HOOH + O2
O• → (L5CoIII-O2•, slow) O, H, O—OCoIIIL5
O, H, O—OCoIIIL5 → O, O + L5CoIIIOH
L5CoIIIOH + OH → O• + L5CoII + H2O
2 O• + 1/2 O2 → O, O + H2O

Drago and co-workers also observed that H_2O_2 decreased the rate of autoxidation, and the presence of benzoic acid or HCl stopped the autoxidation because the oxidation of Co(II) to Co(III) occurs.

Another type of mechanism involves the hydrogen abstraction by dimeric μ-peroxocobalt (III) complex in the initial step, followed by a nucleophilic displacement that would regenerate the organocobalt (II) complex (Scheme II):[36-38]

Scheme II



Although these two mechanisms can explain some kinetic phenomena and oxidation results, many aspects of the mechanisms of the autoxidation are just speculative. The mechanisms of different autoxidations catalyzed by the cobalt complex should depend on the nature of the catalytic species, nature of the substrate, solvent, and other reaction conditions. It is still unknown whether the monomeric $LCo^{III}O_2$ or dimeric $LCo^{III}O_2Co^{III}L$ is the key species for the autoxidation.

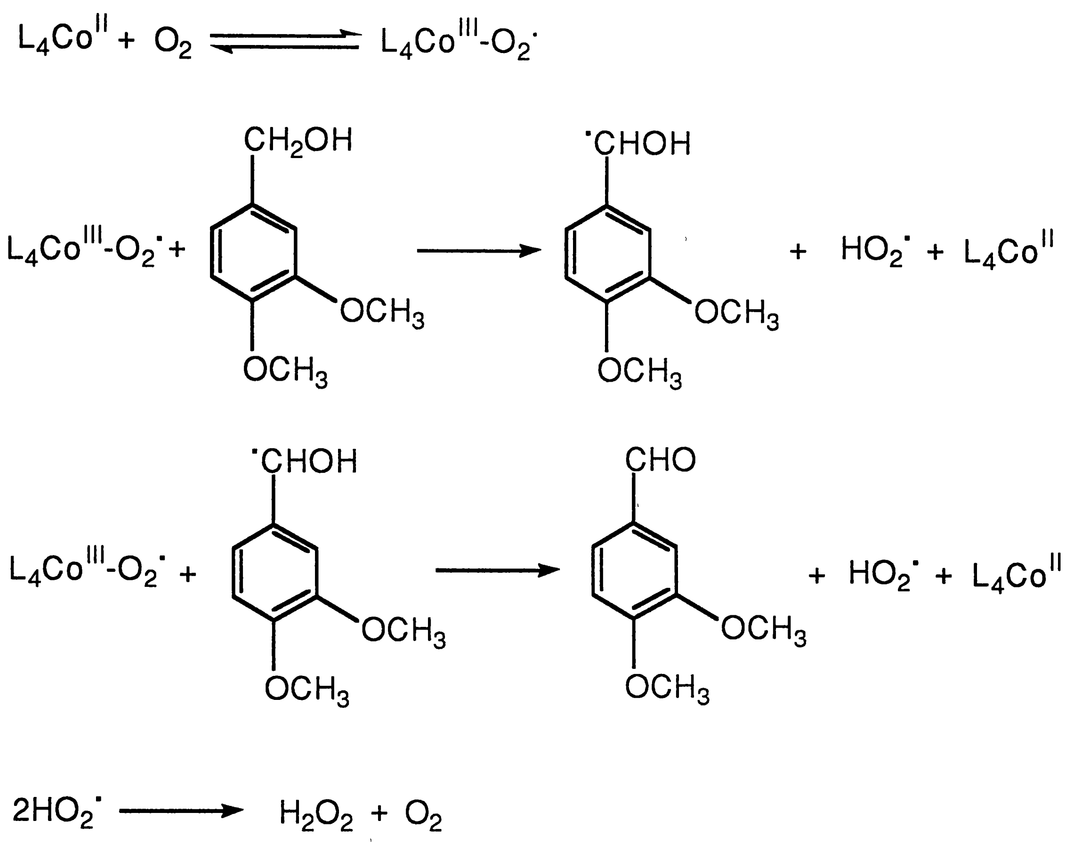
The previous research using UV-vis spectrophotometry showed the existence of dimeric CoPcTs and oxygen adduct (possibly TSCoPc-O_2-PcCoTS) in the alkaline solution (pH ≥ 12). In the neutral solution, no oxygen adduct complex was formed.[39-41] The further study indicated that monomeric TPPCo-O_2 complex and dimeric TPPCo-O_2-CoTPP complex form an equilibrium in solution and the oxygenation may proceed via the successive reactions of eq 6:[39]

$$\mathrm{TPPCo^{II}} \xrightleftharpoons{\mathrm{O_2}} \mathrm{TPPCo^{III}\text{-}O_2\cdot} \xrightarrow{\mathrm{TPPCo^{II}}} \mathrm{TPPCo^{III}\text{-}O\text{-}O\text{-}Co^{III}TPP} \tag{6}$$

The formation of LCo-O_2· might be a rate-determining step. In a nonpolar solvent (such as toluene), the equilibrium is shifted to dimeric complex, while in a polar solvent (such as DMF) the amount of monomeric complex is high.[32] Moreover, ligands (L) of cobalt complex also play an important role in the equilibrium. Schiff base systems and phthalocyanines tend to form the monomeric complex,[32,34] while polyamines gave almost all dimeric oxygen adduct.[38] Therefore, the formation of cobalt-oxygen complex is complicated by the nature of ligands, solvents, and temperature. But it is agreed that this cobalt-oxygen complex is essential to initiate the autoxidation.

The mechanism for our autoxidation of **1** and **3** should be similar to those proposed in the literature. The following mechanism is proposed for the autoxidation of **1**:

Scheme III



As observed by Drago and co-workers,[34] $HO_2\cdot$ and H_2O_2 hinder the autoxidation, and our control experiment also shows that the deliberate addition of H_2O_2 reduces the autoxidation rate (Table V). A pH decrease in the absence of the buffer solution was also observed (Tables III and IV). The pH of 0.41 M H_2O_2 solution was measured to be 5.15. As the reaction proceeds, more H_2O_2 is produced, and once the reaction mixture becomes acidic, the formation of $L_4Co\text{-}O_2\cdot$ probably stops. That is why the yield of aldehyde **2** could not be increased by simple increase of the reaction time (Table III) or by increase of the concentration of CoPcTS (Table IV).

Adjustment of the pH of the aqueous phase to basic conditions with buffer solutions enables formation of $L_4Co\text{-}O_2\cdot$, and the autoxidation can proceed further. In basic solution, the predominant superoxide ion $O_2^{-\bullet}$ is unstable, and may decompose as indicated below:[42]

$$HO_2^{\bullet} + OH^{-} \rightleftharpoons O_2^{-\bullet} + H_2O \tag{7}$$

$$pK_a\,(HO_2\cdot) = 4.88$$

$$2\,O_2^{-\bullet} + H_2O \rightleftharpoons O_2 + HO_2^{-} + OH^{-} \tag{8}$$

$$K_{eq} = 2.5 \times 10^{8}$$

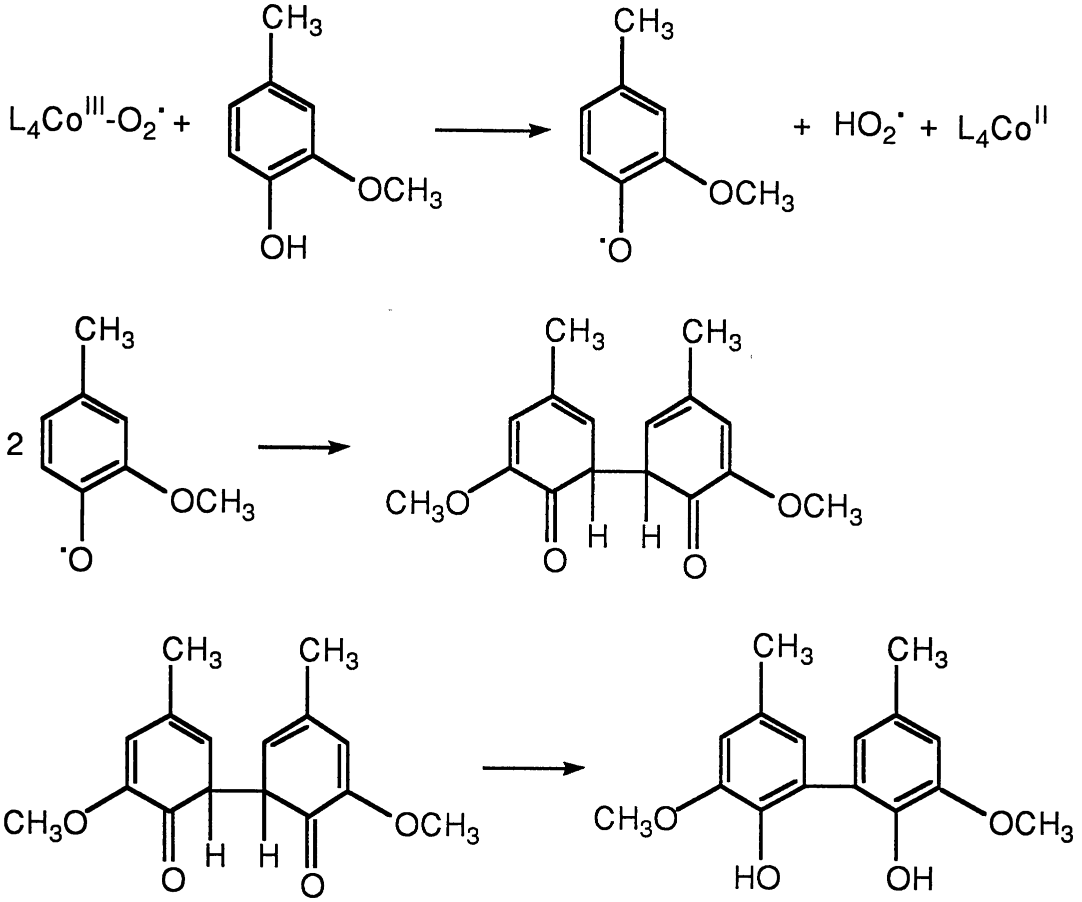
$$O_2^{-\bullet} + HO_2^{\bullet} \longrightarrow HO_2^{-} + O_2 \tag{9}$$

$$k = 8.5 \times 10^{7}\ M^{-1}s^{-1}$$

The decrease of the autoxidation rate by H_2O_2 is not fully understood. H_2O_2 alone oxidizes DMBA with CoPcTS at pH 11, presumably because H_2O_2 decomposes into water and O_2, and O_2 might be the actual oxidant in the oxidation (Table V).

A possible pathway to produce compound **4** is also proposed:

Scheme IV



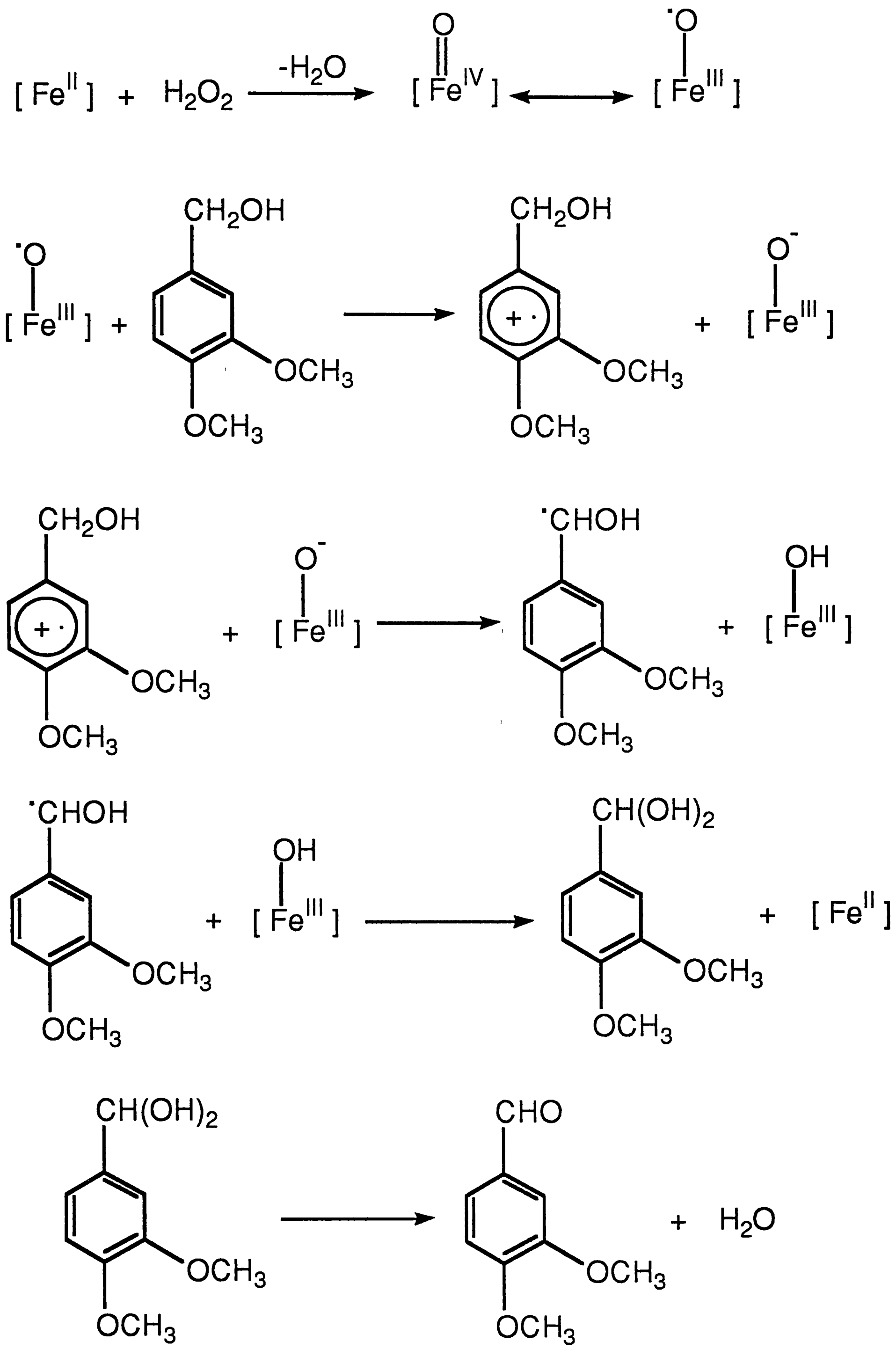
In conclusion, the CoPcTS/O_2 system can oxidize benzyl alcohol and phenols under slightly basic conditions. The presence of OH^- helps form the O_2-CoPcTS complex and helps decompose $HO_2\cdot$ and hence helps the autoxidation.

Oxidation of Lignin Model Compounds with H_2O_2. Metalloporphyrins and metallophthalocyanines in the presence of a single oxygen donor (such as H_2O_2) could mimic the oxidative capability of natural oxygenases. Our results confirm such biomimetic capability of Pcs and porphyrins. Of the six metallophalocyanines and metalloporphyrins used in this research, FePcTS is the most active catalyst, which surprises us because Pcs usually have lower catalytic activity for oxidation (except the autoxidation described above) than metalloporphyrins.[43] The catalytic activity of metal complexes should depend on not only the type of metal complex, but also substrates and reaction conditions. Furthermore, FePcTS reportedly catalyzes the decomposition of H_2O_2 in the pH range from 5.5 to 10.[44] The decomposition of H_2O_2 depends on the solution pH, concentration of the catalyst and H_2O_2, and ionic strength. H_2O_2 decomposes fast in the basic solution with a maximum rate at pH 8-8.5. Under acidic conditions (pH 5.5) the decomposition is relatively slow. According to Waldmeier and Sigel,[44] the initial decomposition rate taken within first 20 sec is 5.01×10^{-7} mol L^{-1} s^{-1} at pH 5.5 and 6.31×10^{-6} mol L^{-1} s^{-1} at pH 8.4. In our control experiment at initial pH 4.75 without buffer, we found that about 22% of the original amount of H_2O_2 decomposed after 1h reaction at 25 ^{o}C, which gives a rate of 1.81×10^{-5} mol L^{-1} s^{-1}.

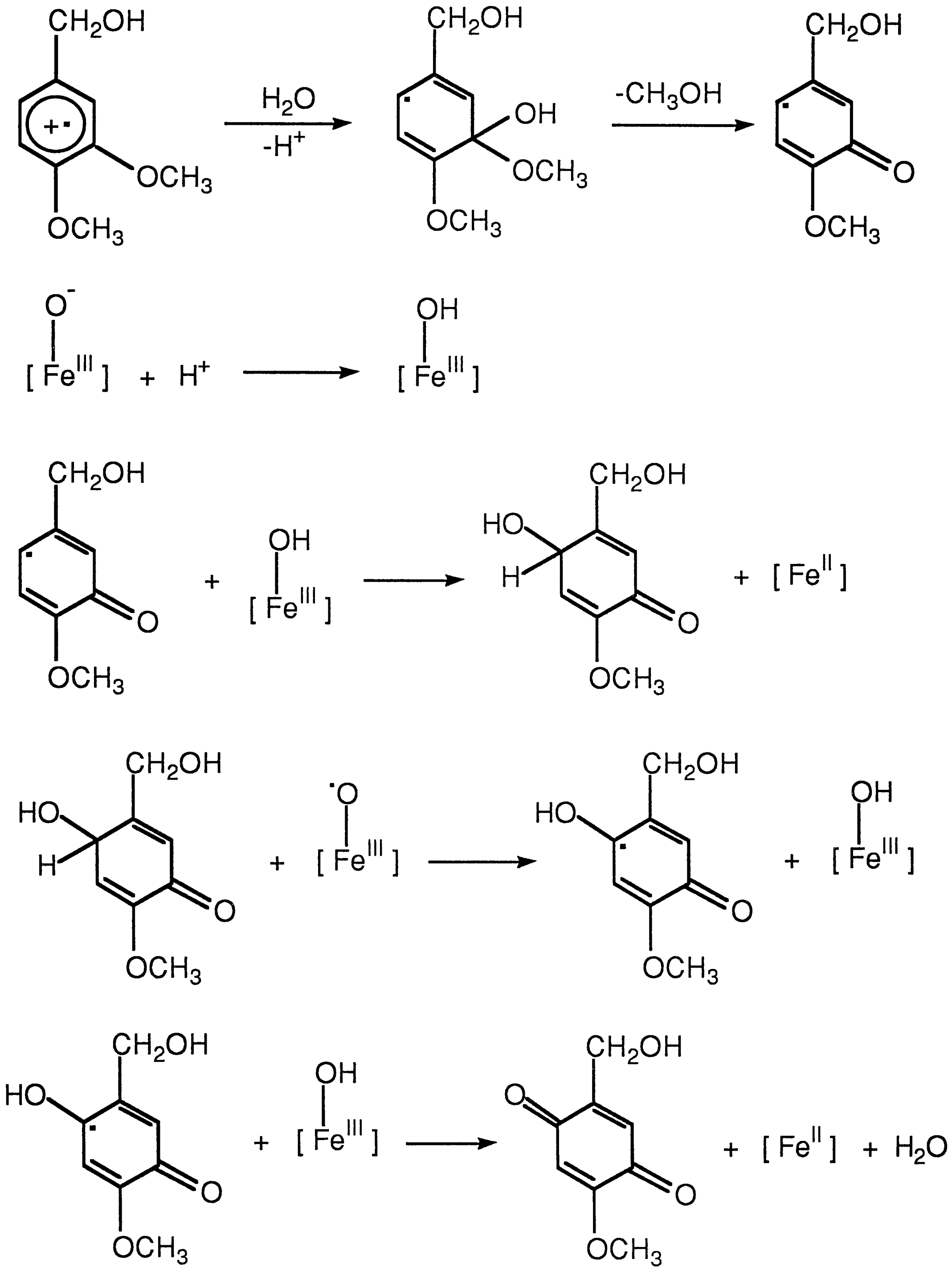
High temperature is necessary for the FePcTS catalyzed H_2O_2 oxidation of **1**, and FePcTS is unstable under oxidative conditions.

