# CHAPTER 1

# INTRODUCTION

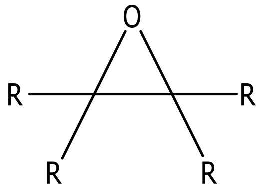
## 1.1 Introduction

The methods of production of various compounds have been received considerable attention for a long time because they are important in processes to produce raw materials for manufacturers. Although some reactions can occur easily, it takes a long time to be converted to products. Many catalysts were developed for further applications. Several works were focused on catalytic synthesis, including both homogeneous and heterogeneous catalysis.

Epoxidation is one of the fundamental oxidation reactions in industry that is a highly attractive topic in current chemical research (Arnold, et al., 2001). Epoxide can react with other chemicals to yield various substances such as halohydrin (Soroka and Goldeman, 2005), polyethers (Wuu and Ping, 2004), diols (Thakur, et. al., 2005), and amino alcohols (Kamal, et. al., 2005).

### 1.1.1 Synthesis of epoxides

Epoxidation is a chemical reaction in which an oxygen atom is joined to an olefinically unsaturated molecule to form a cyclic, three-membered ether. This cyclic is called epoxide ring or oxirane ring (Morrison and Boyd, 1983). Most of their characteristics are quite similar to the linear ether.



R = H or alkyl group

**Figure 1** The structure of oxirane ring (epoxide ring)

Epoxidation of alkenes can be achieved by variety of oxidants. These include m-chloroperbenzoic acid (the most widely used reagents for epoxidation), dioxiranes, alkylhydroperoxide, hydrogen peroxide, bleach, iodosylbenzene and molecular oxygen. Examples of epoxide preparation with some reagent are summarized below.

#### 1.1.1.1 Epoxidation with peracids

Peracids are electrophilic due to the presence of the electron withdrawing groups on alkyl group. Electron-rich alkenes are more reactive to them than electron defective double bond. The general mechanism of this reaction is shown in Figure 2.

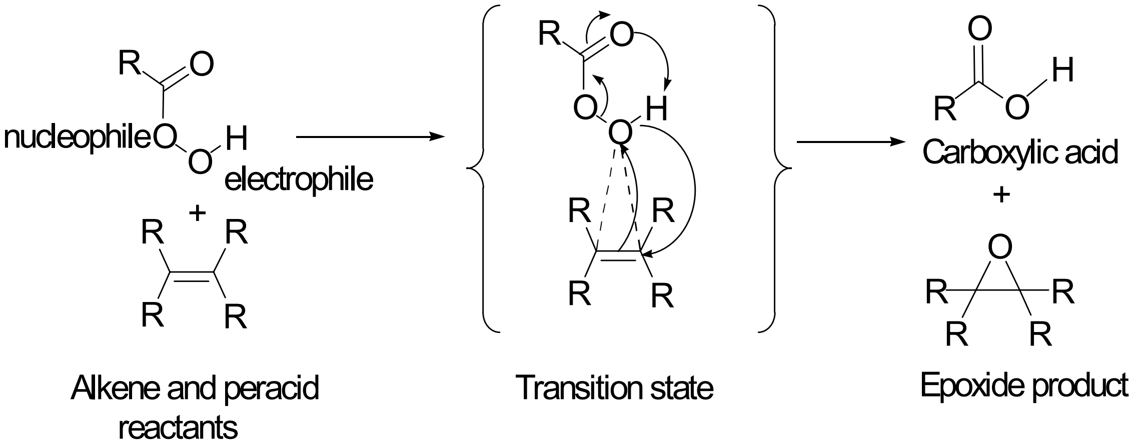


**Figure 2** The general mechanism of alkene epoxidation by peracids (Shi, Zhang and Wang, 2005)

Epoxidation occurs when the double bond is induced by electrophilic oxygen. The collision of the oxygen and the double bond leads to an activated complex. This state is called butterfly transition state, a single step reaction involving several changes. The process starts at the double bond functioning as the nucleophile. A bond to the slightly electrophilic oxygen is made. The weak O-O bond is broken and a C=O is formed. The original C=O is broken to form a new O-H bond. The original O-H and C=C are broken to form the new C-O bond of epoxide ring (Shi, Zhang and Wang, 2005).

Although peracids are a popular oxidising agent in laboratory, they are very expensive, hazardous to handle, non-selective for the epoxide formation and also able to form undesirable products, creating a lot of waste (Patil et. al., 2004). Therefore, it is not interesting to use in industry.

### 1.1.1.2 Epoxidation with hydroperoxides and alkyl hydroperoxides

For hydrogen peroxide, the reaction can be handled easily, leaving only water as a byproduct which is easily to be separated. In this reaction, two molecules of $H_2O_2$ are converted into two molecules of water and molecular oxygen. $H_2O_2$ and alkyl hydroperoxides require the presence of the transition metals or metal complexes (such as alumina (Mandelli, et. al., 2001), metalloporphyrin (Rebelo et. al., 2001)) to initiate epoxidation. Tert-butyl hydroperoxide (TBHP) is favorable because it is not expensive, soluble and stable in anhydrous solvents. The mechanism of alkene epoxidation by hydrogen peroxide in the case of $Al_2O_3$ is shown in Figure 3.

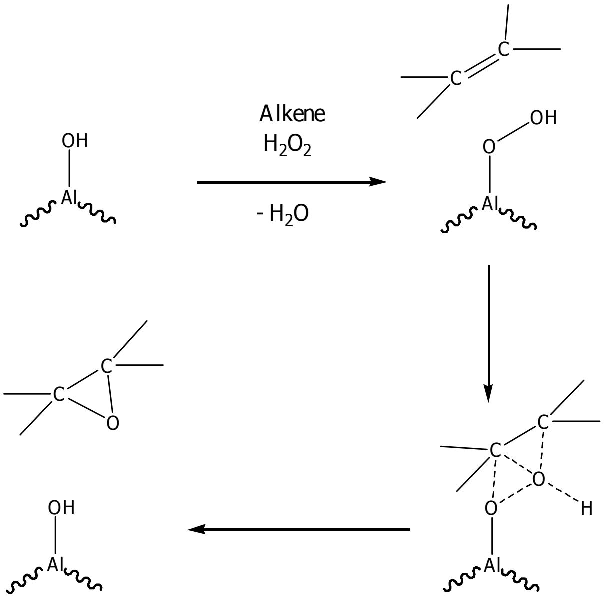
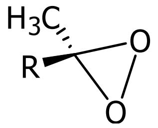


**Figure 3** Proposed mechanisms for the $Al_2O_3$-catalyzed alkene epoxidation (Mandelli, et. al 2001)

### 1.1.1.3 Epoxidation with dioxirane

The dioxiranes, 3-membered ring cyclic peroxides (Figure 4), are highly strained peroxides that serve as powerful oxidants in synthetic organic chemistry (Baboul et. al., 1998). They were found to be powerful oxidizing reagents with high reactivity towards both electron-rich and electron-deficient olefin epoxidation.



