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Biomimetic homogeneous oxidation catalyzed by metalloporphyrins with green oxidants

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Abstract

Cytochrome P-450 mono-oxygenase enzymes play a key role in the oxidative transformation in living systems. As one kind of cytochrome P-450 models, metalloporphyrins have been widely used in selective oxygenation of hydrocarbons under mild conditions. The chapter focuses on reviewing the biomimetic homogeneous oxidation of organic compounds catalyzed by metalloporphyrins with green oxidants such as dioxygen or hydrogen peroxide, in which the oxidized substrates include alkanes, olefins, alcohols, aldehydes, sulfides etc. The mechanisms for the oxidation of different substrates were also described. We can assume that the coming decade is going to be dedicated to the development of metalloporphyrins biomimetic catalyst in petrochemical and fine chemical industries.

Keywords: Biomimetic, Cytochrome, Metalloporphyrins, Oxidation, Homogeneous

1. Introduction

Cytochrome P-450 enzymes are heme-containing monooxygenases and play a key role in the oxidative transformation of endogenous and exogenous molecules.¹⁻⁵ They are virtually ubiquitous in nature and are present in all forms of life like plants and mammals, as well as in some prokaryotic organisms such as bacteria.⁶⁻⁸ The active site of P-450s contains a highly conserved prosthetic heme IX complex coordinated by a thiolate ligand from a cysteine residue (Figure 1).

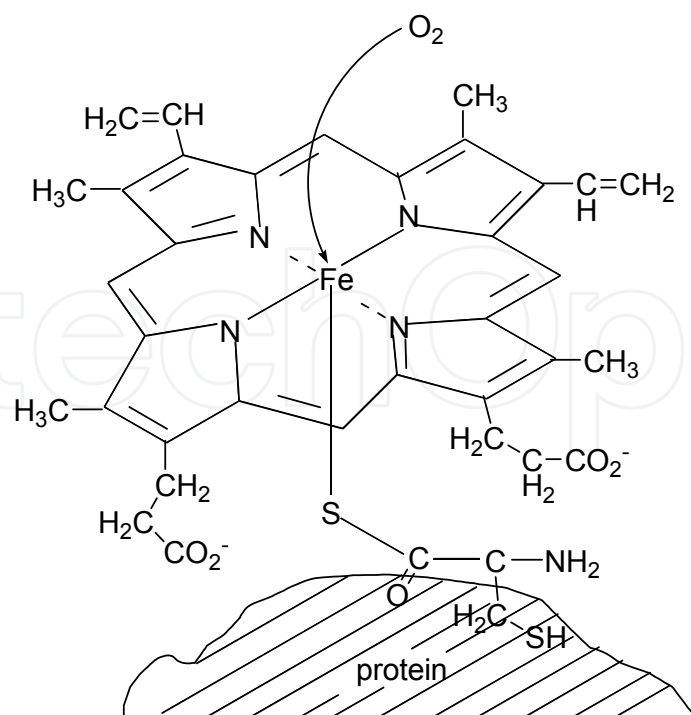
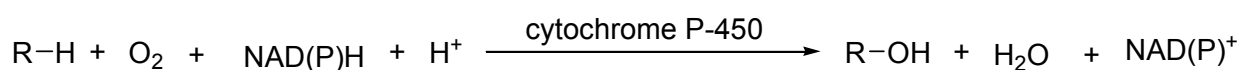


Fig. 1. Prosthetic of cysteinato-heme enzymes: an iron(III) protoporphyrin-IX covalently linked to the protein by the sulfur atom of a proximal cysteine ligand.

The primary function of cytochrome P-450 enzymes is the oxygenation of a wide variety of organic substrates by inserting one oxygen atom from O_2 to the substrate and reducing the other oxygen atom with reducing equivalents to a water molecule, utilizing two electrons provided by NAD(P)H via a reductase protein (Scheme 1).



Scheme 1. Overall oxygenation reaction catalyzed by cytochrome P-450

Being a triplet (two unpaired electrons in ground state), molecular oxygen is unreactive toward organic molecules at low temperatures. The reaction of dioxygen with the single state of organic substrates is spin-forbidden.⁹ Consequently, the oxygenation of organic molecules at physiological temperatures must involve the modification of the electronic structure of one of the partners. Living systems mainly use enzymes like cytochromes P-450 to modify the electronic structure of dioxygen to form which is adapted for the desired oxidation reaction. The mechanism of its catalytic activity and structural functions has been the subject of extensive investigation in the field of biomimetic chemistry. The high-valent iron(IV)-oxo intermediate, formed by the reductive activation of molecular oxygen via peroxo-iron(III) and hydroperoxy-iron(III) intermediates by cytochrome P-450, is responsible for the *in vivo* oxidation of drugs and xenobiotics. This high valent iron(IV)-oxo intermediate and probably other intermediates of the P450 catalytic cycle can be formed by the reaction of iron(III) porphyrins with different monooxygen donors.¹⁰⁻¹²

Therefore, cytochrome P-450 enzymes are potent oxidants that are able to catalyze the

hydroxylation of saturated carbon-hydrogen bonds, the epoxidation of double bonds, the oxidative dealkylation reactions of amines, oxidations of aromatics, and the oxidation of heteroatoms,¹³⁻¹⁵ as shown in Figure 2.