A plausible pathway for oxidation of **1** is suggested in Scheme V, which is similar to those proposed in the literature.[6,9]

Scheme V



$[Fe^{II}] + H_2O_2 \xrightarrow{-H_2O} [Fe^{IV}=O] \longleftrightarrow [Fe^{III}-O^{\bullet}]$
CH2OH
OCH3
OCH3
+ ·
O⁻
[FeIII]
•CHOH
OH
CH(OH)2
[FeII]
CHO
H2O


CH2OH
OCH3
OCH3
H2O
-H+
OH
-CH3OH
O
O-
[FeIII]
+ H+
[FeII]
+ H2O

The above process involves single electron transfer as reported before in the biooxidation of **1** with lignin peroxidase.[6,9] The oxidation of **1** with lignin peroxidase and H_2O_2 also gave the same aldehyde **2** and quinone **5**.[9] Therefore, CoPcTS and FePcTS may serve as lignin peroxidase models. The oxidation methods reported in this paper could be potential processes for delignification of wood chips, because they are simple, relatively mild, and effective. However, H_2O_2 oxidation catalyzed by FePcTS at 85 °C may not be practical because FePcTS decomposes.

Conclusion

Cobalt phthalocyaninetetrasulfonate (CoPcTS) can efficiently catalyze the autoxidation of lignin model compounds (**1** and **3**) at $pH \geq 8$. The autoxidation at 85 °C and pH 11 converted all of phenol **3** to 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl (**4**) and other oxidation products in 5 h, and quantitatively converted alcohol **1** to aldehyde **2** in 12 h. Compound **8** failed to react at pH 3 and pH 11. All catalysts were active for the oxidation of **1**, **3**, and **8** with H_2O_2, with the order of the catalytic activity: FePcTS > CuPcTS > CoPcTS ≈ FeTCPP > MnTSPP ≈ NiPcTS. The reactivity order of three compounds in the oxidation with H_2O_2 and FePcTS was **3** > **1** > **8**. The H_2O_2 oxidation proceeded faster in acid than in base. The advantage of CoPcTS and FePcTS oxidations is that they are free radical processes which do not require strong acids and bases. Strong acidic or basic conditions are unfavorable in practical pulping processes.

Further research may be devoted to oxidizing dimeric model compounds, such as 1-(3,4-dimethoxyphenoxy)-2-(2-methoxyphenoxy)propane-1,3-diol or other substituted 1,2-bisphenylpropane-1,3-diols, since many basic units of the lignin are phenyl propanediols. Our O_2/CoPcTS and H_2O_2/FePcTS systems may cleave C_α-C_β bonds of those propanediols.

Experimental Section

Instruments and Materials. ^{1}H NMR spectra at 300 MHz and 400 MHz were obtained on a Varian XL-300 and XL-400 instruments. ^{13}C NMR spectra at 75.4 MHz were obtained on a Varian XL-300 instrument. Infrared spectra were taken on a Perkin-Elmer 681 instrument. UV-vis spectra were measured on a Varian DMS-200 spectrophotometer. HPLC was performed on a Partisil 5 ODS-3 reversed phase column (Whatman, eluent: water/methanol, 6.5/3.5 v/v, flow rate 1 mL/min) equipped with Waters-590 pump and detected by a Beckman-153 analytical UV detector at 280 nm. The analytical data were recorded on an Omniscribe D5000 recorder and processed with an IBM PC-XT computer. GLC analyses were carried out on a Hewlett-Packard 5840A GC equipped with columns of 6-ft 5% Carbowax 20M and 6-ft 20% SE-30 packed columns on 80/100 mesh GAS-CHROM® Q in series. 3,4-Dimethoxybenzyl alcohol (**1**), 4-hydroxy-3-methoxytoluene (**3**), 3,4-dimethoxytoluene (**8**), copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid (tetrasodium salt) (CuPcTS), and nickel phthalocyaninetetrasulfonic acid (tetrasodium salt) (NiPcTS, a mixture of isomers) (all from Aldrich) were used as received. *meso*-Tetra(4-carboxyphenyl)porphine (TCPP) was obtained from Strem and used as received. MnTSPP and CoPcTS are gifts from Dr. Turk and were prepared by a known procedure.[25,45] FePcTS was provided by Dr. Srinivasan and was prepared by a literature procedure.[45] Dowex 50W-X4 resin was obtained from J. T. Baker and was washed thoroughly with ethanol, acetone, methanol, and water before use. The purity of chemicals was checked by ^{1}H NMR. The peroxide content of a commercial aqueous hydrogen peroxide (30%, Fisher) was 28.1 wt % or 9.66 mmol/mL which was determined by iodometric titration. The elemental analysis was performed by Galbraith, Inc., Knoxville, TN.

Latexes (L-4 and L-7) were prepared by the method reported in chapter II.

Iron(III) meso-Tetra(4-carboxyphenyl)porphyrin Chloride. A mixture of TCPP (0.24 g, 0.3 mmol), $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ (0.59 g, 1.5 mmol), and 20 mL of water was refluxed for 24 h. The initial pH was adjusted to 9 by addition of 1 N NaOH. The pH of the mixture was maintained at 6-9 by addition of 1 N NaOH, and the final pH was 7.1. After the reaction, the pH of the mixture was adjusted to 12-13 with NaOH. The brown-green mixture was filtered by suction filtration through a glass frit (PYREX, size M) to remove an unidentified solid impurity. The filtrate was dried with a rotary evaporator. The dark solid was dissolved in methanol and passed over a column of 30 g of hydrated Dowex 50W-X4 (H^+ form). The methanol eluate was dried and the solid was dissolved in water, giving a solution of pH $\geq$ 11. The solution was acidified to pH 1 with HCl under stirring, and the dark brown powder precipitated. The dark brown powder was collected and washed with a large amount of water. The dark brown FeTCPP (H^+ form) was suspended in water and the pH of the suspension was adjusted to 9.2 until all solids were dissolved in water. This green-brown solution was dried with a rotary evaporator to give dark green powder which was dried at 80 ^oC for 24 h in vacuo. Yield: 116 mg, 59%. ^1H NMR [D_2O, internal standard: 3-(trimethysilyl)propionic-2,2,3,3-d_4 acid, sodium salt]: δ 13.2 (broad, 8H, β-pyrrole-H), 8.1 (broad, 16H, phenyl-H). IR (KBr, cm^{-1}): 3700-3100 (vs, broad, OH), 1605 and 1590 (s, arom C=C or C=N or COO^-), 1400 (vs, COO^-), 1000 (s, C=N). UV-vis (H_2O, c = 1.68 x 10^{-5}M) λ_{max} (ε, $M^{-1}cm^{-1}$): 407 (66,100), 323 (22,500), 229 nm (37,200). Anal. Calcd. for $C_{48}H_{24}N_4O_8Na_4FeCl{\cdot}(H_2O)_9{\cdot}NaCl$ (FW1188.55): C, 48.50; H, 3.56; N, 4.71; Na, 9.67; Fe, 4.70; Cl, 5.97. Found: C, 48.43; H, 3.30; N, 4.42; Na, 9.95; Fe, 3.81; Cl, 6.39.

Oxidation of 1 with O_2. All oxidations with O_2 were carried out without using the gas buret system. In a typical procedure, a mixture of L-4 (0.5 g, containing 14 mg solid) or water (0.5 mL in the absence of latex) and an aqueous stock solution of catalyst

(2.04 mL, 10.5 µmol, 3 mol % based on **1**) was stirred for several minutes in a three neck flask equipped with a condenser to which the oxygen gas inlet was connected before addition of 0.68 mL of 1 M NaOH, 1.0 mL of 1 M $NaHCO_3$, and **1** (51 µL, 0.35 mmol) at room temperature (25 °C). The pH of the mixture was 11. The oxygen gas was swept into the flask before the reaction and the oxygen pressure over the reaction mixture was 1 atm. The mixture was heated to 85 °C and stirred for 12 h. After being cooled to room temperature, the mixture was extracted with dichloromethane 5 times (total volume: 6 mL). The combined extract was dried over Na_2SO_4 and analyzed by GLC, using tetradecane as an internal standard. The response factors for **1** and **2** were 1.334 and 1.219. Since **1** and **2** could be identified by GLC, the dichloromethane extract was analyzed by GLC to determine the conversion of **1**. The recovery of the starting material and products was 100%. The ^1H NMR and ^{13}C NMR spectra of the product were identical with those of the commercial sample. **2**: ^1H NMR ($CDCl_3$, TMS): δ 9.87 (s, 1H, ArC<u>H</u>O), 7.45 (m, 2H, H-2 and H-6), 7.0 (d, 1H, J = 9 Hz, H-5), 3.99 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, TMS): δ 190.9 (CHO), 154.5 (C-4), 149.6 (C-3), 130.1 (C-1), 126.9 (C-6), 110.4 (C-2 or C-5), 109.0 (C-2 or C-5), 56.2 (OCH_3), 56.0 (OCH_3).

Oxidation of 1 with H_2O_2. A mixture of L-7 (0.5 g, 20 mg solid) or water (0.5 mL in the absence of latex), an aqueous stock solution of catalyst (3.5 µmol, 1 mol % of DMBA), **1** (51 µL, 0.35 mmol), H_2O_2 (0.18 mL, 1.74 mmol), and 2.87 mL of water was stirred at room temperature (25 °C) for 1 h. The mixture was extracted with dichloromethane for 5 times (total volume: 6 mL) and was dried over Na_2SO_4. The extract was analyzed by HPLC.

Aldehyde **2** and quinone **5** were isolated with a preparative TLC plate (silica gel, Analtech, eluent: 95:5 $CHCl_3$/THF, v/v). **5**: ^1H NMR ($CDCl_3$): δ 6.73 (t, 1H, J = 1.8Hz, H-3), 5.92 (s, 1H, H-6), 4.55 (d, 2H, J = 1.8Hz, C<u>H</u>$_2$OH), 3.83 (s, 3H,

OCH_3), 2.20 (s, broad, 1H, OH). ^{13}C NMR ($CDCl_3$): δ187.8 (C-1), 159.1 (C-4), 147.8 (C-5), 129.2 (C-3), 123.8 (C-2), 107.5 (C-6), 59.7 (CH_2OH), 56.4 (OCH_3).

The oxidation of **8** with H_2O_2 and FePcTS was carried out by the same method as that of **1** (see above). The product, 2-methoxy-5-methyl-2,5-cyclohexadiene-1,4-dione (**9**), was isolated by TLC (silica gel, eluent: $CHCl_3$). **9**: ^1H NMR ($CDCl_3$): δ 6.56 (q,1H,J = 1.4Hz, H-6), 5.92 (s,1H, H-3), 3.80 (s, 3H, OCH_3), 2.08 (d, 3H, J = 1.4Hz, $CH_{\underline{3}}$).

Oxidations of **3** with O_2 and H_2O_2/FePcTS were performed by the same methods as those of **1**. The autoxidation of **3** gave one major product, 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl (**4**), which was isolated by TLC (silica gel, eluent: $CHCl_3$/THF = 95:5 v/v). **4**: ^1H NMR ($CDCl_3$): δ 6.72 (d, 4H, J = 2.8Hz), 5.97 (s, 2H, ArO$\underline{H}$), 3.90 (s, 6H, OCH_3), 2.33 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 147.1 (C-3), 140.4 (C-2), 129.6 (C-5), 124.4 (C-1), 123.5 (C-6), 111.3 (C-4), 56.1 (OCH_3), 21.2 (CH_3).

Products from the oxidation of **3** with H_2O_2/FePcTS were isolated by TLC (silica gel, eluent: $CHCl_3$/THF = 95:5 v/v): 4-hydroxy-3-methoxybenzyl alcohol (**6**), 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl (**4**), 4-hydroxy-3-(2-hydroxy-3-methoxy-5-methylphenyl)-5-methoxybenzyl alcohol (**7**). **6**: ^1H NMR ($CDCl_3$): δ 6.90 (m, 3H), 5.62 (s, 1H, ArO$\underline{H}$), 4.61 (s, 2H, C$\underline{H}_2$OH), 3.91 (s, 3H, OCH_3), 2.35 (s, 1H, O$\underline{H}$). This compound contained some unknown impurities. **7**: ^1H NMR ($CDCl_3$): δ 6.96 (d, 1H, J = 1.8Hz), 6.91 (d, 1H, J = 1.8Hz) 6.73 (s, broad, 2H), 6.11 (s, 1H, ArO$\underline{H}$), 5.94 (s, 1H, ArO$\underline{H}$), 4.65 (s, 2H, C$\underline{H}_2$OH), 3.95 (s, 3H, -OCH_3), 3.91 (s, 3H, OCH_3), 2.33 (s, 3H, CH_3). This compound contained some unknown impurities.

The products were identified by ^1H and ^{13}C NMR spectra which were identical with the commercial samples and reported data.[9,16,46]

In the analysis by GLC, a single column of either SE-30 or Carbowax-20M could not separate **1** and **2**, and other oxidation products from **3** and **8** oxidations. Thus columns of Carbowax-20M and SE-30 in series were used to separate **1** and **2**, and to identify **3** and **8**. The GLC conditions are listed as follows:

Table XIII. GLC Conditions for Oxidation Products from 1, 3, and 8[a]

compound	temp 1 °C	time 1 min	rate °C/min	temp 2 °C	time 2 min	retention time, min
DMBA	190	3.0	3.0	220	1.0	6.7
ArCHO	190	3.0	3.0	220	1.0	4.7
$C_{14}H_{30}$	190	3.0	3.0	220	1.0	2.4
HMT	170	3.0	10.0	220	4.0	2.9
DMT	170	3.0	10.0	220	4.0	2.6
$C_{16}H_{34}$	170	3.0	10.0	220	4.0	5.6

[a] Helium gas flow rate: 40 mL/min, injection temperature: 300 °C, TCD temperature: 320 °C.

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CHAPTER IV

SOLVENT FREE OXIDATION OF ALKENES WITH AQUEOUS POTASSIUM PEROXYMONOSULFATE

Introduction

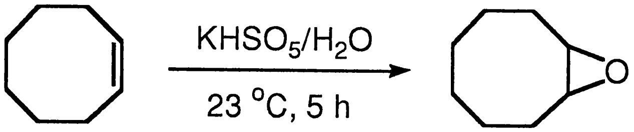
Epoxidation is one of the important reactions for laboratory and industrial syntheses because the epoxides are intermediates which can be converted into other products for various purposes. It is also theoretically and synthetically useful for introducing two stereocenters in one step. Epoxidation by organic peroxy acids is a well known process and has been widely employed due to its versatility, specificity, ease of preparation, and satisfactory yields of the desired product. This process is usually conducted in homogeneous solution in organic solvents to ensure sufficient solubility of organic substrates. Although many inorganic oxidizing agents, such as potassium permanganate and chromic acid, are also effective in oxidation of organic compounds, they often result in difficult-to-handle end products or a mixture of several oxidation products. Few of these inorganic oxidants are applied to epoxidations. Recently, the chemistry of peroxymonosulfuric acid (Caro's acid, H_2SO_5)[1] has been studied increasingly, because Caro's acid is one of the strongest oxidants, and it is also less well-investigated than its analog, peroxydisulfuric acid.

The existence of peroxymonosulfuric acid was first reported by Caro in an attempt to prepare aniline black with a solution of potassium or ammonium persulfate in concentrated sulfuric acid.[1] Caro's acid loses active oxygen so easily that pure, stable H_2SO_5 and its salts have not been obtained. Treatment of 80-90% hydrogen peroxide with concentrated sulfuric acid or chlorosulfuric acid generates an aqueous Caro's acid which is usually used for oxidations without isolation and purification.[3-5] On the other hand, the triple salt of Caro's acid, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ is relatively stable and can be stored at room temperature without appreciable loss of its active oxygen content. The triple salt, potassium peroxymonosulfate, is prepared by reaction of 86% H_2O_2 with concentrated H_2SO_4, followed by neutralizing with K_2CO_3,[6] and is commercially available as Oxone (Du Pont). It is now widely used to replace Caro's acid to carry out oxidations. Griffith and co-workers determined the crystal structure of the active anion HSO_5^- in $KHSO_5 \cdot H_2O$ and $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ by X-ray analysis and comparison with the structures of $(NH_4)_2S_2O_8$ and H_2O_2.[7] The central sulfur atom is bound with a perhydroxyl group and three oxygen atoms, i.e., $H\text{-}O\text{-}O\text{-}SO_3^-$. The bond lengths of three terminal S-O and one S-O (peroxo) are similar to those in $S_2O_8^-$, and the O-O distance is comparable to that in H_2O_2. They believed that the structure of HSO_5^- is close to that in Caro's acid because the Raman spectra of Caro's acid, $KHSO_5 \cdot H_2O$, and the triple salt are similar, although the structure of Caro's acid has not been determined yet.