R = $CH_3$ dimethyldioxirane

R = $CF_3$ methyl(trifluoromethyl)dioxirane

**Figure 4** The structure of some dioxiranes

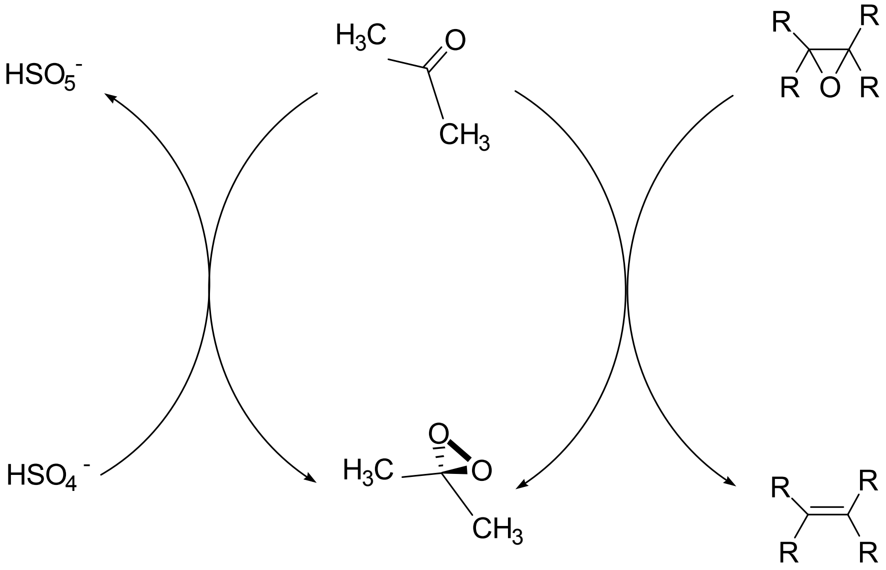


**Figure 5** Catalytic cycle for epoxidation with dioxirane (Kachasakul et. al., 2002)

Two most useful dioxiranes in epoxidation are dimethyldioxirane and methyl(trifluoromethyl)dioxirane. They are generated from ozone and their parent ketones. They can be used either in sito or in solutions as isolated species.

In situ generation of oxirane (biphasic system ($CH_2Cl_2/H_2O$) with ketone catalysts, ozone, olefins and phase transfer agent under an appropriate buffering condition) is suitable and easy for preparative epoxidation. The isolated species method was developed for the reactions where substrates or products are not stable under biphasic condition.

This method is in the fact a modification of ketone/ozone system where the dioxirane generated is isolated by distillation under vacuum and stored at low temperature. Both processes involve the nucleophilic attack of ozone at carbonyl carbon of ketones with subsequent loss of $HSO_4^-$. As shown in Figure 5, it is obvious that after oxygen transfer from dioxirane to olefin, the parent ketone is regenerated and the reaction cycle continues. Thus, in principle, ketones can be used in catalytic amount and the potential for asymmetric epoxidation catalysed by a chiral ketone becomes clear (Kachasakul et. al., 2002).

#### 1.1.1.4 Epoxidation with molecular oxygen

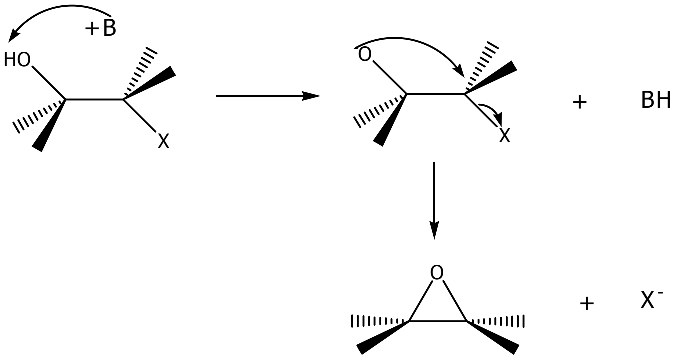
Molecular oxygen is the most attractive oxidant and used on a large scale in industry. Molecular oxygen does not react with alkenes spontaneously but has to be activated with the suitable catalyst. For instance, in the case of the industrial conversion of ethane to ethylene oxide, the technical process employs a catalyst consisting of silver particles supported on $\alpha$-alumina (Lambert et. al., 2005). A silver catalyst transfers one oxygen atom to ethane to form the desired product. The other oxygen atom is not used to produce more of the epoxide but it oxidizes ethylene to CO and water (Muslehiddinoglu et. al., 2003).

#### 1.1.1.5The other methods for epoxides preparation

##### 1.1.1.5.1 Conversion of halohydrins

The conversion of halohydrins into epoxide by the action of base is simple and adapted from the Williamson synthesis. An oxirane compound is obtained because both alcohol and halide happen to be part of the same molecule.

The base deprotonates the alcohol forming an alkoxide intermediate that enhances nucleophilicity. An intramolecular $S_N2$ reaction occurs as the alkoxide nucleophile attacks the electrophilic carbon at the anti position to the C-X bond, displacing the leaving group, the halide ion as shown in Figure 6 (Morrison and Boyd, 1983).



B = base and X = halogen

**Figure 6** Epoxide preparation by halohydrin (Morrison and Boyd, 1983).

### 1.1.1.5.2 Reaction of carbonyl compounds and sulfur ylides

The reaction of sulfur ylides with carbonyl compounds to give epoxides is an important synthetic method. The reaction of a sulfur ylide with an aldehyde initially forms betaine intermediates that undergo subsequent ring closure to furnish an epoxide with regeneration of the sulfide. The mechanism is shown in Figure 7.

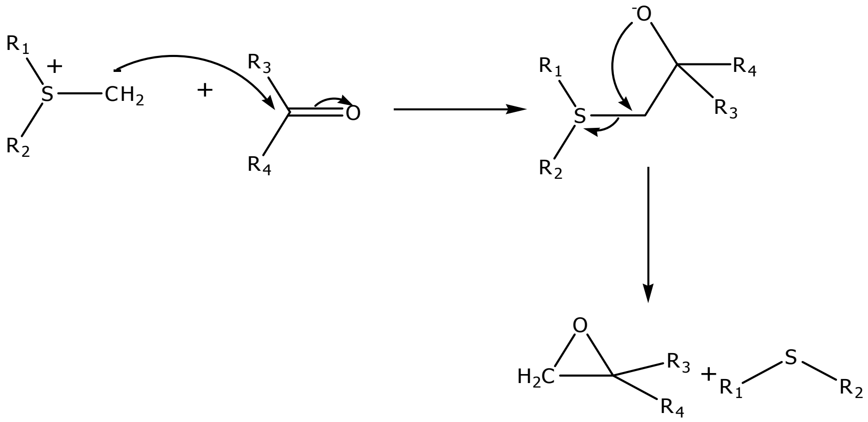


**Figure 7** Epoxide preparations by sulfur ylide (Aggarwal and Winn, 2004)

## 1.1.2 Quinones

### 1.1.2.1 Structured characteristic of quinone

Quinones are the compounds that have two carbonyl functional groups in the cyclic structure as shown in Figure 8.

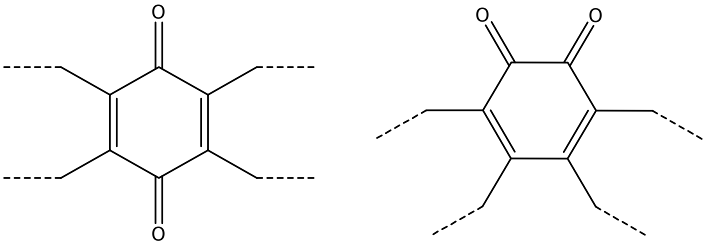


**Figure 8** Two basic structures of quinones

### 1.1.2.1 Role of quinones

Compounds in this group are widely distributed in the nature. Most of them have various bioactivities and play important roles in chemistry. Among a lot of quinones, the naphthoquinone derivatives have variety of bioactivities.

Vitamin K is one of the examples of naphthoquinone. It is the representative of natural naphthoquinones, which is known to have the property of antihemorrhage. It is an essential micronutrient present at low levels in the blood, but at much higher levels in various tissues including liver and bone. The structure of some kinds of vitamin K are shown in Figure 9, 10, and 11.There is an absolute requirement for vitamin K for the γ-carboxylation of specific glutamyl residues in several hepatic and extra-hepatic proteins. The γ-carboxylation of these proteins confers a greater binding affinity for calcium, hydroxyapatite (Reddi et. al., 1995).

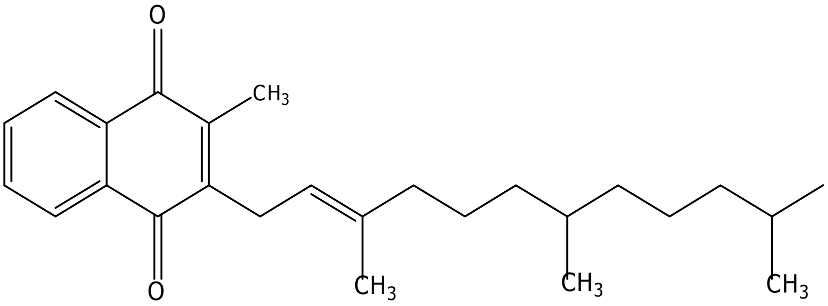


**Figure 9** The structure of phylloquinone (Vitamin $K_1$)

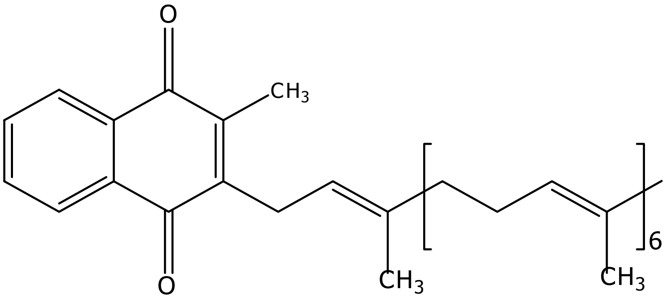


**Figure 10** The structure of menaquinone (Vitamin $K_2$)

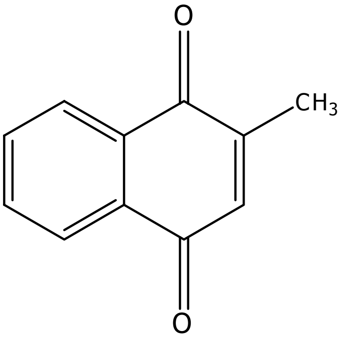


**Figure 11** The structure of menadione (Vitamin $K_3$)

Naphthoquinone derivatives can also be utilized for the animal drugs, antiprotozoal agents and infection drugs such as atovaquone that used for malaria chemotherapy in Africa (Mariga, Gil, Wernsdorfer, Bjorkman, 2005). The compound has the following structural formula:

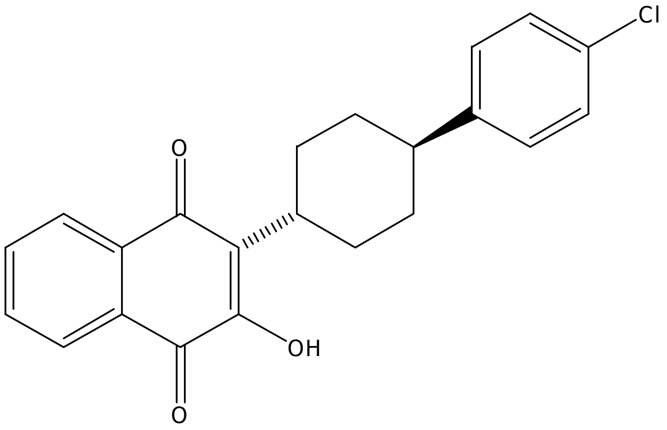


**Figure 12** The structure of mepron (atovaquone)

In the field of agriculture, quinone derivatives are agents that protect the crops by getting rid of pathogenic fungi, harmful insects, weeds and rats and raise the productivity of the farm products by improving or controlling their physiological functions. In the case of cosmetic, Henna has been used for more than 4000 years not only as a hair dye, but also as a body paint and tattoo dye. Today, semi-permanent hair dyes containing Henna as well as its pure dye ingredient Lawsone (2-hydroxy-1, 4-naphthoquinone; HNQ (Figure 13)) are widely used and have become increasingly popular due to their natural origin (Kirkland and Marzin, 2003).

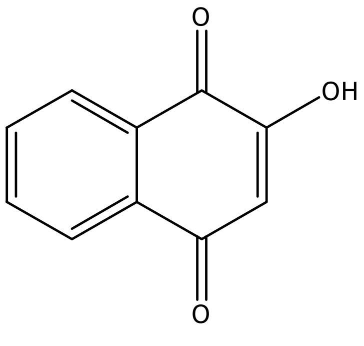


**Figure 13** The structure of 2-hydroxy-1, 4-naphthoquinone (Lawsone) (Knecht, Henseling and Loffler, 2000)

All of plants and cyanobacteria plastoquinone serves as an electron carrier between photosystem (PS) II and the cytochrome b6/f complex. It has been shown that in higher plants an important step of the plastoquinone biosynthesis is the formation of homogentisate from hydroxyphenylpyruvate, catalyzed by the enzyme 4-hydroxyphenylpyruvate dioxygenase (HPPD). This reaction of the plastoquinone biosynthesis pathway is shared by the synthesis of tocopherols and tocotrienols, which are collectively known as vitamin E and produces oxygen from water (Dahnhardt et. al., 2002). The mechanism of the photosynthesis is shown in Figure 14.

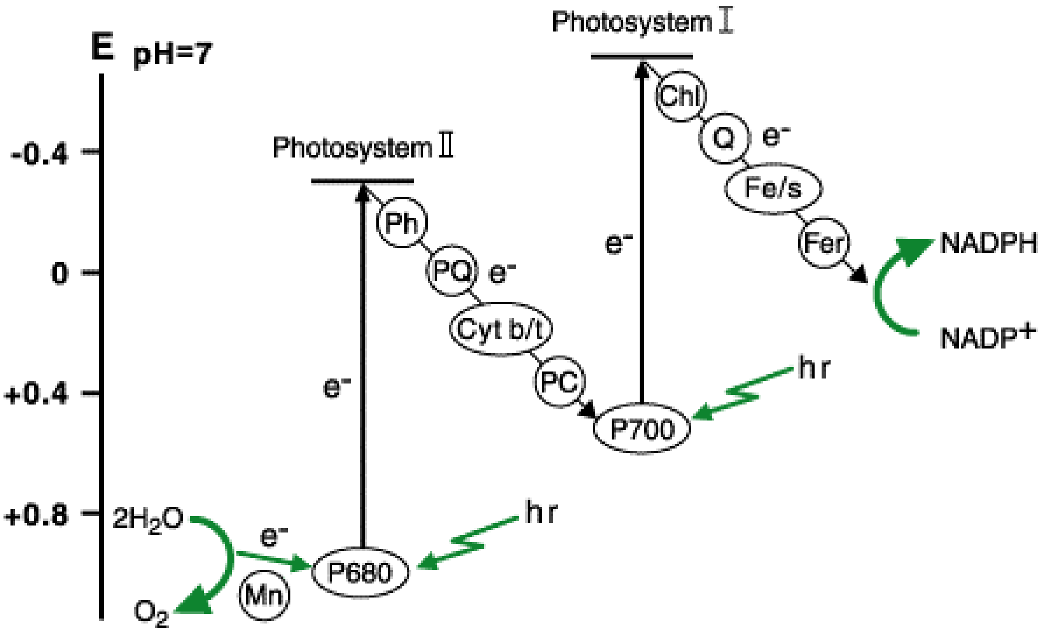


**Figure 14** The Z scheme in the photosynthesis (Prince, 1996)

For the suppression of generation of the hydrogen sulfide, some bacteria use sulfate ion as oxidizing agent to destroy organic substances. The result of this process provides energy for their life and hydrogen sulfide. This gas becomes sulfuric acid when it is oxidized by air. This strong acid is not only dangerous for human, but also effective for the corrosion of concrete. Anthraquinone was used to inhibit the generation of hydrogen sulfide by disturbing the electron transport of enzyme cytochrome C3 in the sulfate - reducing bacteria (Pires, et.al. 2003). The hydrogen sulfide suppression mechanism of anthraquinone in the sulfate-reducing bacteria is shown in Figure 15.