Like Caro's acid, potassium peroxymonosulfate is a powerful oxidant with a variety of applications in organic chemistry. It can oxidize alcohols, ketones, carboxylic acids, alkenes, arenes, phenols, amines and sulfides.[2,8] It can also be used for hydroxylation of alkanes and aromatic compounds[9] and delignification of aspen wood.[10] Epoxidations of alkenes with $KHSO_5$ have been reported. The reported methods of $KHSO_5$ epoxidations can be divided into three types. In the first type, the epoxidation was carried out in a biphasic system mainly developed by Curci and co-workers.[11-15] The epoxidation procedure requires a mixture of water, a ketone (usually acetone), and CH_2Cl_2 and a phase transfer catalyst. The actual oxidant in this system is a dioxirane intermediate generated by reaction of $KHSO_5$ with ketone, and without ketone no epoxidation occured under the reaction conditions. The system must be buffered at pH 7-8 with phosphate solution to avoid Bayer-Villiger oxidation of ketones. The second type of the epoxidation uses organometallic catalysts such as manganese porphyrins[16,17] or platinum complexes.[18] This type of method is impractical, because the organometallic complexes decompose rapidly during the epoxidation. The third type of $KHSO_5$ epoxidation is performed in a mixture of water-methanol (or ethanol), or water-ethanol-acetic acid to overcome the solubility problem of $KHSO_5$ in organic solvents,[2,19] but these organic solvents are also oxidized along with substrates. A large excess amount of $KHSO_5$ is used to convert substrates effectively. This is a disadvantage of previous $KHSO_5$ reactions since mixing of $KHSO_5$ with oxidizable organic solvent may cause combustion.[3] Therefore, a better method for the epoxidation should be developed, not only to fully use the unique oxidizing ability of $KHSO_5$, but also to reduce the possible mixing hazard of organic solvents with $KHSO_5$. In this research aqueous $KHSO_5$ solution was used to oxidize some water-immiscible alkenes in the absence of added organic solvents.

Results

Epoxidation of Cyclooctene. Cyclooctene could be easily epoxidized at room temperature in aqueous $KHSO_5$ mixture without organic solvent (eq 1). Relatively high conversion (83 mol%) was reached within 5 hours with 0.60 mmol $KHSO_5$ (1.7 equiv. of substrate), and cyclooctene oxide was the only product in almost all epoxidations. The colorless crystalline cyclooctene oxide was suspended in the reaction mixture after 70% conversion of alkene, which made separation easy by filtering the reaction mixture to recover the epoxide. The cyclooctene oxide was stable under the acidic conditions. Stirring of 0.35 mmol cyclooctene oxide and 0.44 mmol $KHSO_5$ in 2.3 mL aqueous phase for 5 h at 23 ^{o}C gave only unchanged epoxide. Its stability is presumably due to its low solubility in the aqueous ophase. Several factors controlling the epoxidation yields were also investigated.



(1)

Effect of Stirring Speed. The stirring speed had an important effect on the yield of epoxidation as expected with the biphasic reaction. The yield increased as stirring speed increased (Table I), and the highest yield (75 %) was obtained at 2500 rpm. Yields were reproducible at ≥1800 rpm but not at<1000 rpm. Magnetic stirring proved sufficient to carry out the reaction on a 2.3 mL scale, while mechanical stirring also gave a high yield. Therefore, magnetic stirring with ≥1800 rpm was used in all subsequent small-scale experiments to ensure high conversion and reproducibility.

Table I. Effect of Stirring Speed on the Yield of Epoxidation[a]

run	stirring speed (rpm)	epoxide %
1	< 1000	52
2	1800	67[b]
3	800[c]	70
4	2500	75

[a] All experiments were carried out at 23 °C for 5 h using 0.35 mmol of cyclooctene, 0.16 M (0.37 mmol) of $KHSO_5$ in 2.3 mL of aqueous mixture.

[b] Average mol% of three runs with a standard deviation ± 2%.

[c] Mechanical stirring.

Effect of $KHSO_5$ Concentration on the Epoxidation. The epoxidation yields increased as the amount of $KHSO_5$ was increased at constant amounts of cyclooctene and water (Table II), for high concentration of oxidant accelerated the epoxidation. A solution of 0.26 M $KHSO_5$ gave 83 mol% of cyclooctene oxide. However, at very high concentration of $KHSO_5$ (run 4), the epoxidation yield decreased instead, which could be attributed to lower solubility of cyclooctene in the aqueous phase at high ionic strength. The solubilities of cyclooctene at 23 °C in deionized water and in a solution of 0.46 M $KHSO_4$ and 0.15 M K_2SO_4 (ionic strength = 0.91 M, which is the same as that of reaction run 3) were experimentally determined to be 1.7×10^{-4} M and 1.0×10^{-4} M respectively. Previously the solubility in pure water was estimated to be 2×10^{-4} M by extrapolation from literature data on solubilities of related cycloalkanes and cycloalkenes.[20]

Table II. Effect of $KHSO_5$ Concentration[a]

run	$KHSO_5$ (M)	mol $KHSO_5$/mol alkene	epoxide %
1	0.16	1.06	65
2	0.19	1.28	78
3	0.26	1.70	83
4	0.39	2.55	80

[a] Reactions were carried out using 0.35 mmol (39 mg) of cyclooctene in 2.3 mL aqueous $KHSO_5$ at 23 °C for 5 h.

Experiments were conducted varying the amount of oxidant and water (Table III). These results showed that the simple increase of oxidant concentration hardly increased the epoxidation conversion (run 4 and 8), and the yield decreased between 0.26 M and 0.39 M $KHSO_5$ as indicated in Table II. The highest conversion was obtained with a large excess of $KHSO_5$ and a large volume of water, which reduced the ionic strength of solution and increased the amount of substrate in the aqueous phase. Highest yield was in run 5 of Table III, which had lower $KHSO_5$ concentration than run 1. Results showed that 97 mol% cyclooctene was converted to epoxide after 5 h in 12 mL of reaction mixture, while only 41 mol% cyclooctene was converted in 1 mL of reaction mixture. However a more diluted $KHSO_5$ solution is unfavorable for large scale experiments because large volume would be required to produce a small amount of product. In a typical laboratory scale experiment, treatment of 3 g (28 mmol) of cyclooctene with a 185 mL solution of 0.26 M $KHSO_5$ at 23 °C produced 2.85 g cyclooctene oxide (81%) in 5 h, which proves this epoxidation method to be synthetically useful.

Table III. Combined Effects of Amount of $KHSO_5$ and Aqueous Volume[a]

entry	$KHSO_5$ (mmol)	volume (mL)	$KHSO_5$ (M)	epoxide %
1	0.44	4.5	0.10	84
2	0.44	2.3	0.19	78
3	0.44	2.0	0.22	77
4	0.44	1.8	0.25	73
5	0.60	12.0	0.05	97
6	0.60	4.5	0.13	88
7	0.60	2.3	0.26	83
8	0.60	2.0	0.30	78
9	0.60	0.98	0.61	41

[a] All experiments were carried out under conditions reported in Table II unless noted otherwise.

Time Dependence of Epoxidation. Fig.1 shows the epoxidation yield as a function of reaction time. More than 90% of the epoxide was produced in the first 5 h. After 10 h about 1 % of cyclooctanediol was found also, presumably from ring-opening hydration of the epoxide.

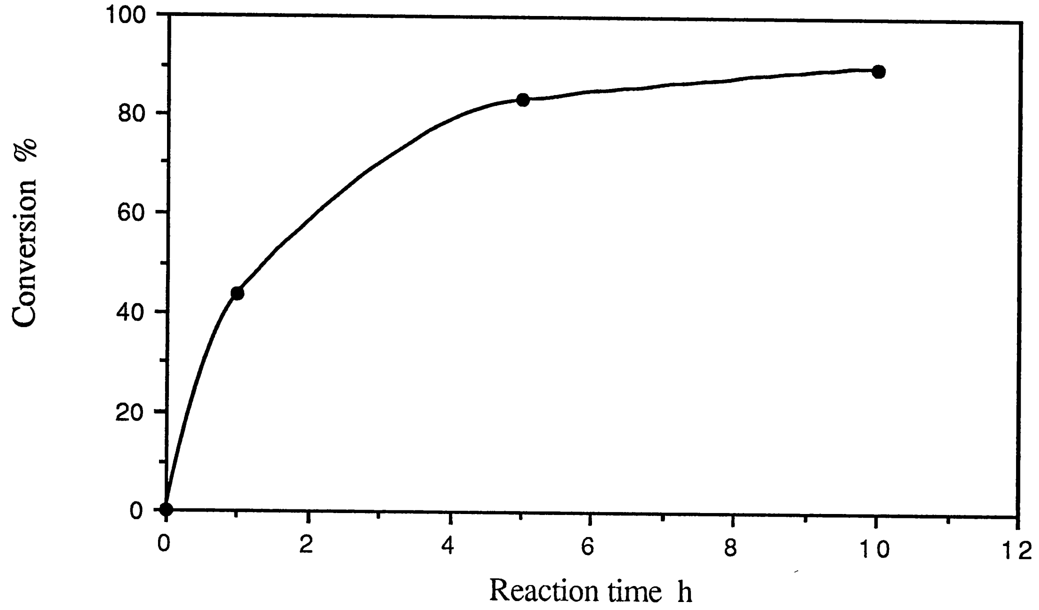


Figure 1. The conversion of cyclooctene epoxidation vs. reaction time. Experiments were carried out with 0.60 mmol of $KHSO_5$ under conditions reported in Table II.

Influence of Phase Transfer Catalysts and Colloidal Particles on the Epoxidation. The common phase transfer catalysts (tetrabutylammonium hydrogen sulfate, benzyltriethylammonium chloride and Aliquat 336), a cationic colloidal polymer and a cationic surfactant microemulsion had little effect on the epoxidation (Table IV). This phenomenon is unusual since phase transfer catalysts accelerate many similar biphasic reactions. A phase transfer catalyst (18-crown-6 ether or tetrabutylammonium hydrogen sulfate) is necessary in Curci's biphasic epoxidation with $KHSO_5$.[11-14]

The presence of PTC agents may not increase the solubility of cyclooctene in aqueous reaction media. The solubility of cyclooctene in a solution of 0.46 M $KHSO_4$, 0.15 M K_2SO_4 and 0.0030 M benzyltriethylammonium chloride (BTAC) is 1.0×10^{-4} M, the same value as that in the absence of BTAC. This fact could account for such a small effect of PTC on the epoxidation.

Table IV. Influence of Phase Transfer Catalysts, Cationic Colloidal Particles, and Microemulsion on Epoxidation of Cyclooctene[a]

PTC or colloids	$KHSO_5$ M	cyclooctene recovered mol %	epoxide mol %
-	0.33	44	56
Aliquat 336	0.35	45	55
Bu_4NHSO_4	0.35	40	60
$C_6H_5CH_2NEt_3Cl$	0.35	37	63
-	0.21	31	61
$C_6H_5CH_2NEt_3Cl$	0.22	38	62
-	0.16	35	65
L-7[b]	0.16	28	70
-	0.21	31	69
L-7[b]	0.21	25	72
μE-1[c]	0.21	30	70
-	0.26	22	78
L-7[b]	0.26	18	78
μE-1[c]	0.26	19	80
-	0.35	44	56
L-7[b]	0.35	37	57

---

[a] All reactions were performed at 23 °C for 5 h with 0.35 mmol of cyclooctene and 7 mmol of PTC agents.

[b] These reactions were carried out in the presence of 20 mg of L-7 that consists of 74 mol% of styrene, 1 mol% of divinylbenzene, 2 mol% of vinylbenzyl chloride and 23 mol% of trimethyl(vinylbenzyl)ammonium chloride units.[22]

[c] Experiments were done in the presence of 0.5 g of μE-1 which is a microemulsion of 17.7 mM of 1-octadecanol and 3.5 mM of hexadecyltrimethylammonium bromide.

Epoxidation of Cyclohexene. The typical epoxidation conditions used with cyclooctene produced *trans*-1,2-cyclohexanediol due to acid-catalyzed hydration of the epoxide at pH 1.58. In a control experiment using cyclohexene oxide in place of cyclohexene under identical conditions, the epoxide was converted completely to *trans*-1,2-cyclohexanediol. To obtain the epoxide, the pH of the aqueous phase was adjusted to nearly neutral using sodium bicarbonate. Results in Table V indicate that the only product was diol if the initial pH was below 6.38, and 99% of final products were cyclohexene oxide at pH $\geq$ 6.75. With $NaHCO_3$ at pH 7.1, the reaction conversion decreased due to either the high ionic strength of the solution or a high decomposition rate of $KHSO_5$. Ball and Edwards[4] found that the second-order rate constant of decomposition of Caro's acid in phosphate buffer solution doubled from 0.071 to 0.148 L mol^{-1} min^{-1} when pH increased from 6.7 to 7.1. $KHSO_5$ is relatively stable at pH < 6 and at pH 12, and it decomposes fastest at pH around the pK_a of caroate (pK_a 9.4 at 25 ^oC in water).[4,5] In the absence of alkene only 19% of active $KHSO_5$ remained after stirring the $KHSO_5$ solution of initial pH 6.75 at 23 ^oC for 5 h with final pH 6.85. Therefore, the epoxidation and HSO_5^- decomposition are two competing reactions in the aqueous phase. The epoxidation is favored in the presence of organic substrates and with large reaction volume.

Table V. Epoxidation of Cyclohexene in the Presence of $NaHCO_3$[a]

$NaHCO_3$ mmol	pH before reaction	pH after reaction	cyclohexene recovered, mol %	epoxide mol %	diol mol %
0	1.58	1.30	0	0	100
0.50	6.38	2.42	0	0	100
0.60	6.60	4.18	0	30	70
0.65	6.68	7.65	6	90	4
0.70	6.75	8.16	4	95	1
0.80	6.86	8.68	11	88	1
1.0	7.10	8.48	16	83	1

[a] Reactions were performed at 23 °C for 5 h by using 0.35 mmol of cyclohexene and 0.44 mol (0.19 M) of $KHSO_5$ in 2.3 mL of aqueous mixture.

Although the $NaHCO_3$ did not maintain constant pH value throughout the reaction, it did prevent the ring opening of the epoxide. The $NaHCO_3$ buffering method could be applied to other reactions in which approximate control of pH is required. In contrast, use of KOH in place of $NaHCO_3$ failed to stop formation of diol (Table VI), and high concentration of KOH decreased the conversion. This may be due to accelerated decomposition of $KHSO_5$.

Table VI. Epoxidation of Cyclohexene in the Presence of KOH[a]

KOH mmol	pH before reaction	pH after reaction	cyclohexene recovered, mol%	epoxide mol%	diol mol%
0.20	2.55	1.60	0	0	100
0.25	5.50	1.72	0	0	100
0.40	8.50	1.88	37	1	62

[a] Reaction conditions were the same as in Table V except that $NaHCO_3$ was replaced by KOH.

Epoxidation of Other Alkenes. Under the standard conditions used for cyclooctene, epoxidations of 2,3-dimethyl-2-butene, 1-methylcyclohexene, allylbenzene and styrene derivatives yielded diols (Table VII and VIII). Neutral conditions (initial pH ≥6.7) selectively produced some epoxides, but usually in low yields. Increase of temperature under neutral conditions did not raise the yield of epoxidation, possibly due to faster decomposition of the oxidant at pH 6.7 at elevated temperature, while higher conversions were observed at higher reaction temperature under acidic conditions (pH ≤ 1.68). Only 2% conversion of 1-octene was observed after 24 hour reaction. Tetrachloroethylene did not react under either acidic or neutral conditions. Again, diluted reaction mixture resulted in high yields of epoxides, and 79 mol % and 44 mol % of β-methylstyrene oxide and styrene oxide were obtained when the epoxidation was carried out in 12 mL of aqueous phase (see the last experiment for each substrate in Tables VII and VIII).

Table VII. Epoxidation of Alkenes at pH ≤ 1.68[a]

substrate	temp °C	initial pH	final pH	alkene mol %	epoxide mol %	diol mol %	solubility[b] M x 10^4
2,3-dimethyl-2-butene[c]	23	1.56	1.46	0	0	100	2.9[d]
2,3-dimethyl-2-butene[e]	23	1.68	1.32	11	0	89	
1-methyl-cyclohexene[c]	23	1.56	1.48	0	0	100	5.4[f]
1-methyl-cyclohexene[e]	23	1.68	1.35	26	0	74	
cyclohexene[c]	23	1.56	1.32	0	0	100	26[f]
cyclohexene[e]	23	1.68	1.40	51	0	49	
cyclooctene	23	1.58	1.30	22	78	0	1.7
α-methylstyrene	23	1.58	1.40	43	1	56	1.7[g]
α-methylstyrene[h]	23	1.58	1.40	23	6	66	
α-methylstyrene	40	1.58	1.40	0	5	95	
β-methylstyrene	23	1.58	1.40	65	0	35	1.7[g]
β-methylstyrene	40	1.58	1.30	3	7	90	
styrene	23	1.58	1.40	76	0	24	7.0[i]
styrene	40	1.58	1.20	23	0	77	
p-methylstyrene	23	1.58	1.60	95	0	5	1.7[g]
p-methylstyrene	40	1.58	1.30	29	0	68	
allylbenzene	23	1.58	1.70	98	2	0	1.7[g]
allylbenzene	50	1.58	1.30	70	0	30	
1-octene	23	1.58	1.70	100	0	0	0.24[f]
1-octene[j]	23	1.58	1.60	98	0	2	
1-octene	50	1.58	1.62	99	0	1	
tetrachloroethylene	23	1.56	1.80	100	0	0	9.0[k]

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[a] All experiments were carried out under the same conditions as reported in Table V unless noted otherwise.

[b] Solubility of alkenes in water at 23 °C.

[c] These experiments were done by using 0.70 mmol of alkenes, 0.88 mmol of $KHSO_5$ in 4.6 mL of aqueous phase at 23 °C for 1 hour.

[d] This value was estimated from the solubility of 2-methylpropene[20] and a decrease of the solubility by a factor of about 4 per additional CH_3 group.[24]

[e] Reactions were performed with 0.70 mmol of alkenes, 0.70 mmol of $KHSO_5$ in 4.6 mL of aqueous phase for 30 min.

[f] See reference 20.

[g] This value was estimated from the solubility of styrene[23] and a decrease of the solubility by a factor of about 0.25 per additional CH_2 or CH_3 group.[24]

[h] The reaction was carried out in the presence of 20 mg of latex L-7.

[i] See reference 23.

[j] The reaction was carried out for 24 h.

[k] See reference 28.