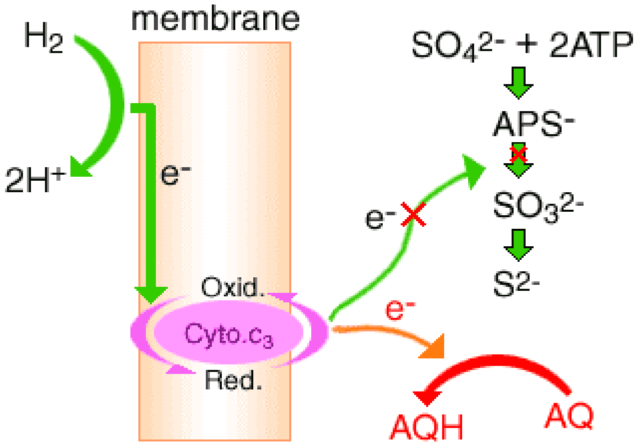


**Figure 15** $H_2S$ suppression mechanism of anthraquinone in the sulfate-reducing bacteria (www.quinone.com).

The characteristics of quinones are very important in living organism and are applied in many industrial processes such as desulfurization, generation control of hydrogen sulfide, recovery of precious metals, absorption of oxygen and catalytic reaction in hydrogen peroxide manufacturing.

### 1.1.2.3 Acid-base and redox properties of quinones

Some quinones have proton transfer coupled with electron transfers which play an important role in biological systems as shown in Figure 16 (Pekmez, Can and Yildiz, 1993).

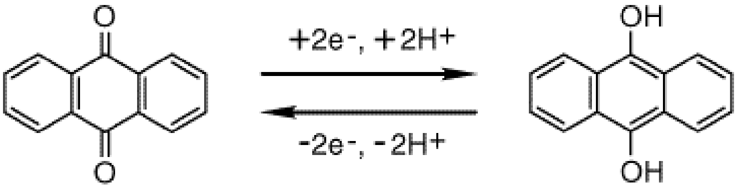


**Figure 16** Redox reaction of anthraquinone

Redox reaction is the most important property of quinones especially benzoquinone, naphthoquinone and anthraquinone. Oxidation – reduction potential of quinones can be utilized to reduce some metal ions to the element forms if they have the redox potential higher than quinones. The relationship of redox potential between metals and quinone are shown in Figure 17.

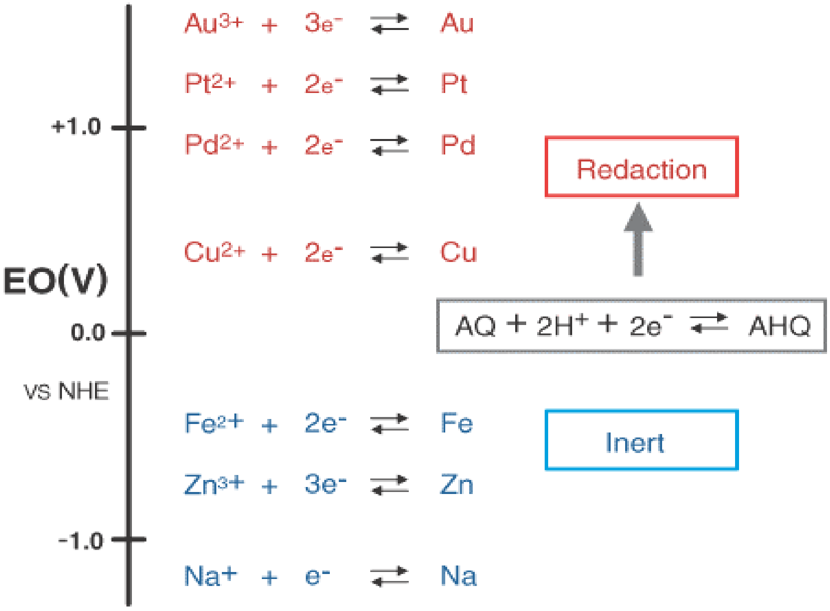


**Figure 17** The relationship of redox potential between metals and quinone (www.quinone.com)

Because the potential is lowered when pH rises, it is possible to control the potential of the quinones to the desirable value by the control of pH.

Proton transfer is one of the most fundamental reactions and it plays crucial role in many systems (Arzhantsev, Takeuchi and Taharos, 2000). This reaction can occur and is the characteristic of dihydroxyanthraquinones. The acidic functional group in their structures is a hydroxy group in the form of phenolic. Proton transfers of these phenolic compounds occur via tautomerization.

Not only proton can be transfered to carbonyl group in their structures but also dihydroxyanthraquinones are deprotonated to proton acceptor in the solution.

From Ab initio investigation of 1, 4 - dihydroxyanthraquinone, 1, 5-dihydroxyanthraquinone and 1, 8 - dihydroxyanthraquinone, the computational study explained that 1, 4 - dihydroxyanthraquinone and 1, 5 - dihydroxyanthraquinone can undergo two intramolecular proton transfers but only one in 1, 8 - dihydroxyanthraquinone. Delocalizations of proton in their structures are shown in Figure 18-20 (Ferreiro and Otero, 2001).

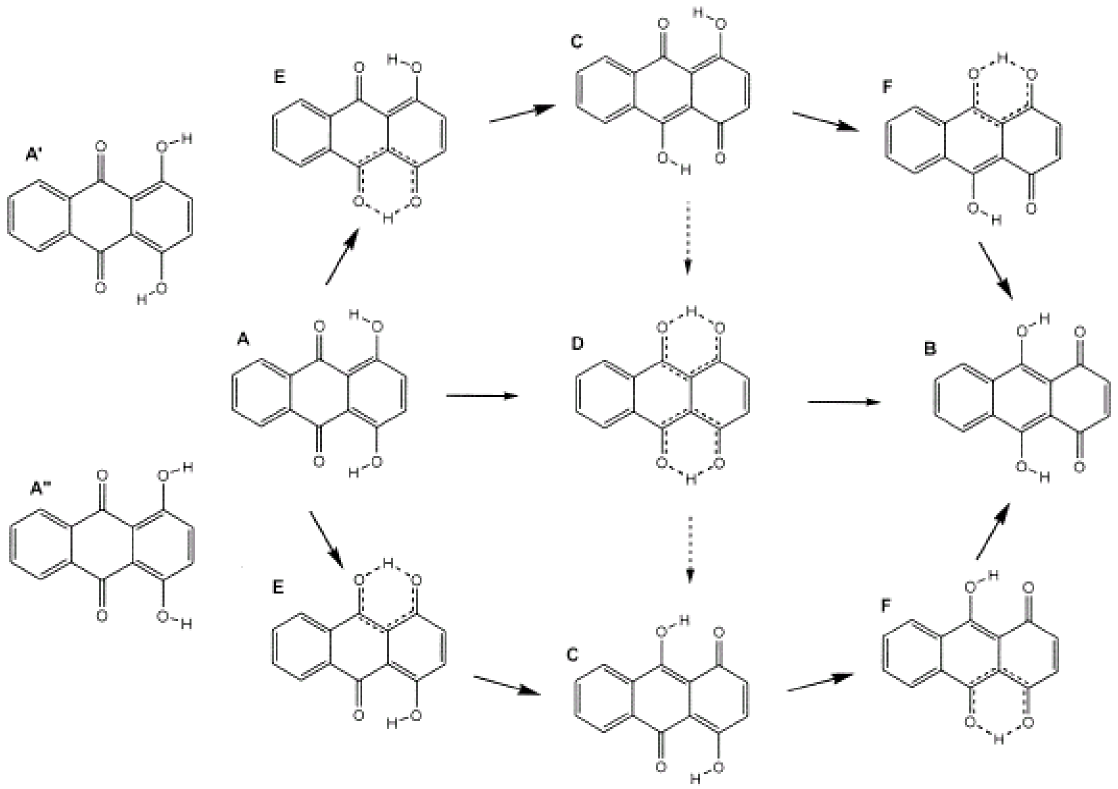


**Figure 18** Tuatomeric structures resulting from proton transfer in 1, 4-DHAQ (A-F) and structures bearing no hydrogen bond (A′, A″)

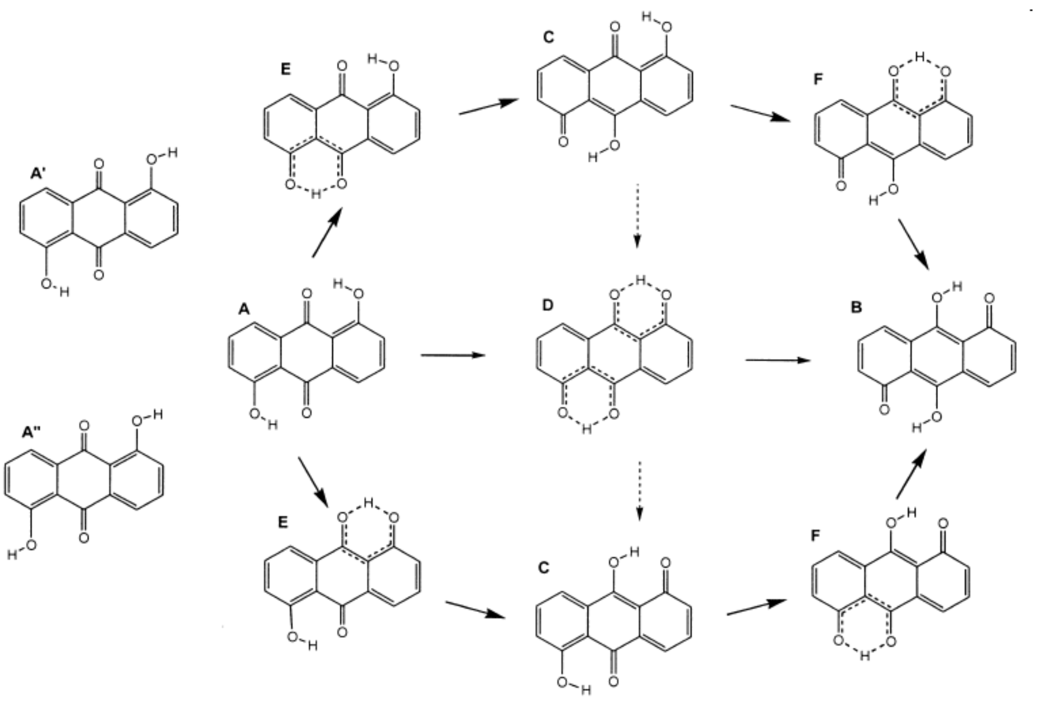


**Figure 19** Tuatomeric structures resulting from proton transfer in 1, 5-DHAQ (A-F), and structures bearing no hydrogen bond (A′, A″)

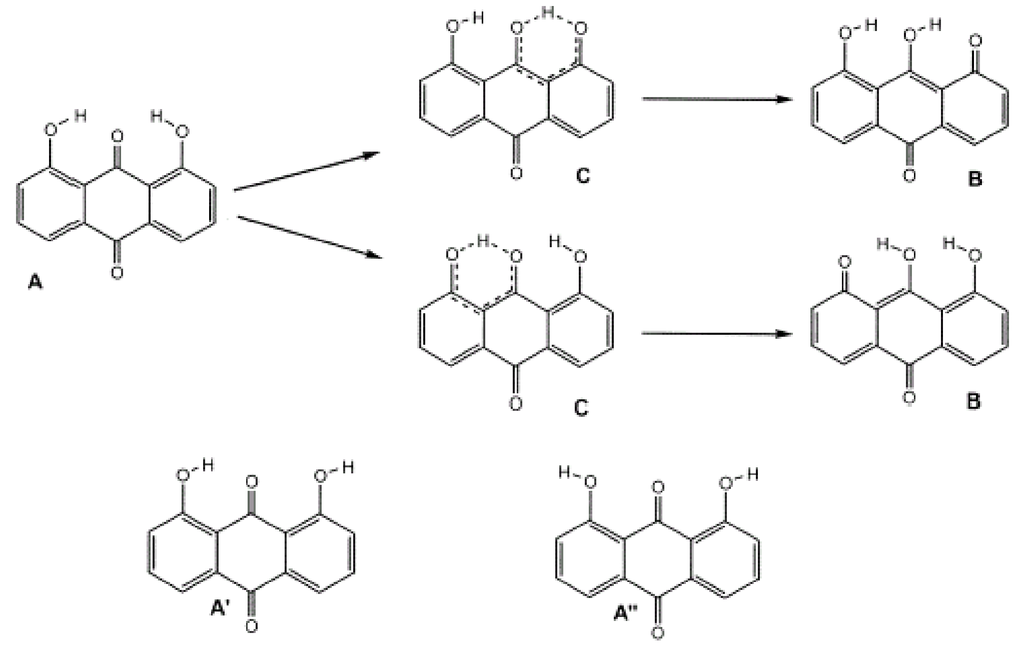


**Figure 20** Possible tautomeric structures of 1, 8-DHAQ

For intermolecular proton transfer property, it was studied by means of potentiometry. An example plot of e.m.f. versus log $(C_{AO-} / C_{AOH})$ for all three anthraquinones in acetonitrile is shown in Figure 21.

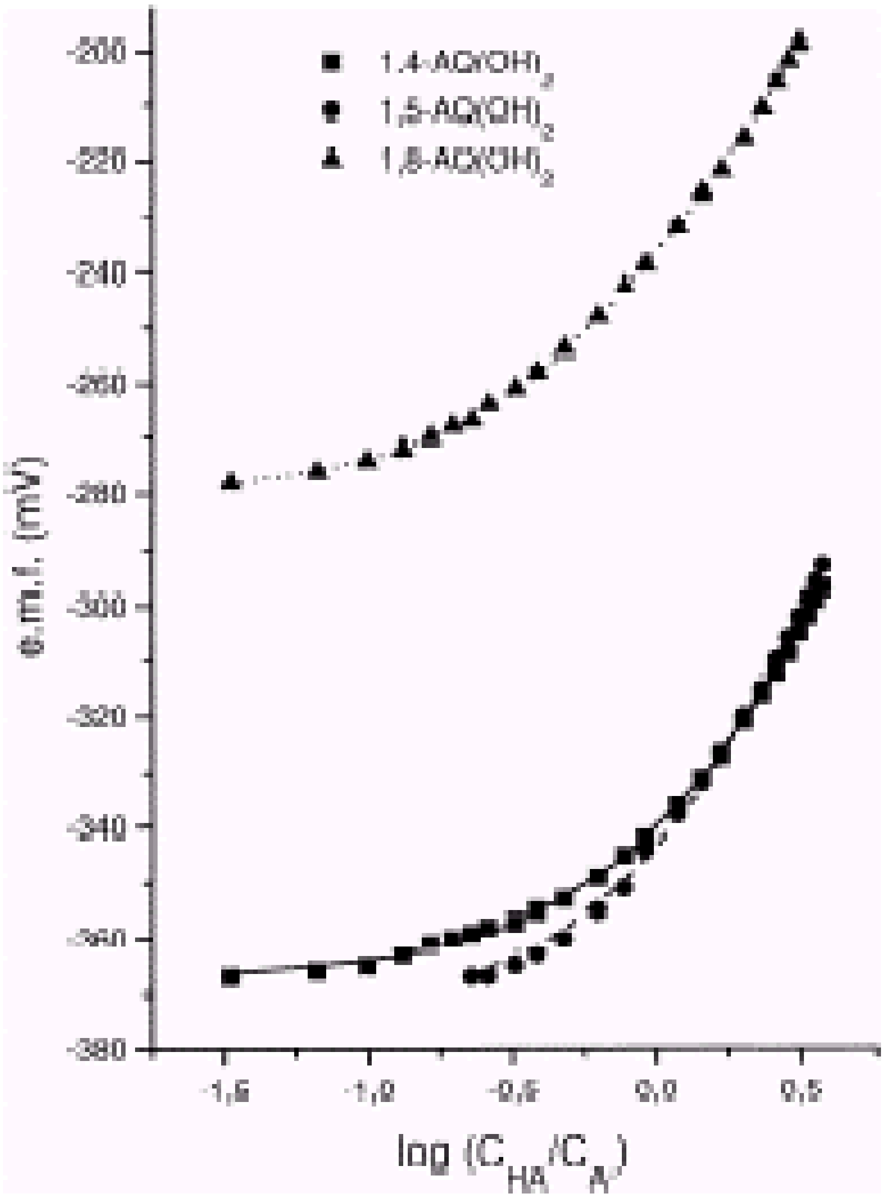


**Figure 21** Titration curves of the dihydroxyanthraquinonate/dihydroxyanthraquinone systems in acetonitrile.

The acid dissociation and anionic homoconjugation constants of them as well as the acid dissociation constant of water are summarized in Table 1