Table VIII. Epoxidation of Alkenes at pH $\geq$ 6.68[a]

substrate	temp °C	initial pH	final pH	alkene mol %	epoxide mol %	diol mol %
2,3-dimethyl-2-butene[b]	23	6.68	8.20	0	98	2
2,3-dimethyl-2-butene[c]	23	6.68	8.32	12	88	0
1-methylcyclohexene[b]	23	6.68	7.60	9	91	0
1-methylcyclohexene[c]	23	6.68	7.76	40	60	0
cyclohexene[c]	23	6.68	7.92	38	62	0
cyclohexene	23	6.75	8.16	1	95	0
α-methylstyrene	23	6.70	7.20	82	13	5
α-methylstyrene	40	6.70	6.75	85	3	12
α-methylstyrene[d]	23	6.80	7.60	30	18	49
α-methylstyrene[e]	23	7.05	7.18	44	33	22
β-methylstyrene	23	6.70	6.70	63	37	0
β-methylstyrene	40	6.70	8.30	63	37	0
β-methylstyrene[d]	23	6.80	7.56	21	79	0
styrene	40	6.70	7.10	84	12	4
styrene[d]	23	6.80	7.70	56	44	0
tetrachloroethylene	23	6.68	7.80	100	0	0

---

[a] All experiments were carried out under the same conditions as reported in Table V unless noted otherwise.

[b] These experiments were done by using 0.70 mmol of alkenes, 0.88 mmol of $KHSO_5$ in 4.6 mL of aqueous phase at 23 °C for 1 hour.

[c] Reactions were performed with 0.70 mmol of alkenes, 0.70 mmol of $KHSO_5$ in 4.6 mL of aqueous phase for 30 min.

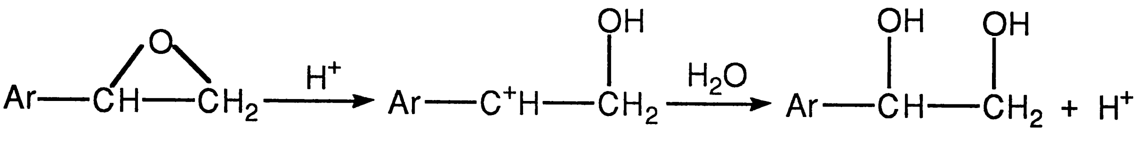
[d] 0.60 mmol of $KHSO_5$ (0.05 M) and 0.87 mmol of $NaHCO_3$ (0.07 M) in 12 mL of aqueous mixture was used in these reactions.

[e] This reaction was done using 1.4 mmol of alkene, 2.40 mmol of $KHSO_5$ (0.05 M) and 4.08 mmol of $NaHCO_3$ (0.085 M) in 48 mL of aqueous phase.

Use of more $NaHCO_3$ to attain higher pH (6.80 vs 7.05) of the aqueous phase nearly doubled the yield of α-methylstyrene oxide (18% to 33%), but gave lower alkene conversion. More $NaHCO_3$ favors production of the epoxide, but decreases the solubility of the alkene in aqueous phase because of the high ionic strength.

2, 3-Dimethyl-2,3-butanediol was stable at pH 1.5, and did not undergo pinacol rearrangement under such acidic conditions as usually expected.

Epoxidation of β-methylstyrene (*cis*/*trans*: 8/92) at pH 6.8 gave a mixture of *cis*- and *trans*-β-methylstyrene oxides (*cis*/*trans*: 10/90) in 79% yield, which suggests that the epoxidation is stereospecific. The oxidation at pH 1.58 produced two racemic diols in equal quantities: *erythro*- and *threo*-1-phenyl-1,2-propanediol. Under acidic condition the diols could be formed via a benzylic cation generated by acid-opening of the epoxide.



In acidic $KHSO_5$ solution (pH 1.58), the reactivity order is: 2,3-dimethyl-2-butene > 1-methylcyclohexene > cyclohexene > cyclooctene > α-methylstyrene > β-methylstyrene > styrene > *p*-methylstyrene > allylbenzene > 1-octene, and in neutral solutions (pH ≥ 6.7), the reactivity order was the same except 1-methylcyclohexene ≈ cyclohexene and β-methylstyrene > α-methylstyrene.

This reactivity order is similar to that of epoxidation by peroxyacetic acid in acetic acid:[25] 2-methyl-2-butene > cyclopentene > cyclohexene > β-methylstyrene > styrene > allylbenzene. The electron-donating groups on the double bond cause an increase in epoxidation rate. This indicates that the process of $KHSO_5$ oxidation resembles to that of electrophilic peroxy acid epoxidation.

Table IX lists some of our results and literature data. Our oxidation conditions are simple, since the only substances in the reaction media are alkene, $KHSO_5$, $KHSO_4$, K_2SO_4 and water. This method has high selectivity for diols from cycloalkenes and styrene derivatives but fails to oxidize 1-alkenes. In many cases, simple removal of starting alkene by the rotary evaporator or in vacuo results in the final product in high purity, and further purification is not necessary. Our method of control of the pH of the reaction by adding $NaHCO_3$ solution once at the beginning of the reaction, is more convenient than the continuous addition of KOH solution used in previous $KHSO_5$ oxidations.[11-14,19]

Table IX. Comparison of Alkene Epoxidation Methods

alkene	$KHSO_5$ (equiv)	alkene conv, %	epoxide, %[a]	reference
cyclohexene	2.4	97	80	11[b]
cyclohexene	1.26	96	99	this work
cyclooctene	1.5		94	19[c]
cyclooctene	1.7	97	100	this work
β-methylstyrene			85	14[b]
β-methylstyrene	1.7	79	100	this work

[a] Epoxide yields are based on the alkene reacted.

[b] 5.1 mmol of alkene, 12 mmol of $KHSO_5$, 1 mmol of $Bu_4N^+HSO_4^-$ in 50 mL of CH_2Cl_2, 50 mL of water and 4 mL of acetone at pH 7.5 buffered by phosphate solution and controlled by addition of KOH solution during the reaction at 2-10 °C for 4 h.

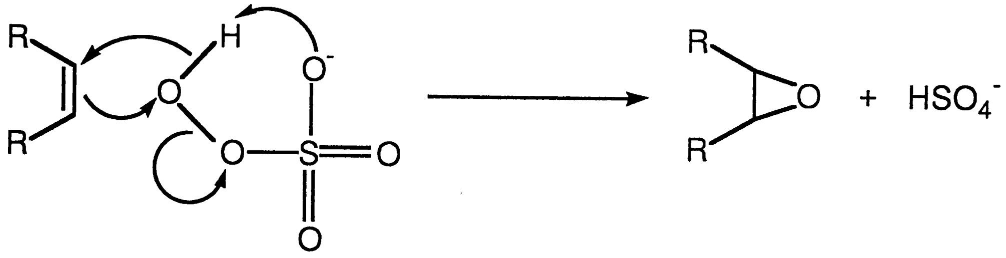
[c] 10 mmol of alkene and 15 mmol of $KHSO_5$ in 20 mL of methanol and 20 mL of water at room temperature for 4 h.

Discussion

The $KHSO_5$ oxidation described here is a biphasic reaction of aqueous $KHSO_5$ solution and organic substrate. The oxidation takes place in the aqueous phase. This suggestion is based on the fact that the diluted $KHSO_5$ solution produced high yield of cyclooctene oxide, while the concentrated $KHSO_5$ solution resulted in low yield (Tables II and III). Normally the rate of a chemical reaction increases with higher concentration of a reactant. The lower yield of the epoxide at higher $KHSO_5$ concentration could be due to the lower concentration of cyclooctene in the aqueous phase of high ionic strength. The solubility of cyclooctene decreases from 1.7×10^{-4} M to 1.0×10^{-4} M with the change of the solution from deionized water to a solution of ionic strength 0.9 M. Increasing the $KHSO_5$ concentration decreases the concentration of cyclooctene in the aqueous phase, and hence decreases the epoxidation rate since the reaction occurs in the aqueous phase.

Mechanism of the Epoxidation. A possible mechanism for epoxidations of cyclohexene and cyclooctene is transfer of the electrophilic oxygen atom of perhydroxyl group of $KHSO_5$ to the substrate (Eq 2 in Scheme I), similar to that of epoxidation by organic peroxy acids. This process generates epoxide and $KHSO_4$, which is more acidic than $KHSO_5$. The pK_a of $KHSO_4$ is 1.9, while that of $KHSO_5$ is about 9.4. A decrease of pH (1.58 to 1.30) was usually observed during the epoxidation in the absence of base.

Scheme I



(2)

$$HSO_4^- + HCO_3^- \longrightarrow H_2CO_3 \longrightarrow H_2O + CO_2\uparrow \qquad (3)$$

After $NaHCO_3$ solution is added to nearly neutral pH, the reaction mixture becomes a buffer solution if CO_2 does not evolve completely because of the presence of sizeable amounts of both HCO_3^- and H_2CO_3. The pH of this solution follows eq. (4):

$$\text{pH } (25\ ^{o}\text{C}) = 6.37 + \log([HCO_3^-]/[H_2CO_3]) \qquad (4)$$

Thus the initial pH is nearly neutral even when the amount of $NaHCO_3$ is an excess at the beginning of the reaction. As the epoxidation proceeds, the generated $KHSO_4$ is neutralized by the remaining $NaHCO_3$. If we assume that the CO_2 produced from $NaHCO_3$ and $KHSO_4$ evaporates from the solution during the reaction, equilibrium calculations predict approximately the final pH values of all of the reaction mixtures in Table V (see Experimental section). If the amount of $NaHCO_3$ added is less than the amount of $KHSO_4$ + $KHSO_5$, the solution becomes acidic as HSO_4^- is formed (eq 1). If the amount of $NaHCO_3$ added is greater than the amount of $KHSO_4$ + $KHSO_5$ and CO_2 evaporates, the solution becomes basic due to loss of acid as CO_2.

This buffer system is similar to that of blood.[21] Acidic metabolites, principally CO_2, are produced in greater quantities than basic metabolites, and carbon dioxide is the principle one. The control of CO_2 in blood to maintain pH is fulfilled by several buffer systems, including bicarbonate and $H_2PO_4^-/HPO_4^{2-}$.

The CO_2/HCO_3^- balance in blood is related to the pH of the blood by the following equation,

$$\text{pH } (37\ ^{o}\text{C}) = 6.10 + \log([HCO_3^-]/[H_2CO_3]) \qquad (5)$$

where H_2CO_3 is equal to the concentration of dissolved CO_2 in the blood; 6.10 is pK_{a1} of carbonic acid in blood at 37 ^{o}C. The normal pH in blood is 7.40.

This HCO_3^-/H_2CO_3 system is the most important one in buffering blood in the lung. As oxygen from inhaled air combines with hemoglobin, the oxygenated hemoglobin ionizes, releasing a proton. This excess acid is neutralized by HCO_3^-, which would result in a decrease of the pH as the ratio of HCO_3^-/H_2CO_3 decreases. Fortunately, the H_2CO_3 produced is rapidly decomposed to CO_2 and H_2O by decarboxylase, and the CO_2 is exhaled by the lung. The pH remains constant at 7.40.

The relative reactivities of different alkenes may be explained by both solubility and nucleophilicity of the substrate towards the oxidant. Since the oxygen transfer in $KHSO_5$ oxidation is electrophilic, the electron-donating group ($-CH_3$) facilitates the epoxidation, leading to high conversion as observed in epoxidations of α-methylstyrene and styrene. Solubility of the substrate could also be a key factor in the reaction. Literature and estimated values of the solubilities are given in Table VII. Styrene is more soluble in water than *p*-methylstyrene, and hence is more reactive..

Conclusion

Aqueous solution of potassium peroxymonosulfate oxidized water-immiscible alkenes at room temperature in the absence of organic solvent. The acidic $pH \leq 1.7$ solutions of commercial $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ in water produced diols from all reactive alkenes investigated except cyclooctene. Adjustment of initial pH to ≥ 6.7 with $NaHCO_3$ enabled selective epoxidation of 2,3-dimethyl-2-butene, 1-methylcyclohexene, cyclohexene, styrene, and β-methylstyrene. The order of decreasing reactivity of alkenes investigated was: 2,3-dimethyl-2-butene > 1-methylcyclohexene ≥ cyclohexene > cyclooctene > α-methylstyrene ≥ β-methylstyrene > styrene > *p*-methylstyrene > allylbenzene. 1-Octene and tetrachloroethylene did not react. Phase transfer catalysts, a colloidal cationic polymer, and a cationic surfactant microemulsion had little effect on the reaction. The above simple oxidation procedure could be practical for laboratory and industrial process.

In further research, I suggest oxidizing more complicated alkenes (such as polyolefins) to determine the selectivity of $KHSO_5$ oxidations. It may be worth while to perform asymmetric epoxidations of allylic alcohols by $KHSO_5$ in the absence of organic solvents.

Experimental Section

Instruments and Materials. IR spectra were recorded on a Perkin-Elmer 681 instrument. ^{1}H NMR spectra at 300 MHz and 400 MHz were obtained on a Varian XL-300 and XL-400 instruments. ^{13}C NMR spectra at 75.4 MHz were obtained on a Varian XL-300 instrument. GLC analyses were performed on a Hewlett-Packard 5840A microprocessor-controlled gas chromatograph equipped with a 6 ft x 1/8 in Tenax® packed column from Supelco Inc. and a thermal conductivity detector. Magnetic stirrers (VWR Scientific 400 HPS, this stirrer allows precise control of stirring speed from 0 to 2500 rpm; Corning PC-320, max speed: 1800 rpm; Corning PC-353, max speed: 1000 rpm) were used to conduct the reactions. pH of reaction mixtures was measured with a semimicro combination glass electrode calibrated at pH 2, 7, and 10. Cyclooctene (Fluka), cyclohexene, cyclohexene oxide, 1-octene, allylbenzene, styrene, α-methylstyrene, β-methylstyrene, *p*-methylstyrene (all from Aldrich) and $KHSO_5$ (Aldrich, obtained in the form of OXONE) were used as received.

Iodometric titration[26] showed that 1 g of Oxone contained 2.75 mmol $KHSO_5$. A solution of 0.0101 g of Oxone and 10 mL of water had pH 2.93. The solution contained 0.0042 g or 2.77×10^{-3} M of $KHSO_5$ and 0.0059 of both $KHSO_4$ and K_2SO_4. Since the pK_{a2} of $KHSO_4$ is 1.92, equilibrium calculation shows that the above solution contained 0.0022 g or 1.60×10^{-3} M of $KHSO_4$ and 0.0037 g or 2.14×10^{-3} M of K_2SO_4. Thus, the molar ratio of $KHSO_5$:$KHSO_4$:K_2SO_4 in Oxone was 1.73:1.0:1.34.

GLC conditions: Temp 1: 60-175 °C, varying with different alkenes (see below). Time 1: 1.5 min. Temp 2: 275 °C. Time 2: 1.0 min. Rate: 15 °C/min. He flow rate: 40 mL/min. Sample concentration: 7 mg/mL. Injection quantity: 10 μL.

Table X. GC Conditions for Analysis of $KHSO_5$ Oxidation Mixtures

compound	temp 1, °C	retention time, min
2.3-dimethyl-2-butene	60	8.80
2,3-dimethyl-2,3-epoxybutane	60	9.82
2,3-dimethyl-2,3-butanediol	60	10.27
cyclooctene	150	4.63
cyclooctene oxide	150	6.52
cyclooctanediol	150	8.81
cyclohexene	85	6.60
cyclohexene oxide	85	8.67
cyclohexanediol	85	11.01
1-methylcyclohexene	115	5.52
1-methylcyclohexene oxide	115	6.92
1-methylcyclohexanediol	115	9.11
α-methylstyrene	175	4.0
α-methylstyrene oxide	175	5.37
α-methylstyrene diol	175	7.18
β-methylstyrene	175	4.44
β-methylstyrene oxide	175	5.26
β-methylstyrene diol	175	7.14
styrene	175	3.17
styrene oxide	175	5.04
styrene diol	175	7.25
p-methylstyrene	175	4.15

p-methylstyrene diol	175	7.87
allylbenzene	175	3.58
allylbenzene diol	175	7.86
1-octene	135	4.20
tetrachloroethylene	130	4.74

Solubility of Cyclooctene in Water and in a Solution of 0.46 M $KHSO_4$-0.15 M K_2SO_4. A mixture of cyclooctene (2 mL, 1.6 g) and water (400 mL) or $KHSO_4$-K_2SO_4 solution (400 mL) in a separatory funnel was shaken vigorously 6 times. After standing at 23 °C overnight, the first 25 mL of aqueous solution was discarded, and 350 mL of solution was collected. The solution was extracted with hexane (3 x 2 mL), and GC analysis of the third extract showed no cyclooctene peak. The combined extract was dried over $NaSO_4$ and analyzed by GC, using *n*-hexadecane as an internal standard with a response factor of 1.2193. The solubilities of cyclooctene in water and in 0.46 M $KHSO_4$-0.15 M K_2SO_4 were 1.7×10^{-4} M (0.019 g/L) and 1.0×10^{-4} M (0.011 g/L) respectively.

The solubility of cyclooctene in a solution of 0.46 M $KHSO_4$-0.15 M K_2SO_4 and 0.0030 M benzyltriethylammonium chloride was determined to be 1.0×10^{-4} M by the same method.

Epoxidation. Method 1. A mixture of deionized water (1.57 mL), cyclooctene (0.35 mmol, 46 μL) and freshly prepared Oxone solution (0.73 mL, 0.45 mmol $KHSO_5$) was stirred magnetically for 5 h at 23 °C. The mixture was then extracted with ethyl ether (5 times, total volume: 6 mL). The ether layer was transferred into a vial and the combined ether extract was dried over Na_2SO_4, and then analyzed by GC, using *n*-octane as an internal standard. Response factors for cyclooctene and cyclooctene oxide were 1.031 and 1.125 respectively. GC analyses accounted for 90-100% of the starting cyclooctene in all experiments.

Method 2. A 500 mL flask was charged with deionized water (185 mL) and Oxone (17.2 g, $KHSO_5$: 48 mmol). The solution was allowed to warm to 23 °C. After addition of cyclooctene (3.09 g, 28 mmol), the mixture was stirred mechanically at 23 °C for 5 h. The colorless crystals suspended in the aqueous phase were collected by suction filtration (1.80 g, yield 51 %). GLC, IR and NMR (^1H and ^{13}C) analyses of this crystalline product were identical with those of authentic cyclooctene oxide. Cyclooctene oxide obtained by this method showed high purity (> 98.5 %). ^1H NMR also detected <1.5 % cyclooctene in the product. The filtrate was extracted with CH_2Cl_2 (5 x 70 mL), and dried over sodium sulfate. Evaporation of the solvent gave colorless crystals (1.09g), and GLC and NMR showed the presence of epoxide and *trans*-1,2-cyclooctanediol (96.5:3.5, w/w). Total epoxide yield: 2.85 g, 81%. Diol: 0.038g, <1%.