**Table 1** Acid dissociation (expressed as $pK_a$ values) and logarithms of homoconjugation constants ($\log K_{homo}$) of the three anthraquinones investigated and the acid dissociation constant of water [expressed as $pK_a$ ($H_2O$)] in the non-aqueous solvents under study and 298 K (Bogdanska et al., 1999).

| Solvent | Anthraquinone | $pK_a$(AOH) | $\log K_{homo}$ | $pK_a(H_2O)$ |
|---|---|---|---|---|
| Acetonitrile | 1,4-AQ$(OH)_2$ | 23.77(0.11)[a] | 2.63(0.02) | 24.23(0.11) |
| | 1,5-AQ$(OH)_2$ | 23.82(0.30) | 2.85(0.06) | 24.44(0.30) |
| | 1,8-AQ$(OH)_2$ | 21.92(0.09) | 2.35(0.02) | 23.22(0.09) |
| Methanol | 1,4-AQ$(OH)_2$ | 13.22(0.04) | 2.22(0.11) | 13.42(0.05) |
| | 1,5-AQ$(OH)_2$ | 14.26(0.39) | 1.86(0.66) | 12.81(0.36) |
| | 1,8-AQ$(OH)_2$ | 12.47(0.09) | 2.03(0.09) | 13.35 (0.06) |
| Dimethylsulfoxide | 1,4-AQ$(OH)_2$ | 11.14(0.01) | 2.31(0.02) | 12. 27(0.01) |
| | 1,5-AQ$(OH)_2$ | 14.13(0.15) | 2.64(0.08) | 16.71(0.67) |
| | 1,8-AQ$(OH)_2$ | 11.85(0.37) | 3.17(0.08) | 15.48(0.72) |

[a] Standard deviations in parentheses

### 1.2 Literature review

Catalysis of olefin epoxidation in both homogeneous and heterogeneous systems has been investigated by many researchers for their excellent yields of interesting products. The investigations of the catalysis systems are focused on high reactivity, high selectivity and operational simplicity. Catalysts were developed for investigating reactions many years ago. Examples of this work area are shown as the following.

### 1.2.1 Heterogeneous olefin epoxidation catalysis

Heterogeneous catalysts are used in a different phase from the reactants. They are widely used in industry because of high reaction rate. Not only they are easily separated from products but also they can be recycled. Although heterogeneous systems have many advantages, they have the difficulty in selectivity or tenability. The effective concentration of catalysts is lower than that of homogeneous system because the reactions are depending on the exposed active surface only. The catalyst is thinly spreaded on a sturdy support so that its surface is maximized. Researches in the area of the heterogeneous catalysis are as follows:

Chimentao et al. (2005) studied different morphologies of silver nanoparticles affecting the selective oxidation of styrene in the gas phase using oxygen as an oxidant. Silver nanoparticles (nanowires and nanopolyhedra), prepared using the polyol process and supported on $\alpha$-$Al_2O_3$.Phenylacetaldehyde (Phe) and styrene oxide (SO) were the main products for nanoparticles catalysts. The promotion effect on the catalytic activity of potassium and cesium on the silver nanowires catalysts was also studied. At 573 K, the styrene conversion and selectivity to styrene oxide with the silver nanowires catalyst were 57.6 and 42.5%, respectively. Silver nanopolyhedra catalyst showed 57.5% conversion and 30.8% selectivity to styrene oxide.

Tang et al. (2005) prepared co-containing molecular sieves, mainly co - faujasite zeolite and co-MCM - 41. They studied the epoxidation of styrene with molecular oxygen. The Co(II) sites located in the molecular sieves catalyze the epoxidation of styrene by oxygen with higher activity than $Co_3O_4$ (ca. 2.6 times based on the same cobalt amount). On the other hand, in homogeneous reactions, $Co(NO_3)_2$and $Co(Ac)_2$ are almost inactive for the conversion of styrene with oxygen, whereas $CoCl_2$ and $Co(acac)_3$ show some activity, but the selectivity for epoxide is remarkably lower as compared with the

Co(II)-containing molecular sieves. Among various oxidants examined, oxygen is found to be the best one for the epoxidation of styrene over the Co(II)-containing molecular sieve catalysts. The solvent plays an important role in epoxidation, and superior catalytic performances have been obtained with an acylamide such as N, N-dimethylformamide (DMF) as the solvent. The oxygen species with a radical nature generated by the activation of molecular oxygen over the solvent-coordinated Co(II) site has been proposed for the epoxidation reactions.

Choudhary et al. (2005) investigated the epoxidation of styrene by anhydrous hydrogen peroxide over boehmite and alumina catalysts with continuous removal of the reaction water. They found that boehmite and alumina (obtained from the boehmite by its calcinations at different temperatures 300-900 $^{0}$C) are active and stable catalysts for the selective epoxidation of styrene by anhydrous $H_2O_2$ to styrene oxide with continuous removal of the reaction water. In the presence of water, the catalyst shows very poor activity and selectivity for the epoxidation. The catalyst also catalyses $H_2O_2$ decomposition and hence has optimum loading for obtaining high-styrene conversion in the epoxidation.

Tangestaninejad et. al. (2005) studied efficient and selective hydrocarbon oxidation with sodium periodate under ultrasonic irradiation catalyzed by polystyrene-bound Mn (TPyP). This catalytic system showed high selectivity in epoxidation of stilbenes and R-(+)-limonene and exhibited a particular ability to epoxidize linear alkenes such as 1-heptene. This supported catalyst can catalyze the oxidation of very inert saturated hydrocarbons as well as alkylbenzene derivatives with $NaIO_4$ under ultrasonic irradiation. Under mild reaction conditions, this catalyst was consecutively reused five times without detectable catalyst leaching and gave over 95 % epoxide yields in the epoxidation styrene.

Volodkar et. al. (2004) examined the catalytic oxidation of alkanes and alkenes by polymer anchored amino acid ruthenium-complexes. A synthetic strategy was developed to anchor an amino acid, 1-valine, on to chloromethylated styrene-divinyl benzene co-polymer beads with 6 % and 8 % cross-linking. The polymeric ligands containing bidentate N, O donor sites were treated with solution of ruthenium(III)chloride to form the metal complex on the support. Synthesis of this substance is shown in Figure 22.