Method 3. The procedure in Method 1 was employed except that cyclohexene or other alkenes (0.35 mmol, 39 μL) and $NaHCO_3$ (0.65 mmol, 0.65 mL of freshly prepared 1.0 M solution) or 1.0 M KOH solution were used. In most experiments the order of addition to the flask was water, $NaHCO_3$ solution, alkene, and $KHSO_5$ solution. In some cases $KHSO_5$ was added before $NaHCO_3$ solution. The combined ether solution was analyzed by GLC.

All the epoxides and diols were known compounds and their spectral data were identical with those given in the literature[27] or with those of commercial samples.

Control Experiments on Stability of $KHSO_5$. Iodometric titrations of the oxidation mixtures immediately after epoxidations of cyclohexene and of cyclooctene at initial pH 1.58 and of cyclohexene at initial pH 6.75 showed that all of the excess of

$KHSO_5$ remained after 5 h reaction under acidic conditions, and all of excess oxidant disappeared after 5 h reaction under neutral conditions.

Cyclooctene oxide was prepared by method 1. ^1H NMR ($CDCl_3$, TMS): δ 2.90 (m, 2H, -CHCH-), 2.15 (m, 2H), 1.70-1.35 (m, 8H), 1.35-1.20 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS): δ 55.6, 26.5, 26.3, 25.6.

2,3-Dimethyl-2,3-epoxybutane was prepared by method 3. The epoxide was isolated by distillation (yield: 90 %). ^1H NMR ($CDCl_3$, TMS): δ 1.32. ^{13}C NMR ($CDCl_3$, TMS): δ 62.1, 21.1.

2,3-Dimethyl-2,3-butanediol was prepared by method 1. After removing ether solvent by the rotary evaporator, we obtained the diol (yield: 90 %). ^1H NMR ($CDCl_3$, TMS): δ 2.26 (broad s, 2H, 2OH), 1.25 (s, 12H, CH_3). ^{13}C NMR ($CDCl_3$, TMS): δ 75.1, 24.8.

1-Methylcyclohexene oxide was prepared by method 3. The epoxide was isolated by the same procedure as that for 2,3-dimethyl-2,3-butanediol (yield 91 %). ^1H NMR ($CDCl_3$, TMS): δ 2.96 (d, J=3.3 Hz, 1H), 2.88-1.25 (m, 11H). ^{13}C NMR ($CDCl_3$, TMS): δ 59.6, 57.5, 29.8, 24.7, 24.0, 20.0, 19.7.

1-Methylcyclohexane-trans-1,2-diol was prepared by method 1. The diol was isolated by the same procedure as that for 2,3-Dimethyl-2,3-butanediol (yield 92 %). ^1H NMR ($CDCl_3$, TMS): δ 3.49 (dd, J=10.3 Hz, J = 4.6 Hz, 1H), 2.87 (broad s, 2H, 2OH), 1.86 (m, 1H), 1.71 (m, 2H), 1.61 (m, 1H), 1.32 (m, 4H), 1.19 (s, 3H). ^{13}C NMR ($CDCl_3$, TMS): δ 77.2, 54.3, 38.7, 31.1, 24.3, 23.2, 19.5.

Cyclohexene oxide was prepared by method 3. The epoxide yield and recovery were determined by GLC with hexadecane as an internal standard. The response factors for cyclohexene and cyclohexene oxide were 0.979 and 1.127 respectively. Recoveries were from 76.3 % to 88.6 %. ^1H NMR ($CDCL_3$, TMS): δ 3.13 [m, 2H, -C(O)H-], 1.95 (m, 2H), 1.82 (m, 2H), 1.42 (m, 2H), 1.24 (m, 2H). ^{13}C NMR ($CDCl_3$, TMS): δ 52.1, 24.4, 19.4.

trans-1,2-Cyclohexanediol was prepared by method 1. The reaction conversion and recovery were determined by GC with hexadecane as an internal standard. Response factor of 1.404 was used for cyclohexanediol. Recovery: 34.0 %. ^{1}H NMR ($CDCl_3$, TMS): δ 3.36 [m, 2H, 2C(O)H], 2.48 (s, broad, 2H, 2OH), 1.98 (m, 2H), 1.71 (m, 2H), 1.27 (m, 4H). ^{13}C NMR ($CDCl_3$, TMS): δ 75.7, 32.9, 24.4.

2-Phenyl-1,2-propanediol was prepared by method 1. Removal of ethyl ether by the rotary evaporator and unreacted alkene in vacuo at room temperature for 24 h gave pure diol (29.1 mg, 55%). ^{1}H NMR ($CDCl_3$, TMS): δ 7.35 (m, 5H, arom-H), 3.78, 3.60 (dd, J = 11.3 Hz, 2H, $2CH_2$), 2.30 (broad, 2H, 2OH), 1.52 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS): δ 145.0, 128.4, 127.2, 125.1, 74.9, 71.1, 26.0. IR (neat): 3250-3450 (O-H), 3060-3080 (arom-H), 2880-2980 (C-H), 1600 and 1500 cm^{-1} (arom C=C).

α-Methylstyrene, α-methylstyrene oxide and 2-phenyl-1,2-propanediol was also obtained by method 3. Removal of ether by the rotary evaporator starting gave a mixture of starting alkene, epoxide and diol (molar ratio: 30:18:49) confirmed by GLC, ^{1}H and ^{13}C NMR.

β-Methylstyrene oxide was prepared by method 3. Removal of ether solvent by rotary evaporation gave a mixture (38 mg) which contained 54.4 % starting material and 45.6 % epoxide based on ^{1}H NMR. The pure epoxide was isolated by preparative TLC (silica gel, eluent: CH_2Cl_2/hexane 8:2 v/v). Yield: 37%. This product has two isomers, *cis* and *trans*-β-methylstyrene oxide with molar ratio of 10:90. *cis*-β-Methylstyrene oxide: ^{1}H NMR ($CDCl_3$, TMS): δ 7.3 (m, 5H, arom-H), 4.07 (d, J = 4.2 Hz, 1H, PhC$\underline{H}$O), 3.34 (qq, J = 4.2, 5.3 Hz, 1H, OCH), 1.09 (d, J = 5.3 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS): δ 147.9, 127.5, 126.6, 124.5, 57.5, 55.1, 12.6.

trans-β-Methylstyrene oxide: ^{1}H NMR ($CDCl_3$, TMS): δ7.3 (m, 5H, arom-H), 3.58 (d, J = 2.1 Hz, 1H, PhC<u>H</u>O), 3.08 (dq, J = 2.1, 5.2 Hz, 1H, OCH), 1.45 (d, J = 5.2 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS): δ137.7, 128.4, 128.0, 125.5, 59.5, 59.0, 17.9.

1-Phenyl-1,2-propanediol was prepared by method 1. After evaporation of ether using the rotary evaporator, the product was dried in vacuo at room temperature for 24 h to remove unreacted alkene. Diol yield: 42%. NMR showed a 50/50 mixture of 2 racemic diols: *erythro*- and *threo*-1-phenylpropane-1,2-diols. *erythro*-1-Phenylpropane-1,2-diol: ^{1}H NMR ($CDCl_3$, TMS): δ 7.35 (m, 5H, arom-H), 4.67 (d, J = 4.4 Hz, 1H, PhC<u>H</u>O), 4.0 (dq, J = 4.4, 6.3 Hz, 1H, CHO), 2.52 (broad, 2H, OH), 1.06 (d, J = 6.3 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS): δ 141.0, 128.5, 128.1, 126.8, 79.5, 72.2, 18.7. *threo*-1-Phenylpropane-1,2-diol: ^{1}H NMR ($CDCl_3$, TMS): δ 7.35 (m, 5H, arom-H), 4.37 (d, J = 7.8 Hz, 1H, PhCHO), 3.85 (dq, J = 6.3, 7.8 Hz, 1H, CHO), 2.52 (broad, 2H, OH), 1.05 (d, J = 6.3 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS): δ 140.3, 128.4, 127.8, 126.6, 77.5, 71.3, 17.2. IR (neat): 3250-3550 (O-H), 3060-3080 (arom-H), 2880-2980 (C-H), 1600 and 1500 cm^{-1} (arom C=C). *erythro*- and *threo*-1-phenylpropane-1,2-diols were identified by comparison of their ^{1}H NMR spectra with reported spectra data.[27(f)]

Styrene oxide was prepared by method 3. Evaporation of ether and unreacted styrene using the rotary evaporator gave nearly pure styrene oxide (yield: 46%). ^{1}H NMR ($CDCl_3$, TMS): δ 7.35 (m, 5H, arom-H), 3.87 (dd, J = 2.7, 3.8 Hz, 1H, PhCHO), 3.15 (dd, J = 3.8, 5.3 Hz, 1H, CHO), 2.81 (dd, J = 2.7, 5.3 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$, TMS): δ 137.5, 128.5, 128.2, 125.5, 52.4, 51.2.

1-Phenyl-1,2-ethanediol was prepared by method 1. The same work up procedure was used as that for purification of 1-Phenyl-1,2-propanediol, giving pure diol product (yield: 29%). ^{1}H NMR ($CDCl_3$, TMS): δ 7.35 (m, 5H, arom-H), 4.80 (m, 1H, PhCHO), 3.70 (m, 2H, CH_2O), 2.90 (broad, 1H, OH), 2.46 (broad, 1H, OH), 1.78 (m, 0.7H, H_2O). ^{13}C NMR ($CDCl_3$, TMS): δ 140.5, 128.5, 128.0, 126.1, 74.7, 68.1. IR (KBr): 3220-3340 (O-H), 3040 (arom C-H), 2880-2980 (C-H), 1500 (arom C=C), 1450 and 1350 cm^{-1} (C-H).

1-(4-Methylphenyl)-1,2-ethanediol was prepared by method 1. The same work up procedure was used as that for purification of 1-Phenyl-1,2-propanediol. Yield: 71%. ^1H NMR ($CDCl_3$, TMS): δ 7.18 (dd, J = 7.5 Hz, 4H, arom-H), 4.76 (dd, J = 3.5, 8.3 Hz, 1H, PhCHO), 3.70 (dd, J = 3.5, 10.7 Hz, 1H, CHO), 3.62 (dd, J = 8.3, 10.7 Hz, 1H, CHO), 3.34 (broad, 2H, OH), 2.32 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS): δ 137.7, 137.5, 129.2, 126.0, 74.6, 68.0, 21.1.

3-Phenyl-1,2-propanediol was prepared by method 1. Removal of ether by the rotary evaporator gave a mixture (18 mg) of starting alkene (8 %) and diol (92 %) determined by ^1HNMR. Pure diol was isolated by preparative TLC (silica gel, eluent: CH_2Cl_2). Yield: 31%. ^1H NMR ($CDCl_3$, TMS): δ 7.30 (m, 5H, arom-H), 3.96 (m, 1H, CH), 3.71 (dd, J = 2.6, 8.4 Hz, 1H, CH), 3.54 (dd, J = 5.5, 8.4 Hz, 1H, CH), 2.82 (qq, J = 4.2, 10.6 Hz, 1H, PhCH), 2.76 (dd, J = 5.5, 10.6 Hz, 1H, PhCH), 2.0 (broad, 2H, OH). ^{13}C NMR ($CDCl_3$, TMS): δ 137.6, 129.3, 128.7, 126.7, 73.0, 66.1, 39.8.

Calculation of the Composition of OXONE. Method A. The amount of $KHSO_4$ and K_2SO_4 could be estimated by measurement of pH of different OXONE solutions. Results are listed as follows:

Tot OXONE used (g)	0.0101	0.1005	0.2158
Volume (mL)	10.0	10.0	10.0
$[KHSO_5]$ (M)	2.76×10^{-3}	0.0276	0.0593
(g)	0.0042	0.0421	0.0903
$KHSO_4 + K_2SO_4$ (g)	5.90×10^{-3}	0.0584	0.1254
Measured pH	2.93	2.12	1.47
Ionic strength	0.012	0.113	1.32
Activity coeff. $Y_{HSO_4^-}$	0.894	0.761	0.585
$Y_{SO_4^{2-}}$	0.638	0.335	0.117
Calculated $[KHSO_4]$ (M)	1.60×10^{-3}	0.0209	0.0282
(g)	2.18×10^{-3}	0.0285	0.0384
Calculated $[K_2SO_4]$ (M)	2.14×10^{-3}	0.0165	0.0499
(g)	3.73×10^{-3}	0.0288	0.0870
$[KHSO_5]:[KHSO_4]:[K_2SO_4]$	1.73:1.0:1.34	1.67:1.27:1.0	2.10:1.0:1.77

Ionic strength: $I=0.5 \Sigma C_iZ_i^2$

where C_i is the concentration of species i; Z_i is the ion charge of species i.

Activity coefficients are estimated by Debye-Huckel equation:

$$-\log Y_1 = \frac{0.51 Z_1^2 \sqrt{I}}{1 + 0.33 a_1 \sqrt{I}}$$

a is an ion size parameter, and $a_{HSO_4^-} = a_{SO_4^{2-}} = 4$.

Because the more diluted solution is closer to the real solution, the result from a solution of 0.0101 g of OXONE in 10 mL of water should be considered. Therefore, the molar ratio of $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ in OXONE is 1.73:1.0:1.34.

Method B. The amount of $KHSO_4$ in OXONE can also be estimated by immediately measuring pH after $NaHCO_3$ solution is added to the OXONE solution. This estimation is based on the following equations:

$$NaHCO_3 + KHSO_4 = H_2CO_3 + NaKSO_4$$

provided that no CO_2 evolves, the pH of resulting solution is:

$$pH = pK_{a1} + \log\frac{[HCO_3^-]}{[H_2CO_3]} = 6.37 + \log\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\log\frac{[H_2CO_3]}{[HCO_3^-]} = \log\frac{[NaKSO_4]}{[HCO_3^-]} = 6.37 - pH$$

$[HCO_3^-] = [NaHCO_3]_o - [KHSO_4]$. Since pK_{a1} of HSO_4^- is low, $[NaKSO_4]$ is equivalent to the amount of $KHSO_4$ in OXONE. Results are listed as follows:

$NaHCO_3$ mmol	Oxone g	$KHSO_5$ mmol	water mL	pH	$KHSO_4$ mmol	$KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$
0.50	0.1610	0.443	2.3	6.38	0.253	1.75:1.0:1.34
0.30	0.1612	0.443	2.3	5.55	0.260	1.70:1.0:1.29

Both method A and B gave very close compositions of Oxone.

Calculation of initial and final pH in the oxidation of cyclohexene. The aqueous phase has 0.192 M of $KHSO_5$, 0.111 M of $KHSO_4$ and 0.149 M of K_2SO_4 at the beginning of the oxidation.

I. In the presence of $NaHCO_3$:

A. Initial pH

1. $[NaHCO_3]_o = 0.217$ M

$$pH = 6.37 + \log\frac{[HCO_3^-]}{[H_2CO_3]} = 6.37 + \log\frac{[HCO_3^-]_o-[HSO_4^-]}{[HSO_4^-]} =$$

$$6.37 + \log\frac{0.217-0.111}{0.111} = 6.35, \text{ measured: } 6.38.$$

2. $[NaHCO_3]_o = 0.261$ M

$$\mathrm{pH} = 6.37 + \log\frac{[HCO_3^-]_o\text{-}[HSO_4^-]}{[HSO_4^-]} = 6.37 + \log\frac{0.261\text{-}0.111}{0.111} = 6.50,$$

measured: 6.60.

3. $[HCO_3^-]_o = 0.283$

$$\mathrm{pH} = 6.37 + \log\frac{[HCO_3^-]_o\text{-}[HSO_4^-]}{[HSO_4^-]} = 6.37 + \log\frac{0.283\text{-}0.111}{0.111} = 6.58,$$

measured: 6.68.

4. $[HCO_3^-]_o = 0.304$ M

$$\mathrm{pH} = 6.37 + \log\frac{[HCO_3^-]_o\text{-}[HSO_4^-]}{[HSO_4^-]} = 6.37 + \log\frac{0.304\text{-}0.111}{0.111} = 6.63,$$

measured: 6.75.

5. $[NaHCO_3]_o = 0.348$ M

$$\mathrm{pH} = 6.37 + \log\frac{[HCO_3^-]_o\text{-}[HSO_4^-]}{[HSO_4^-]} = 6.37 + \log\frac{0.348\text{-}0.111}{0.111} = 6.70,$$

measured: 6.86.

6. $[NaHCO_3]_o = 0.434$ M

$$\mathrm{pH} = 6.37 + \log\frac{[HCO_3^-]_o\text{-}[HSO_4^-]}{[HSO_4^-]} = 6.37 + \log\frac{0.434\text{-}0.111}{0.111} = 6.83,$$

measured: 7.10.

B. Final pH

Assume that 0.152 M of $KHSO_5$ was converted to $KHSO_4$ (1 equiv. of substrate), and all CO_2 evolves.

1. $[HSO_4^-] = [HSO_4^-]_o + [HSO_5^-]_{conv} - [HCO_3^-]_o = 0.111 + 0.152 - 0.217 = 0.046$ M

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-} \qquad K_{a2} = \frac{a_H([SO_4^{2-}]Y_{SO_4^{2-}} + a_H)}{[HSO_4^-]Y_{HSO_4^-} - a_H}$$

Ionic strength (I) = 0.99 M, $Y_{HSO_4^-} = 0.605$, $Y_{SO_4^{2-}} = 0.134$, $K_{a2} = 0.012$

$a_H = 0.00827$, pH = 2.08, measured: 2.42.

2. $[HSO_4^-] = [HSO_4^-]_o + [HSO_5^-]_{conv} - [HCO_3^-]_o = 0.111 + 0.152 - 0.261 = 0.002$ M

I = 1.01 M, $Y_{HSO_4^-} = 0.602$, $Y_{SO_4^{2-}} = 0.132$, $K_{a2} = 0.012$

$a_H = 4.49 \times 10^{-4}$ M, pH = 3.35, measured: 4.18.

3. $[HSO_4^-] = [HSO_4^-]_o + [HSO_5^-]_{conv} - [HCO_3^-]_o = 0.111 + 0.152 - 0.283 = -0.02 <$ 0, thus, $HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

$$a_H = \sqrt{\frac{K_{a1}K_w + K_{a1}K_{a2}[HCO_3^-]}{K_{a1} + [HCO_3^-]}} = \sqrt{K_{a1}K_{a2}} = \sqrt{4.3x10^{-7}x4.8x10^{-10}} =$$

4.54×10^{-9} M, pH=8.34, measured: 7.65.

4. pH = 8.34, measured: 8.16.
5. pH = 8.34, measured: 8.68.
6. pH = 8.34, measured: 8.48.

C. Final pH

Assume that 0.152 M of $KHSO_5$ was converted to $KHSO_4$ (1 equiv of substrate), and no CO_2 evolves.

1. $[HSO_4^-] = [HSO_4^-]_o + [HSO_5^-]_{conv} - [HCO_3^-]_o = 0.111 + 0.152 - 0.217 = 0.046$ M

   $[H_2CO_3]$=0.217 M

   $$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-} \qquad K_{a2} = \frac{a_H([SO_4^{2-}]Y_{SO_4^{2-}} + a_H)}{[HSO_4^-]Y_{HSO_4^-} - a_H} = 0.012$$

   $$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

   $$K_{a1(H_2CO_3)} = \frac{a_H' a_{HCO_3^-}}{a_{H_2CO_3}} = \frac{(a_H')^2}{a_{H_2CO_3}} = 4.3 \times 10^{-7}$$

   $a_H' = 3.05 \times 10^{-4}$ M

   Ionic strength (I)= 1.21 M, $Y_{HSO_4^-} = 0.590$, $Y_{SO_4^{2-}} = 0.122$, $K_{a2} = 0.012$

   $a_H = 8.43 \times 10^{-3}$ M, $(a_H)_{tot} = a_H' + a_H = 8.74 \times 10^{-3}$ M, pH = 2.06, measured: 2.42.

2. $[HSO_4^-] = [HSO_4^-]_o + [HSO_5^-]_{conv} - [HCO_3^-]_o = 0.111 + 0.152 - 0.261 = 0.002$ M

   $[H_2CO_3] = 0.261$ M

   The same equilibrium equations can also be applied here.

$I = 1.27$ M, $\gamma_{HSO_4^-} = 0.587$, $\gamma_{SO_4^{2-}} = 0.119$.

$(a_H)_{tot} = a_H' + a_H = 3.35 \times 10^{-4} + 4.67 \times 10^{-4} = 8.02 \times 10^{-4}$ M, pH = 3.10, measured: 4.18.

3. $[HSO_4^-] = [HSO_4^-]_o + [HSO_5^-]_{conv} - [HCO_3^-]_o = 0.111 + 0.152 - 0.283 = -0.02 < 0$

Thus, $[NaHCO_3] = [NaHCO_3]_o - [HSO_4^-]_o - [HSO_5^-]_{conv} = 0.283-0.111-0.152 = 0.020$ M. $[H_2CO_3] = [HSO_4^-]_o + [HSO_5^-]_{conv} = 0.111 + 0.152 = 0.263$ M.

$NaHCO_3 + KHSO_4 = H_2CO_3 + NaKSO_4$

$$pH = 6.37 + \log \frac{[HCO_3^-]}{[H_2CO_3]} = 6.37 + \log \frac{0.020}{0.263} = 5.25, \text{ measured: } 7.65$$

4. $[HSO_4^-] = [HSO_4^-]_o + [HSO_5^-]_{conv} - [HCO_3^-]_o < 0$

$[NaHCO_3] = [NaHCO_3]_o - [HSO_4^-]_o - [HSO_5^-]_{conv} = 0.304 - 0.111 - 0.152 = 0.041$ M. $[H_2CO_3] = [HSO_4^-]_o + [HSO_5^-]_{conv} = 0.111 + 0.152 = 0.263$ M.

$$pH = 6.37 + \log \frac{[HCO_3^-]}{[H_2CO_3]} = 6.37 + \log \frac{0.041}{0.263} = 5.56, \text{ measured: } 8.16.$$

5. $[HSO_4^-] = [HSO_4^-]_o + [HSO_5^-]_{conv} - [HCO_3^-]_o < 0$

$[NaHCO_3] = [NaHCO_3]_o - [HSO_4^-]_o - [HSO_5^-]_{conv} = 0.348-0.111-0.152 = 0.085$ M. $[H_2CO_3] = [HSO_4^-]_o + [HSO_5^-]_{conv} = 0.111 + 0.152 = 0.263$ M.

$$pH = 6.37 + \log \frac{[HCO_3^-]}{[H_2CO_3]} = 6.37 + \log \frac{0.085}{0.263} = 5.88, \text{ measured: } 8.68.$$

6. $[HSO_4^-] = [HSO_4^-]_o + [HSO_5^-]_{conv} - [HCO_3^-]_o < 0$

$[NaHCO_3] = [NaHCO_3]_o - [HSO_4^-]_o - [HSO_5^-]_{conv} = 0.434 - 0.111 - 0.152 = 0.171$ M. $[H_2CO_3] = [HSO_4^-]_o + [HSO_5^-]_{conv} = 0.111 + 0.152 = 0.263$ M.

$$pH = 6.37 + \log \frac{[HCO_3^-]}{[H_2CO_3]} = 6.37 + \log \frac{0.171}{0.263} = 6.18, \text{ measured: } 8.48.$$

The above calculations show that the calculated initial pH values are close to those measured, while the final pH calculated by assuming no CO_2 presence is more comparable with measured data.

II In the presence of KOH:

A. Initial pH

1. $[KOH]_o = 0.087$ M.

$[HSO_4^-] = [HSO_4^-]_o - [KOH]_o = 0.111 - 0.087 = 0.024$ M

$I = 0.837$ M, $Y_{HSO_4^-} = 0.615$, $Y_{SO_4^{2-}} = 0.143$.

$$K_{a2} = \frac{a_H([SO_4^{2-}]Y_{SO_4^{2-}} + a_H)}{[HSO_4^-]Y_{HSO_4^-} - a_H}$$

$a_H = 4.66 \times 10^{-3}$M, pH = 2.33, measured: 2.55.

2. $[KOH]_o = 0.109$ M

$[HSO_4^-] = [HSO_4^-]_o - [KOH]_o = 0.111 - 0.109 = 0.002$ M

$I = 0.859$ M, $Y_{HSO_4^-} = 0.613$, $Y_{SO_4^{2-}} = 0.141$.

$$K_{a2} = \frac{a_H([SO_4^{2-}]Y_{SO_4^{2-}} + a_H)}{[HSO_4^-]Y_{HSO_4^-} - a_H}$$

$a_H = 4.39 \times 10^{-4}$ M, pH = 3.36, measured: 5.50.

3. $[KOH]_o = 0.174$ M

$[KOH] = [KOH]_o - [HSO_4^-]_o = 0.174 - 0.111 = 0.063$ M

pOH = 1.2, pH = 12.8, measured: 8.50.

B. Final pH

Assume that 0.152 M of $KHSO_5$ was converted to $KHSO_4$ (1 equiv. of substrate).

1. $[HSO_4^-] = [HSO_4^-]_o + [HSO_5^-]_{conv} - [KOH]_o = 0.111 + 0.152 - 0.087 = 0.176$ M

$I = 0.837$ M, $Y_{HSO_4^-} = 0.615$, $Y_{SO_4^{2-}} = 0.143$.

$$K_{a2} = \frac{a_H([SO_4^{2-}]Y_{SO_4^{2-}} + a_H)}{[HSO_4^-]Y_{HSO_4^-} - a_H}$$

$a_H = 0.0230$ M, pH=1.64, measured: 1.60.

2. $[HSO_4^-] = [HSO_4^-]_o + [HSO_5^-]_{conv} - [KOH]_o = 0.111 + 0.152 - 0.109 = 0.154$ M

$I = 0.859$ M, $Y_{HSO_4^-} = 0.613$, $Y_{SO_4^{2-}} = 0.141$.

$$K_{a2} = \frac{a_H([SO_4^{2-}]Y_{SO_4^{2-}} + a_H)}{[HSO_4^-]Y_{HSO_4^-} - a_H}$$

$a_H = 0.0210$ M, pH = 1.68, measured: 1.72.

3. $[HSO_4^-] = [HSO_4^-]_o + [HSO_5^-]_{conv} - [KOH]_o = 0.111 + 0.152 - 0.174 = 0.091$ M

$I = 0.924$ M, $Y_{HSO_4^-} = 0.608$, $Y_{SO_4^{2-}} = 0.137$.

$$K_{a2}=\frac{a_H([SO_4{}^{2-}]Y_{SO_4{}^{2-}} + a_H)}{[HSO_4{}^{-}]Y_{HSO_4{}^{-}} - a_H}$$

$a_H = 0.0142$ M, pH = 1.85, measured: 1.88.

The above calculations show that both initial and final pH calculated for each oxidation mixture fit these measured values. This is another evidence that the calculation of OXONE composition is reliable.

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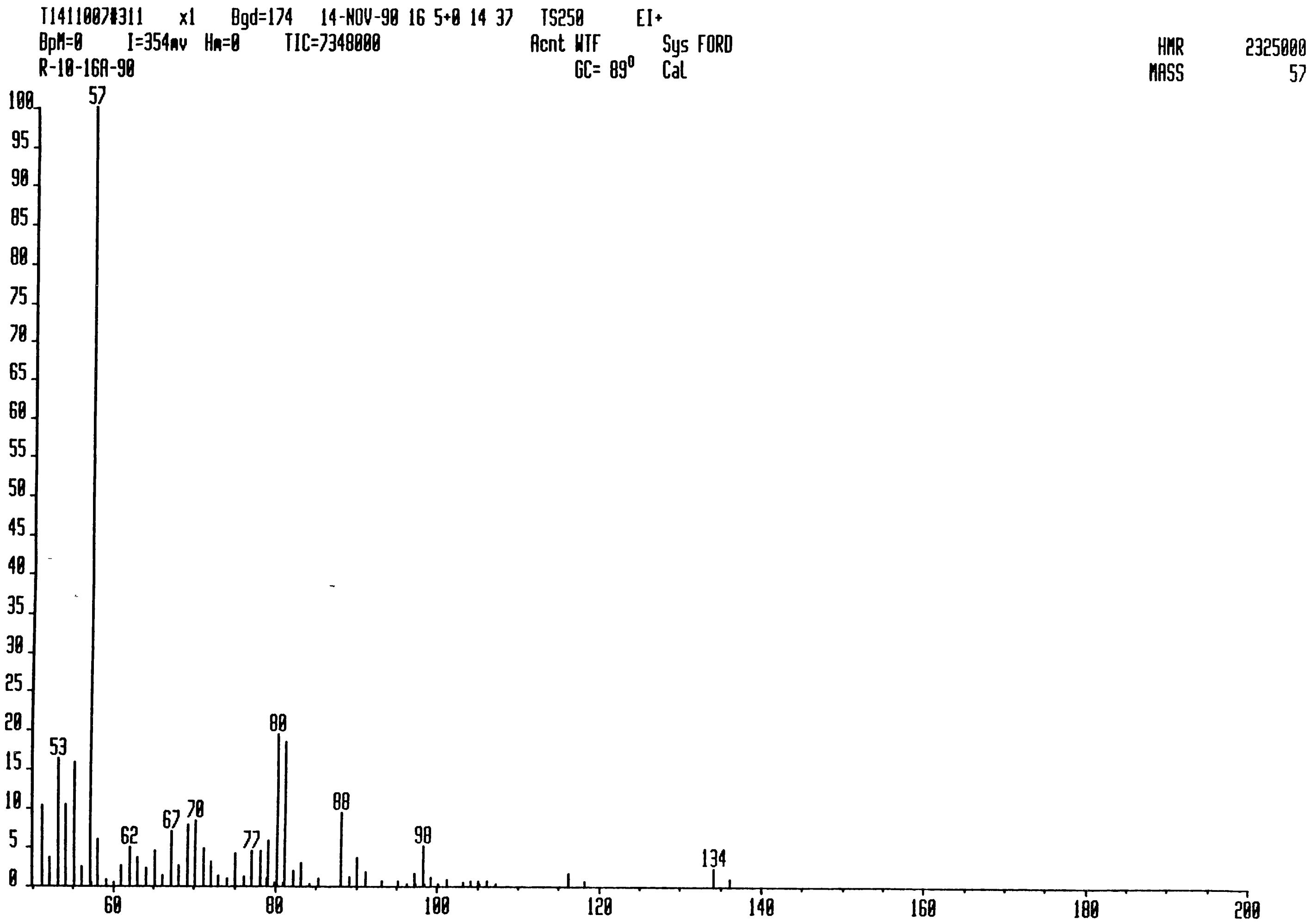
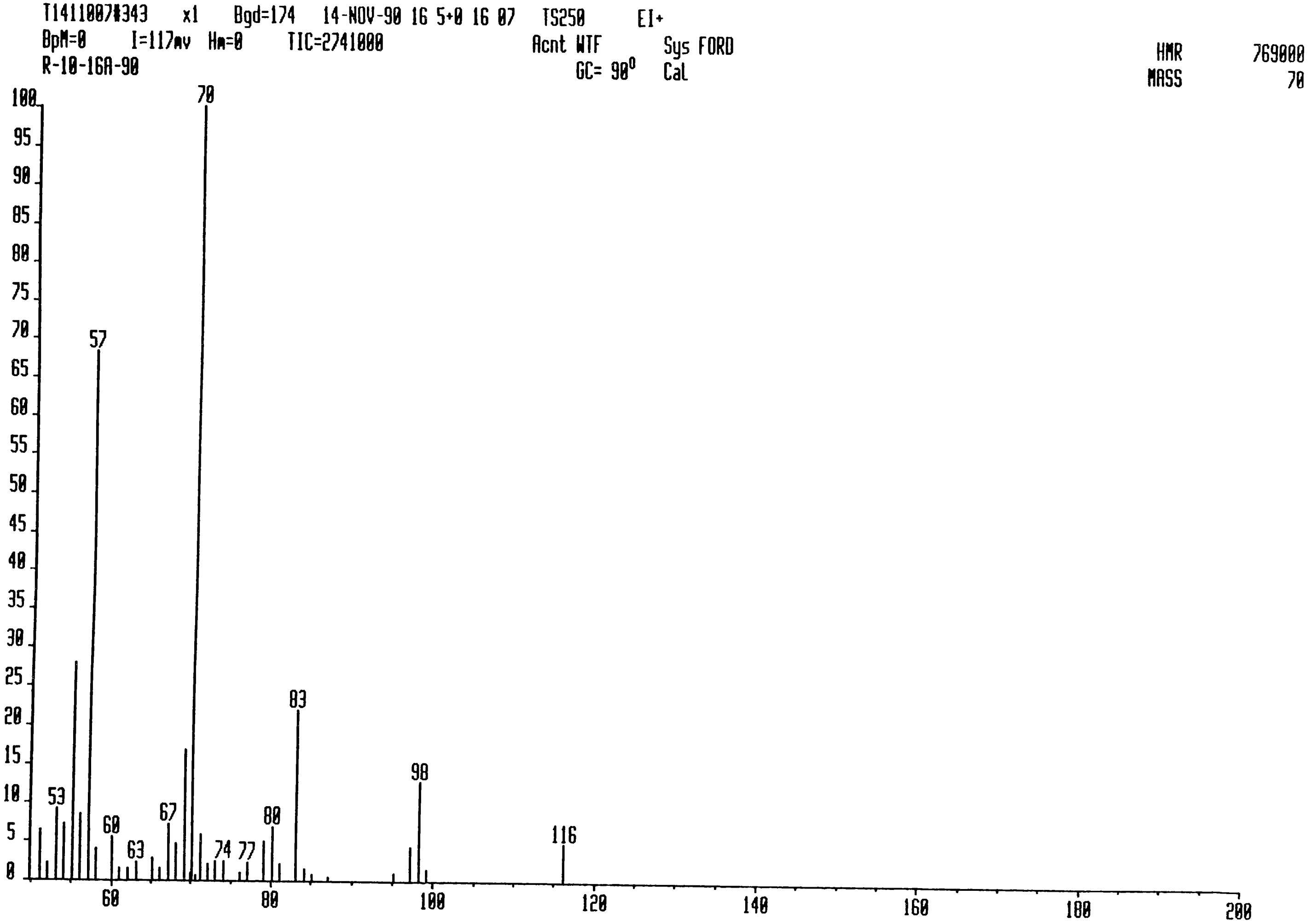
APPENDIX