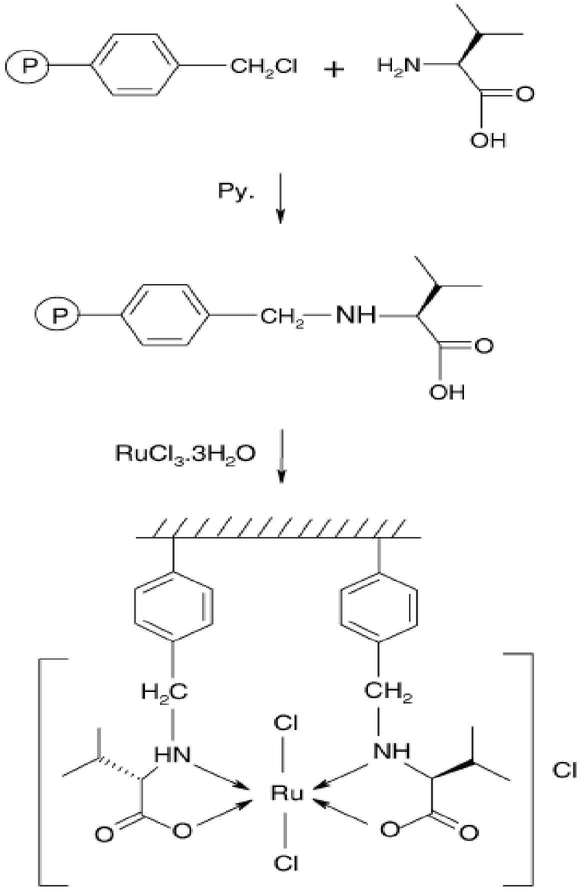


**Figure 22** Synthesis of poly(S-DVB)-supported amino acid-Ru(III)complex

The catalytic oxidation of cyclohexane and toluene were investigated using the catalysts in the presence of tert-butyl hydroperoxide as the terminal oxidant at ambient and at 45 $^0$C. In the case of cyclohexane, the formation of cyclohexanol and cyclohexanone were observed. Benzaldehyde was selectively obtained with toluene as substrate. The catalysts were active in the epoxidation of olefins such as styrene and norbornylene. Recycling studies indicated that the catalyst could be recycled three to four times without significant degradation of polymer matrix.

Patil et. al. (2004) investigated epoxidation of styrene by anhydrous tert-butyl hydroperoxide over number of transition metal oxides ($TiO_2$, $Cr_2O_3$, $MnO_2$, $Fe_2O_3$, $Co_3$ $O_4$, NiO, CuO, ZnO, $Y_2O_3$, $ZrO_2$, $La_2O_3$, and $U_3O_8$) supported nano-size gold catalysts, prepared by homogeneous deposition-precipitation method.

The supported gold catalyst (except Au/ $MnO_2$ and Au/$U_3O_8$) showed good styrene conversion activity and selectivity for styrene oxide in the epoxidation. The Au loading, Au particle size and performance in the epoxidation of the supported gold catalysts are found to be strongly influenced by the transition metal oxide support used in the catalyst. The Au/ $TiO_2$ and Au/ CuO are promising catalysts for the selective epoxidation.

Kirm et. al. (2004) studied the epoxidation of styrene with hydrogen peroxide using hydrotalcites as heterogeneous catalysts. Several Mg/Al hydrotalcite-like materials with atomic ratios of 2, 3, 4, 6 and 10 were tested as heterogeneous catalysts for the epoxidation reaction of styrene, using a combined oxidant of hydrogen peroxide and acetonitrile in the presence of acetone and water as solvents. Several factors such as the Mg/Al ratio, the presence of the pure hydrotalcite phase in the samples, the reconstruction rate of the hydrotalcite-like phase, carried out during the reaction, and the addition of water play an important role in the selective epoxidation of styrene. Possible mechanism is shown in Fugure 23.

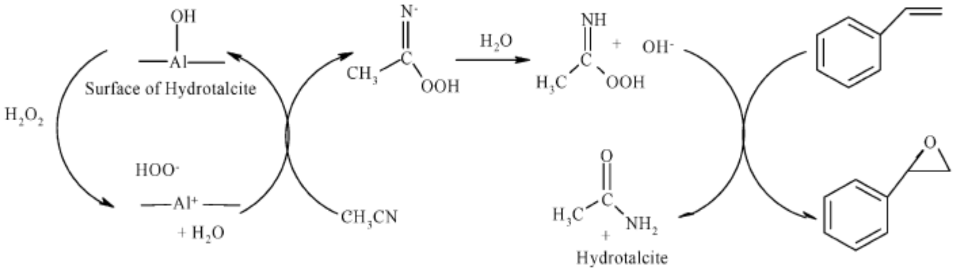


**Figure 23** Possible mechanism of styrene epoxidation catalyzed by hydrotalcite.

Rode, Nehete and Dongare (2003) studied alkali promoted selective epoxidation of styrene to styrene oxide using TS-1 catalysts. The epoxidation of styrene was carried out over titanium silicalite (TS-1) and an alkali (sodium hydroxide) in the reaction medium. This system gave a very high turn over frequency (TOF) (> 200 $h^{-1}$) and selectivity to styrene oxide (> 92 %). Also, further isomerization of styrene oxide to phenylacetaldehyde is nearly suppressed by NaOH, thereby increasing the styrene oxide selectivity remarkably.

Estavillo et. al. (2003) investigated the epoxidation of styrene by human cytochrome P450 1A2 (cyt P450 1A2) by thin film electrolysis and peroxide activation compared to solution reactions. Films of cyt P450 1A2 and poly styrene sulfonate were constructed on carbon cloth electrode using layer-by-layer alternate absorption and evaluated for electrochemical and $H_2O_2$ driven enzyme catalyzed oxidation of styrene to styrene oxide. At -0.6 V with saturated calomel reference electrode in an electrochemical cell, epoxidation of styrene was mediated by initial catalytic reduction of dioxygen to $H_2O_2$ which activates the enzyme for the catalytic oxidation. Slightly larger turnover rates for cyt P450 1A2 were found for the electrolytic and hydrogen peroxide (10 ml) driven reactions compared to conventional enzymatic reactions using cyt P450 1A2, reductases, and electron donors for cyt P450 1A2. cyt P450 1A2 gave comparable turnover rates in film cam (camphore) electrolysis and solution reactions. Results demonstrate that cyt P450 1A2 catalyzes styrene epoxidation faster than cyt P450, and suggests the usefulness of this thin film electrolytic method for relative turnover rate studies of cam P450s. Pathway for electrochemical and peroxide driven catalysis of styrene epoxidation by cyt P450s is shown in Figure 24.

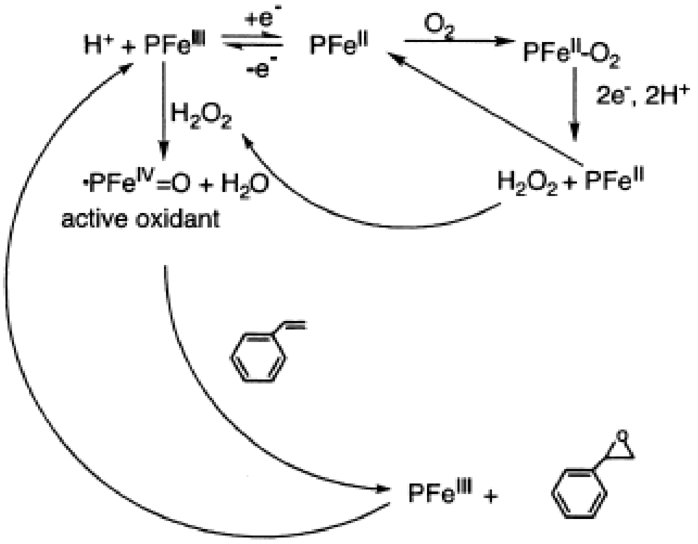


**Figure24** Pathway for electrochemical and peroxide driven catalysis of styrene epoxidation by cyt P450s

Szakacs and Ivan (2004) studied the epoxidation of thermally degraded poly(vinyl chloride). Epoxidation of conjugated polyenes formed by thermal degradation of poly(vinyl chloride) (PVC) was carried out in cyclohexanone and tetrahydrofuran solution with m-chloroperbenzoic acid (mCPBA). Epoxidation of this material is shown in Figure 25. PVC was thermally degraded in the solid state under continuous nitrogen flow at 200 $^{0}$C for 30 min leading to 0.6 mol % double bonds in the polymer chain as determined from the UV-visible spectrum of the degraded polymer. Cyclohexanone proved to be an inappropriate solvent for the epoxidation reaction probably due to its competitive reaction with the peroxide. UV-visible and FTIR spectroscopic analyses indicate that the epoxidation of polyenes by mCPBA in THF occurs in high yields leading to polyepoxy sequences in the PVC chain, and there are no signs of side reactions, such as oxidation of double bonds in polyenes to carbonyl groups. The resulting new epoxidised PVC might be useful in a variety of applications, such as fully miscible secondary epoxy stabilizer for PVC itself without plasticizing effect, starting material for epoxy curing and co-curing for reactive blends.