SELECTED MASS AND NMR SPECTRA

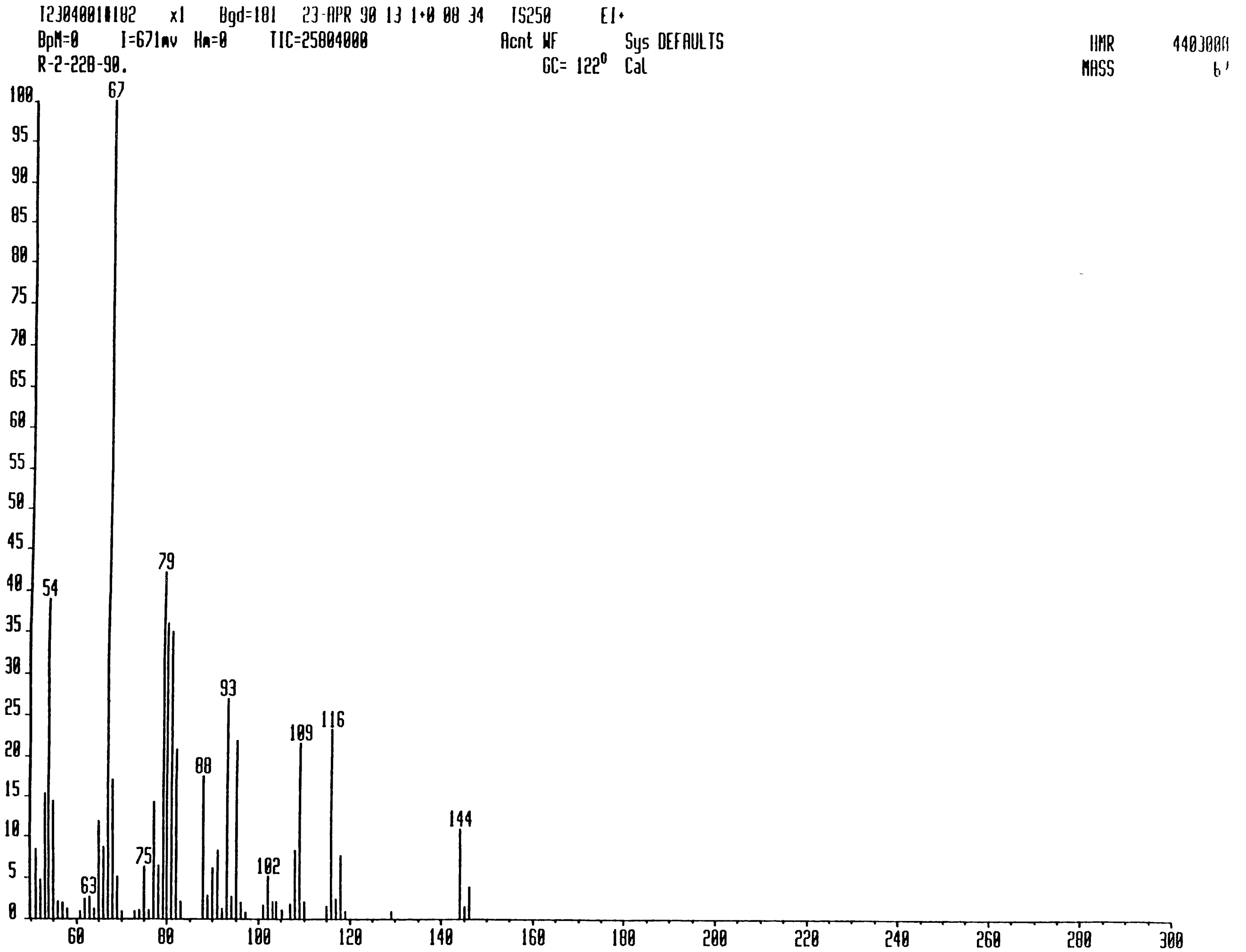


Spectrum 1. Mass Spectrum of *trans*-2-Chlorocyclohexanol

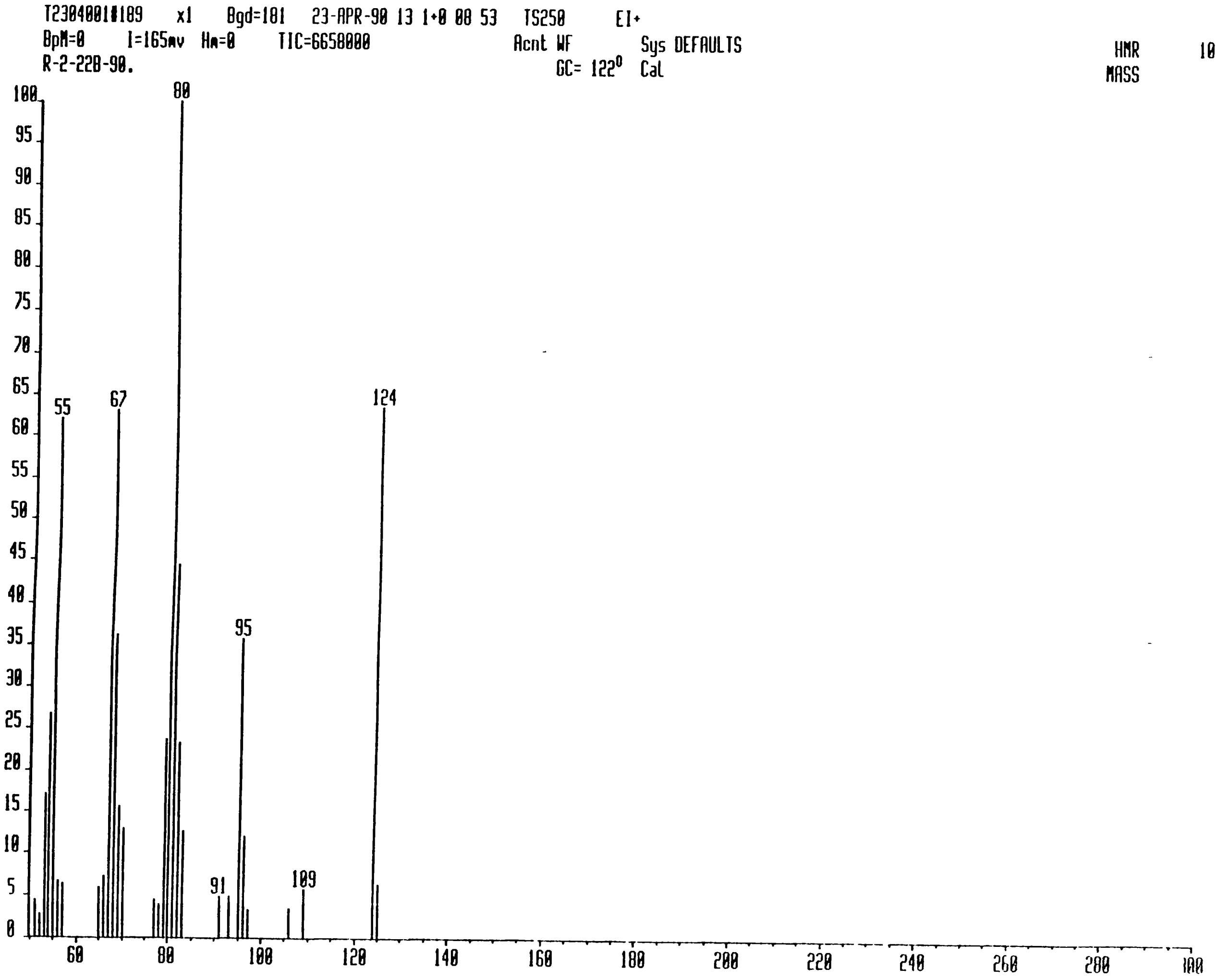
Spectrum 2. Mass Spectrum of 1,2-Cyclohexanediol



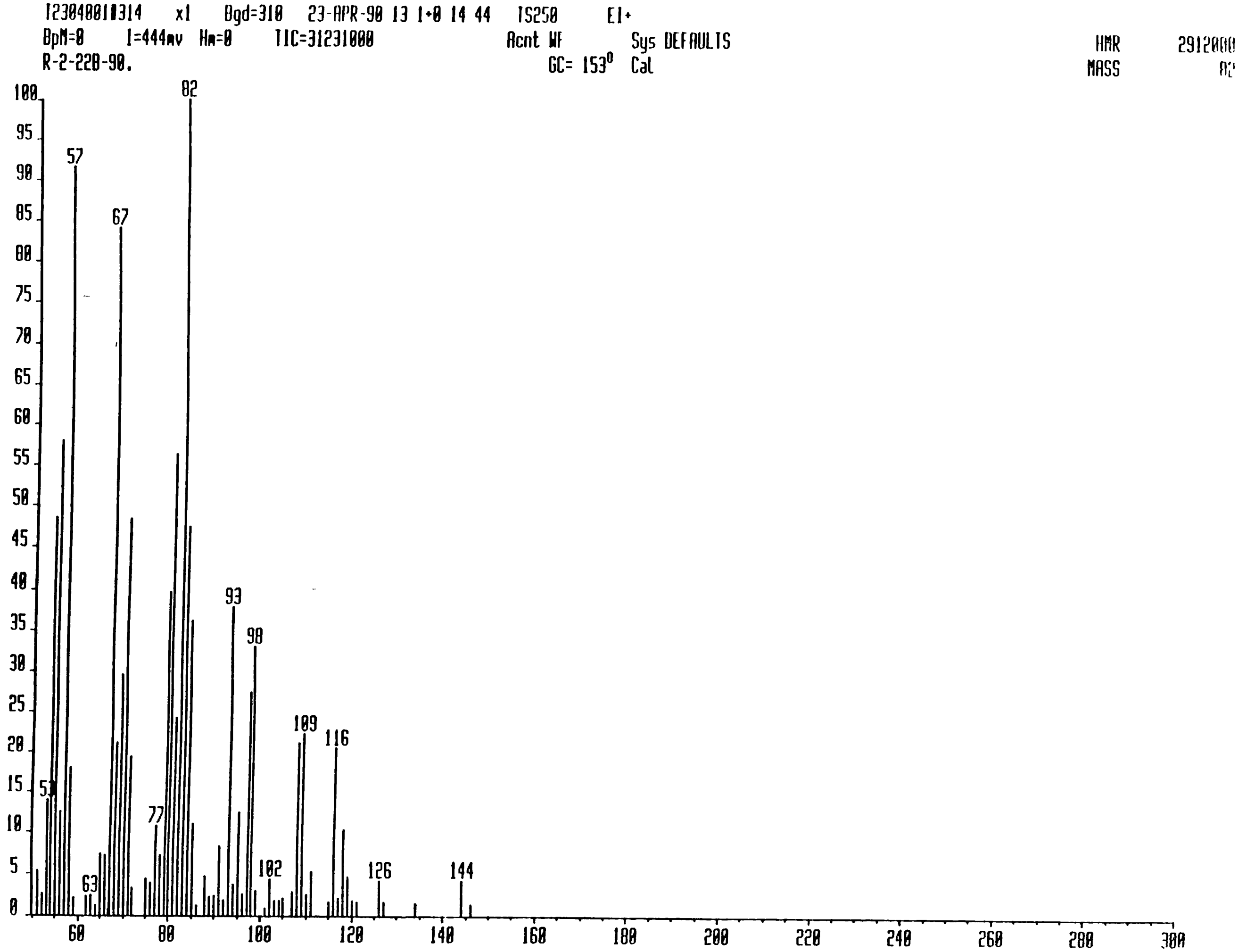
Spectrum 3. Mass Spectrum of 3-Chlorocyclooctene



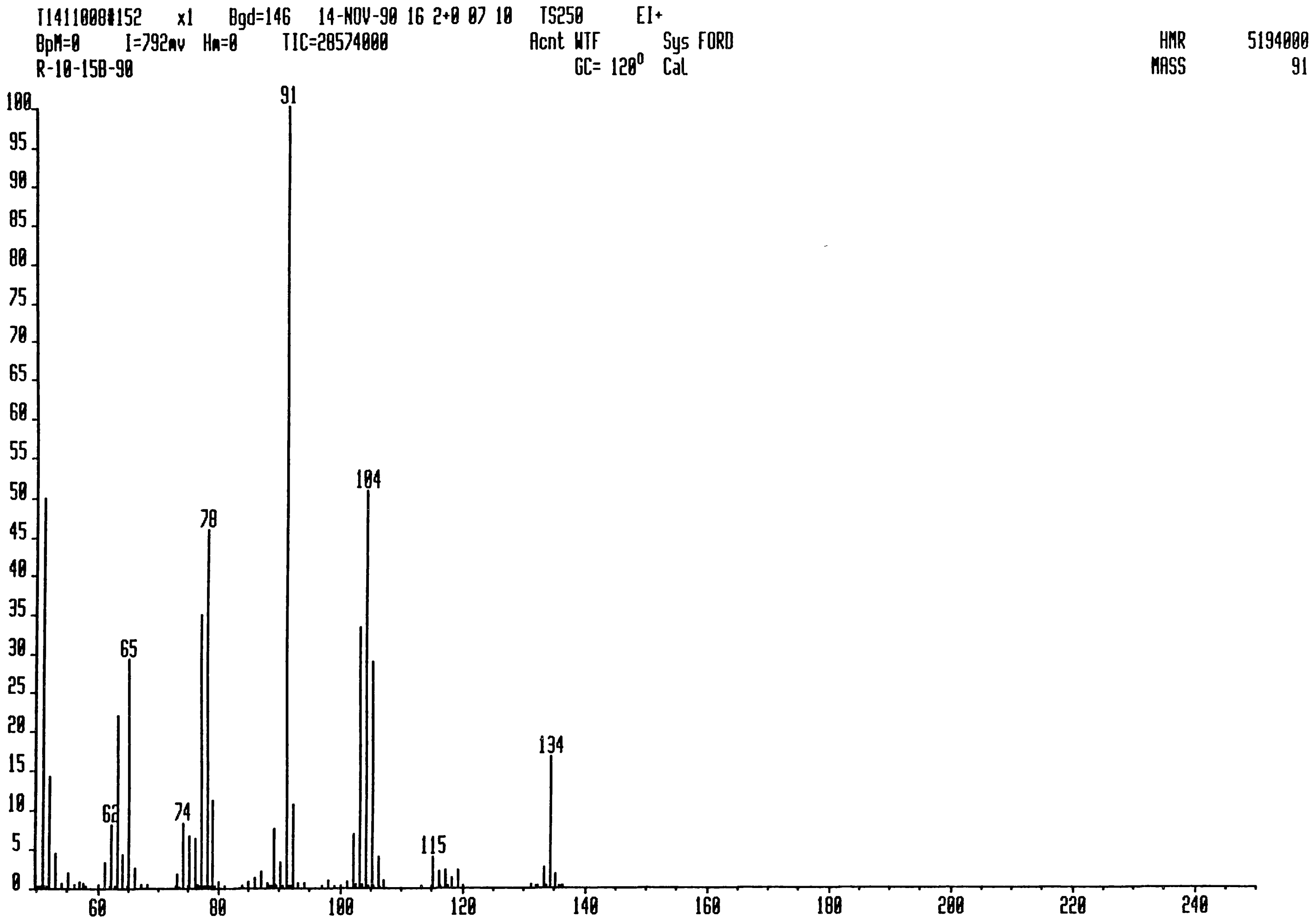
Spectrum 4. Mass Spectrum of 3-Cyclooctenone



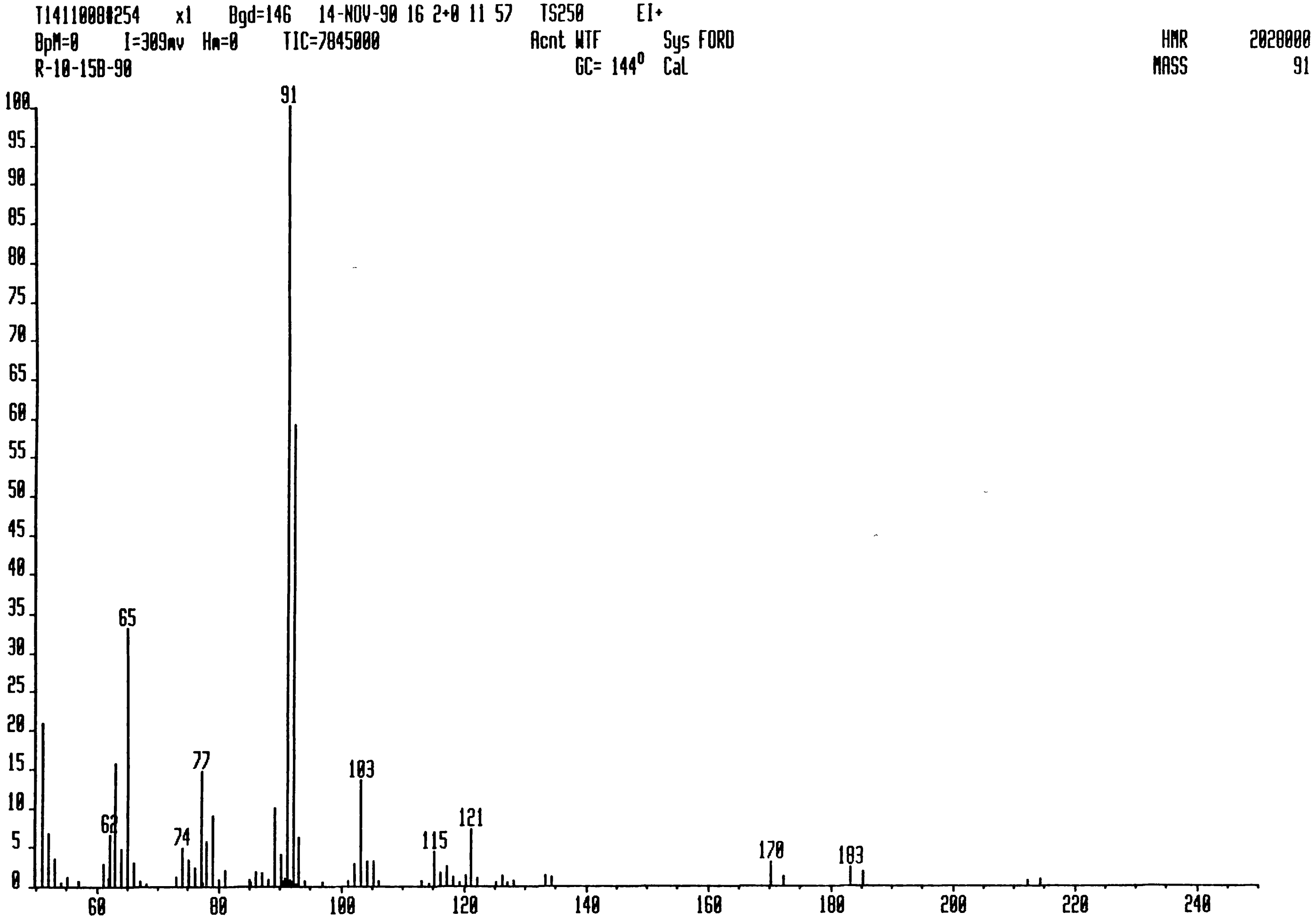
Spectrum 5. Mass Spectrum of 2-Chlorocyclooctanol



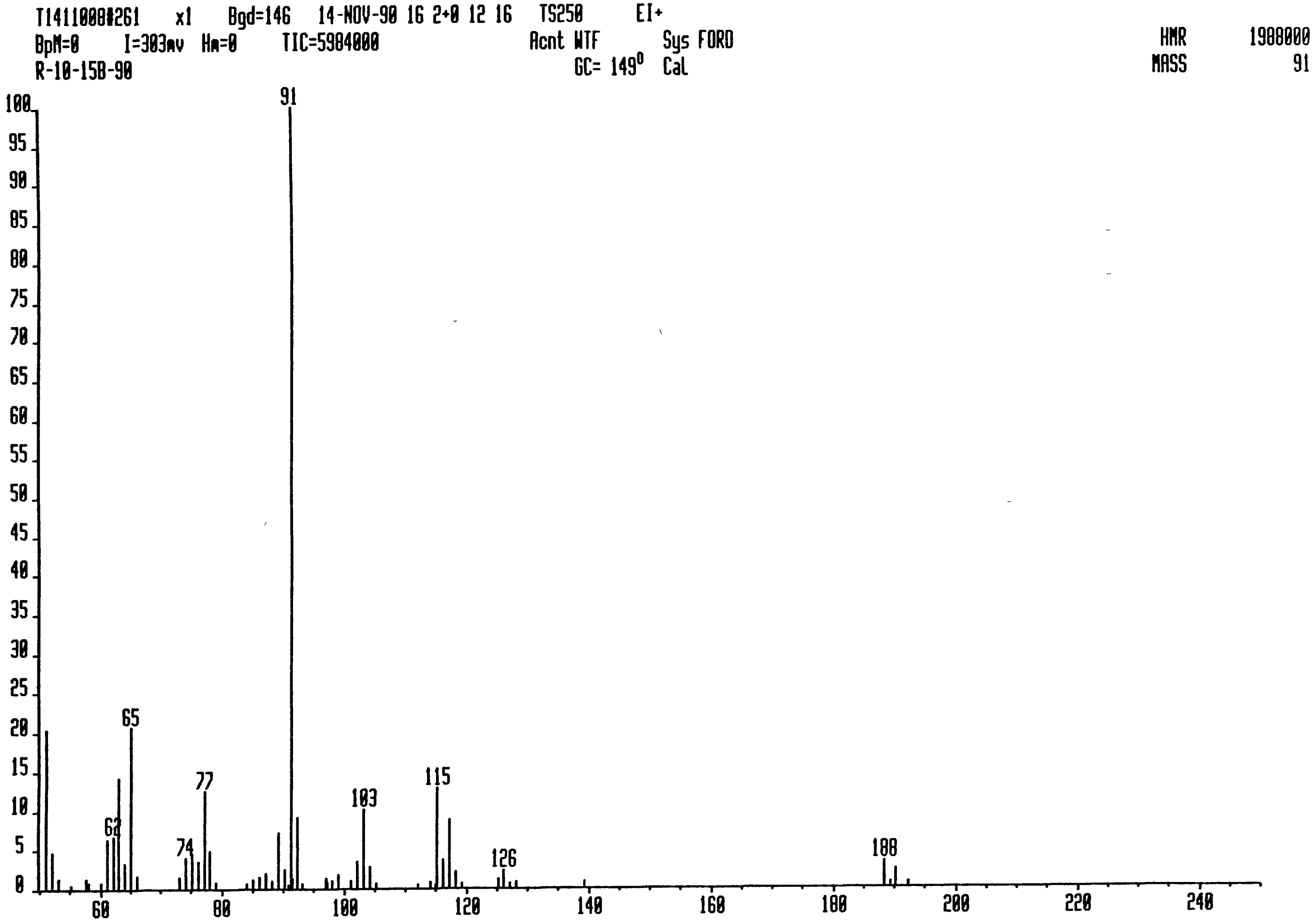
Spectrum 6. Mass Spectrum of 1,2-Epoxy-3-phenylpropane



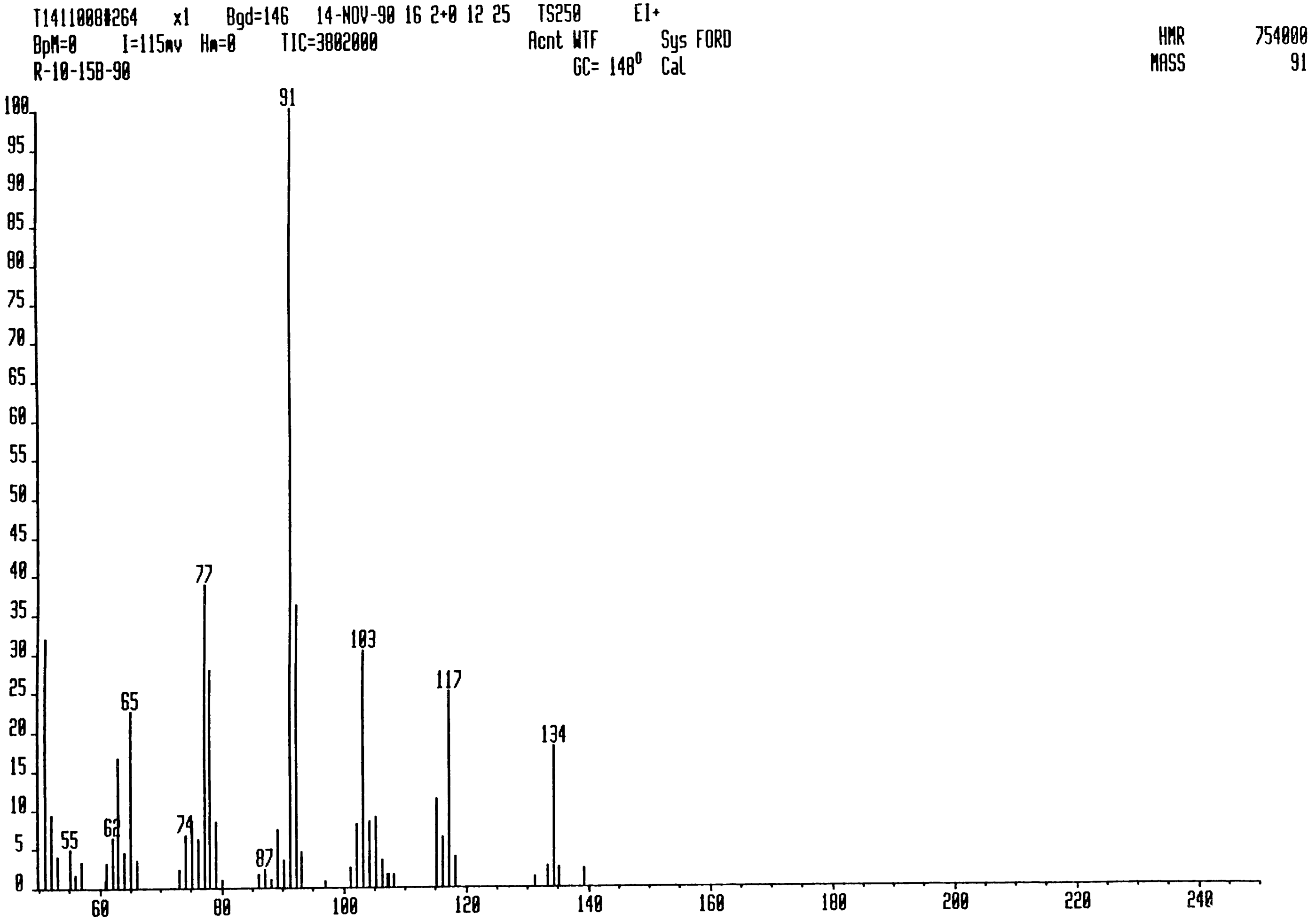
Spectrum 7. Mass Spectrum of 1-Chloro-3-phenylpropan-2-ol



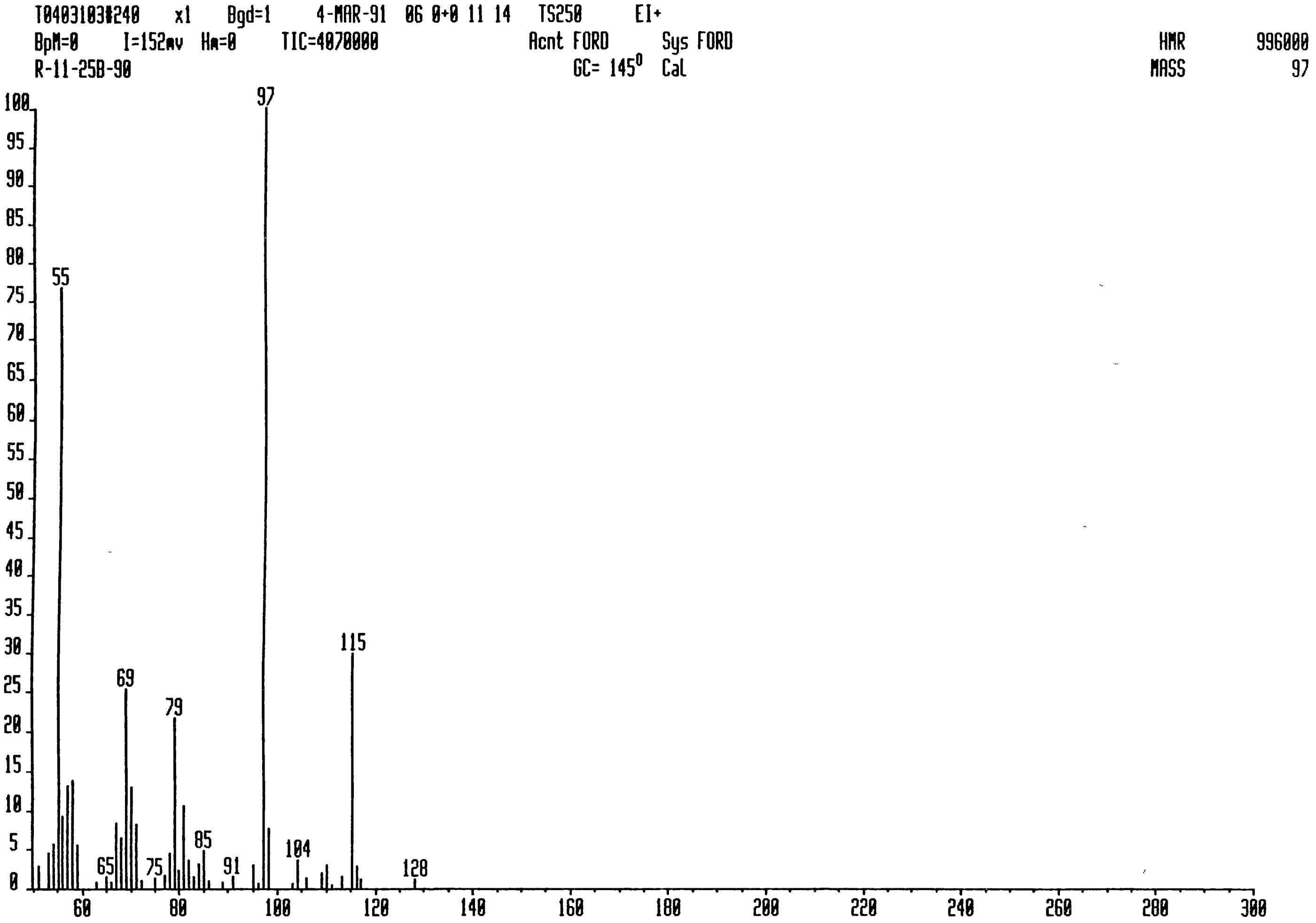
Spectrum 8. Mass Spectrum of 1,2-Dichloro-3-phenylpropane



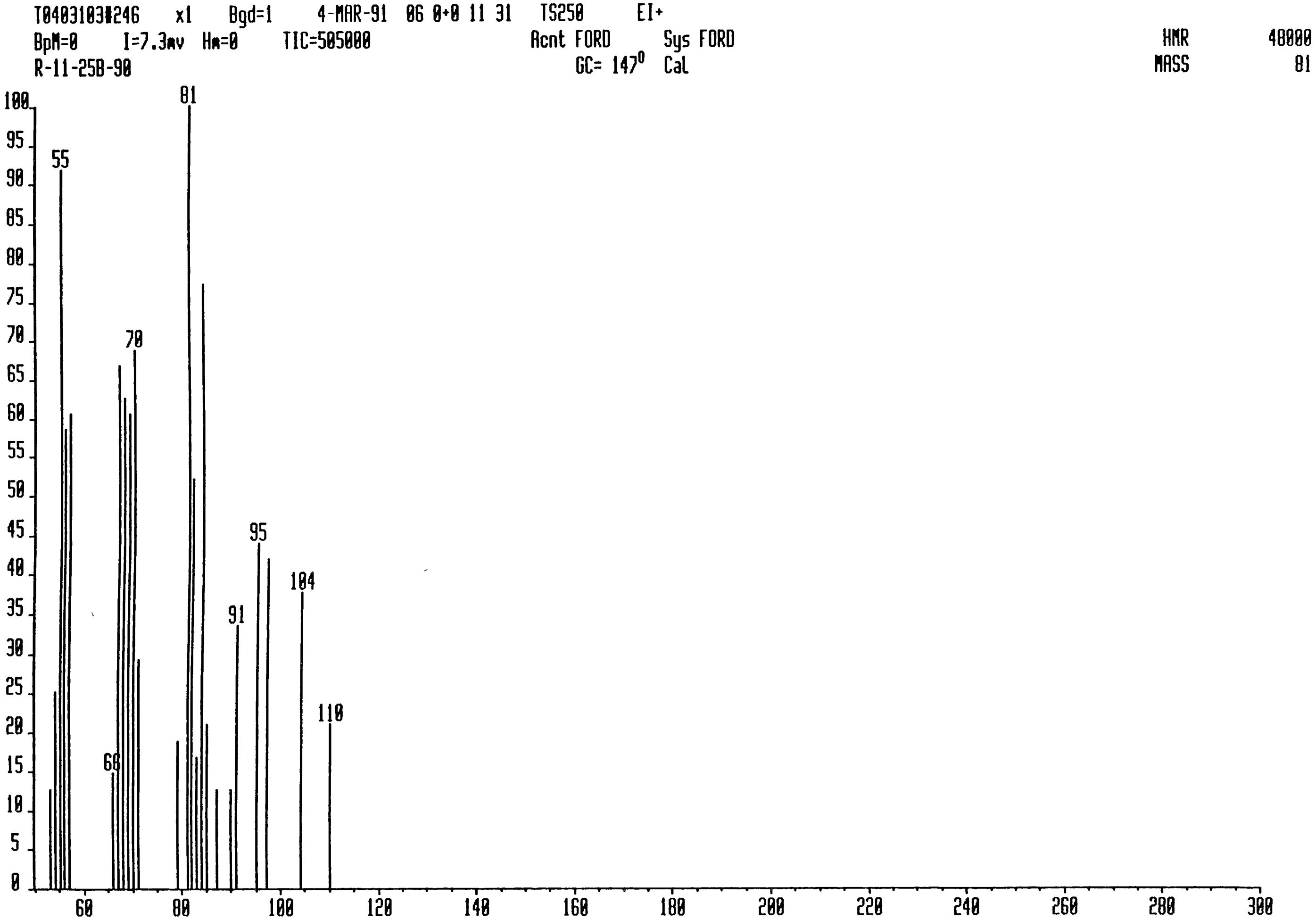
Spectrum 9. Mass Spectrum of 3-Phenyl-1,2-propanediol



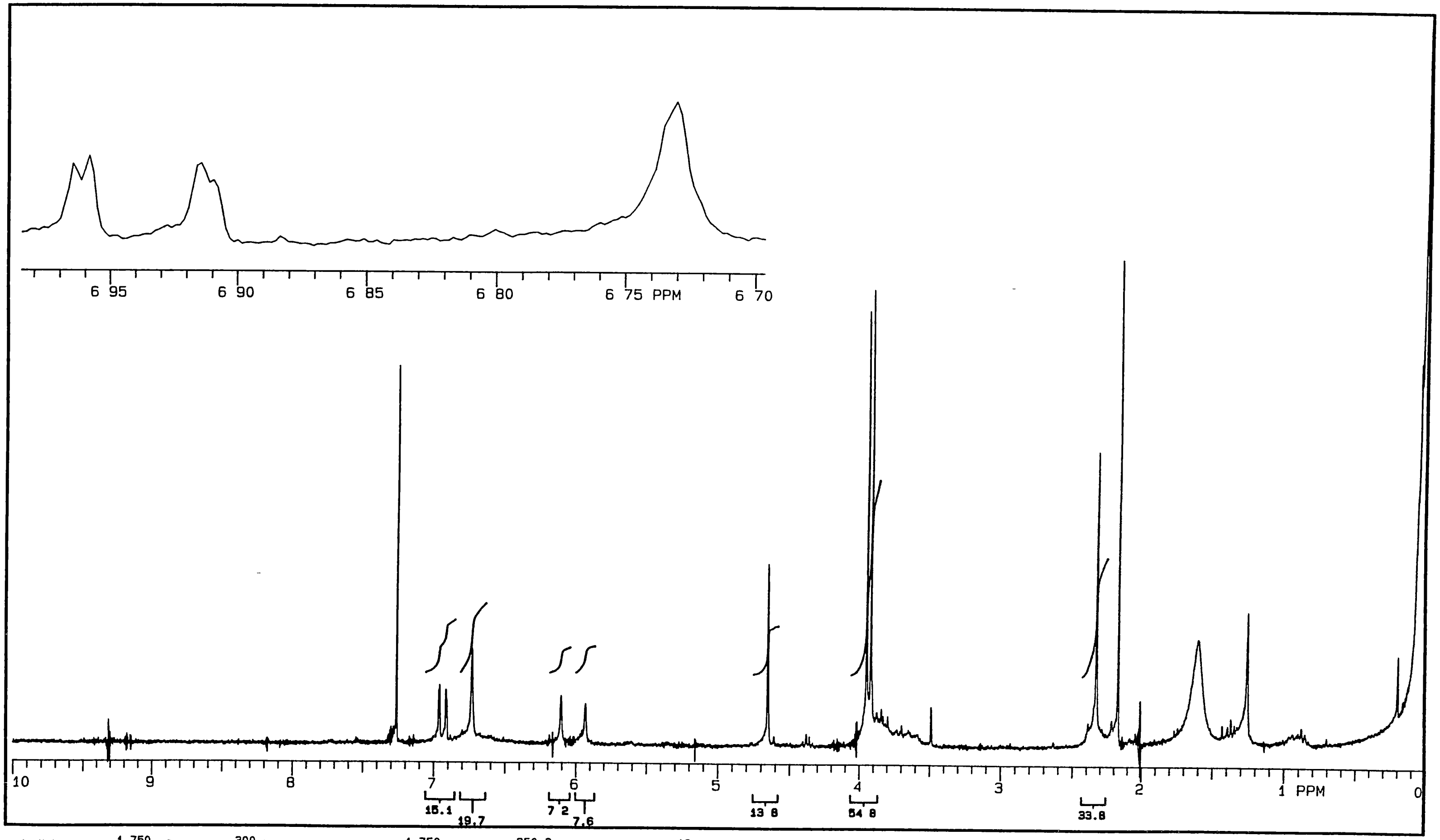
Spectrum 10. Mass Spectrum of 1-Chloro-2-octanol



Spectrum 11. Mass Spectrum of 1,2-Octanediol



Spectrum 12. ^1H NMR Spectrum of 4-Hydroxy-3-(2-hydroxy-3-methoxy-5-methylphenyl)-5-methoxybenzyl Alcohol



OBSERVE

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Offset 700 Hz
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Delay 0 sec
Pulse Width 12 0 µsec
Transients 300

DECOUPLE

Nucleus 1 750
Offset 350 3 Hz
Mode NNN
Power 20 db
Modulation Mode C
Freq 200 Hz
Pulse Width µsec
Power Mode ---

PLOT/PROCESSING

FN 16 K RE --- sec CD --- sec
LB --- Hz AF --- sec CCD ---
Width 2999 4 Hz/ppm Start 0 Hz/ppm
Reference

EXPERIMENT

Pulse Sequence STD1H
Tube OD mm
Temp --- °C
Solvent CDCL3

SAMPLE

BP-2

Number
File WZ005H
Date 09-20-91
XL XLAA 300

2

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