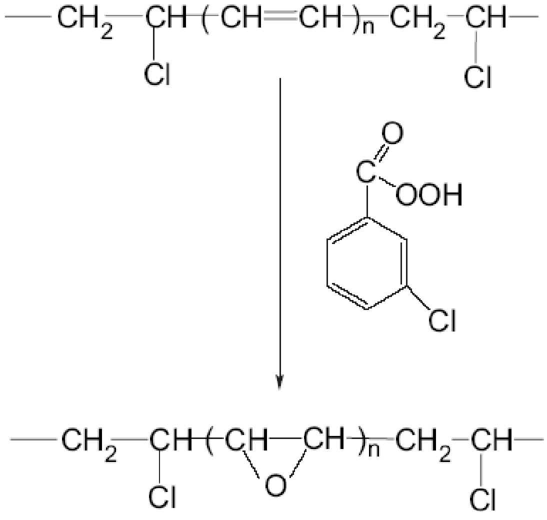


**Figure 25** Epoxidation of thermally degraded poly(vinyl chloride) with mCPBA

### 1.2.2 Homogeneous olefin epoxidation catalysis

The catalyst and the reactant are in the same phase in homogeneous systems. The reactions in this system are usually carried out as the liquid phase. Comparing with the heterogeneous system, the homogeneous system is much more dependent on the concentration of the catalyst. In addition, the solvent effects, including strong solvation to the catalyst and slow mass transfer, result in slow reaction rates. The disadvantages of the system are that the separation of the catalyst from the products is hard and that sometimes the separation method can destroy the catalyst.

Silva et al. (2005) prepared the two chiral manganese (III) salen catalysts, bearing different chiral diamine bridges that were anchored by direct axial coordination of the metal center onto the phenolate groups of a modified commercial activated carbon. The modification of the activated carbon was achieved by reaction between sodium hydroxide and surface phenol groups giving rise to phenolate groups. These materials were active and enantioselective in the epoxidation of styrene and α-methylstyrene in dichloromethane at $0^0$ C using, respectively, mCPBA/NMO (4-methylmorpholine N-oxide) and NaOCl. Only for α-methylstyrene was comparable asymmetric induction was found in the epoxide as the homogeneous phase reactions and catalyst reuse led to no significant loss of catalytic activity and enantioselectivity. Molecular structures and dimensions of the (a) Catalyst 1 and (b) Catalyst 2 are shown in Figure 26.

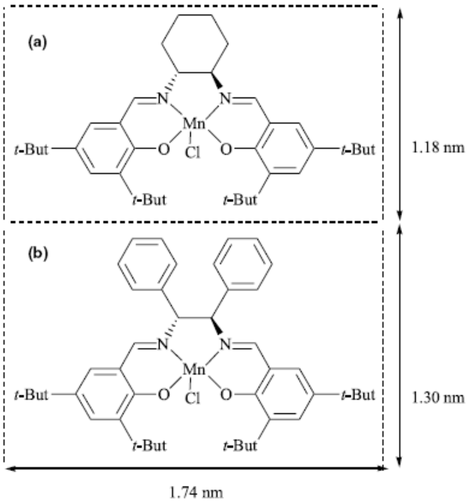
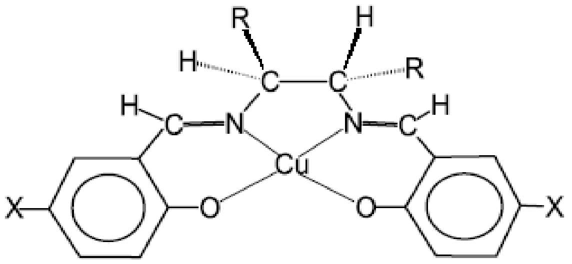


**Figure 26** Molecular structures and dimensions of the (a) Catalyst 1 and (b) Catalyst 2

Zolezzi, Spodine and Decinti (2003) investigated epoxidation of styrene with iodosylbenzene in the presence of copper(II) schiff - base complexes. Copper(II) complexes with salen Schiff-base ligands derived from ethylenediamine or (S, S)-1, 2-diphenylethylenediamine and salicylaldehyde or

5-methoxy, 5-bromo and 5-nitrosalicylaldehyde have been tested as catalysts for the epoxidation of styrene with iodosylbenzene, in dichloromethane as a solvent. The structure of the catalyst is shown in Figure 27.



1: R = H, X = $OCH_3$
2: R = H, X = H
3: R = H, X = Br
4: R = H, X = $NO_2$

1S: R = $C_6H_5$, X = $OCH_3$
2S: R = $C_6H_5$, X = H
3S: R = $C_6H_5$, X = Br
4S: R = $C_6H_5$, X = $NO_2$

**Figure 27** Structure and labeling of the copper(II) Schiff-base complexes

Catalytic activities were found to be dependent upon both the Lewis acidity of the metal complexes and the presence of phenyl substituents on the ethylene moiety. Moderate styrene conversions and epoxide yields were obtained.

Andrus and Poehine (2000) studied the treatment of a wide range of olefins with m-chloroperbenzoic acid (mCPBA) at low temperature in the presence of copper(I) and (II) catalysts in methylene chloride and found that obtained excellent yields. Without added copper, no desirable resulted after 2 day at -78 $^0$C. The catalyst-oxidant system was then employed with a range of electron-rich and deficient olefins to explore the scope of the process.

Heijnen et. al. (2003) studied about the micellar catalysis for selective epoxidations of linear alkenes. The application of surfactant system is an excitingly new concept to perform reactive separation. One of the applications is the incorporation of homogeneous catalysts in micelles to perform reaction: micellar catalysis. Nonpolar reactants are converted into polar products, using the micelles as nanoreactors. The principle of micellar catalysis is shown in Figure 28.

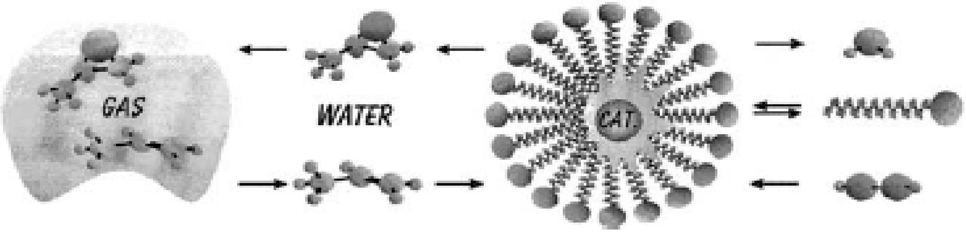


**Figure 28** The principle of micellar catalysis

The polar products are extracted towards the surrounding water phase, allowing catalysis for selectivity tuning. In this study, propene and 1-octene have been successfully epoxidized by hydrogen peroxide, catalysed by micelle-incorporated porphyrin catalysts. Preliminary experiments showed that an ultrafiltration membrane could retain the micelles containing the homogeneous catalyst. This opens up the industrial applications of homogeneous catalysis for the production of commodity chemicals.

It is well known that the protonation on the carbonyl group in peracids is the key step in the epoxidation catalysis. m-chloroperbenzoic acid, one of the peracids which are very reactive to the electron rich alkene, is used in this work. Here, the electron rich alkene used is styrene. The catalyst system chosen for this work is quinones and silver nitrate.

### 1.3 Objective

1. To study styrene epoxidation catalysis by silver nitrate and some quinone compounds.

2. To preliminarily study of a reaction order of non catalyst reaction between styrene and m-chloroperbenzoic acid.

3. To investigate reaction rate of styrene epoxidation catalysis.