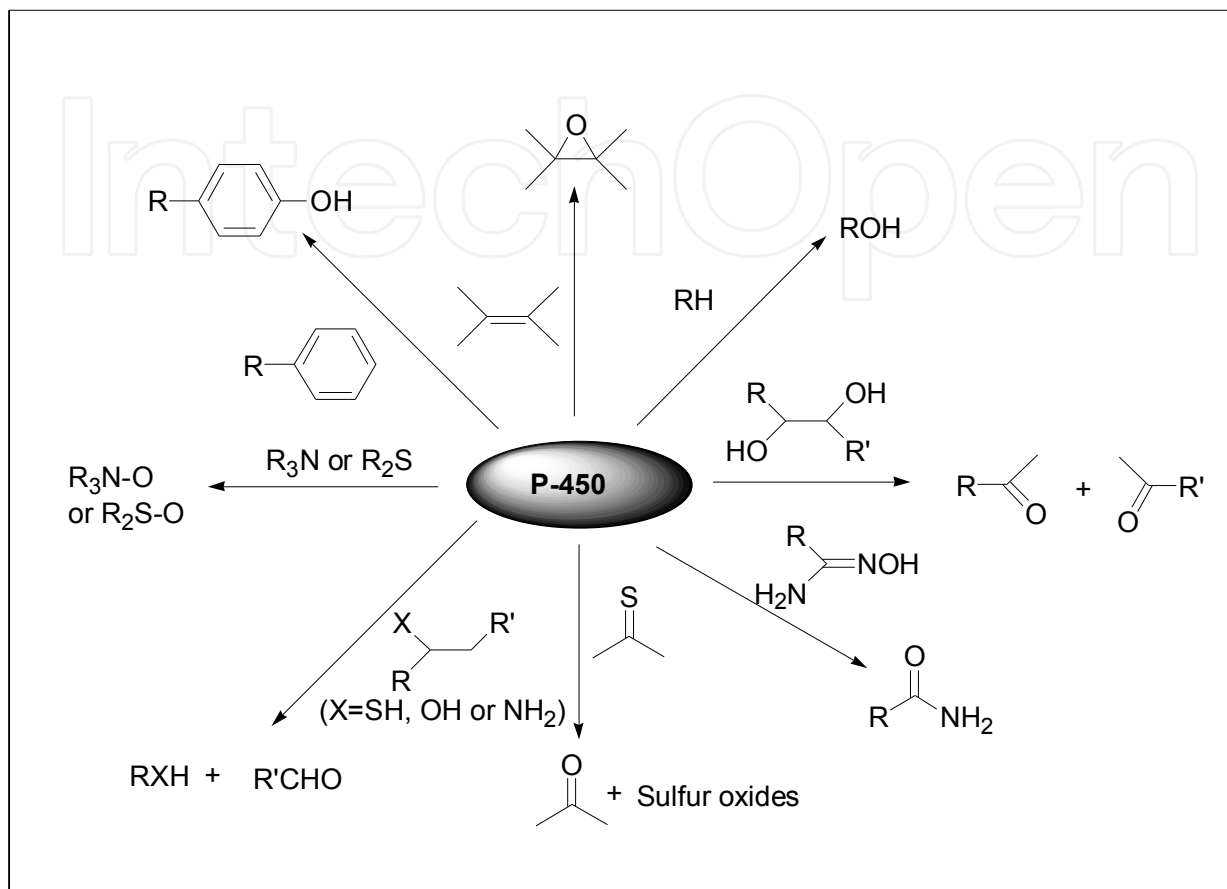


Fig. 2. Oxidations of organic compounds catalyzed by cytochrome P-450

As the isolation of P-450 enzymes from plants is extremely difficult, the first reactions employing this hemoprotein's enzymes were carried out with bacterial and mammalian P-450. Only in recent years have genes of P-450 enzymes been isolated from plants, and the first reactions confirmed that these enzymes take an active part in herbicide detoxification.¹⁶ The use of chemical model systems mimicking P-450 might therefore be a very useful tool for overcoming the difficulty in working with enzymes in vivo and vitro.¹⁷ The synthesis of cytochrome P-450 models is a formidable challenge for chemist to establish a system that is structurally equivalent to the enzymes. The synthetic mimic is not only a structural analogue exhibiting spectroscopic features close to the enzyme's cofactor but also displays a similar reactivity and catalysis.¹⁸ In recent years, the development of efficient catalytic systems for oxidation reactions that mimic the action of cytochrome P-450 dependent monooxygenases has attracted much attention. Synthetic metalloporphyrins have been used as cytochrome P-450 models and have been found to be highly efficient homogeneous or heterogeneous catalysts for oxidation reactions, especially for the alkane hydroxylation and alkene epoxidation.¹⁹⁻²¹

In attempting to mimic the reactivity of cytochrome P-450 enzymes, many researchers have used metalloporphyrins to catalyze a variety of organic compounds oxidations, such as

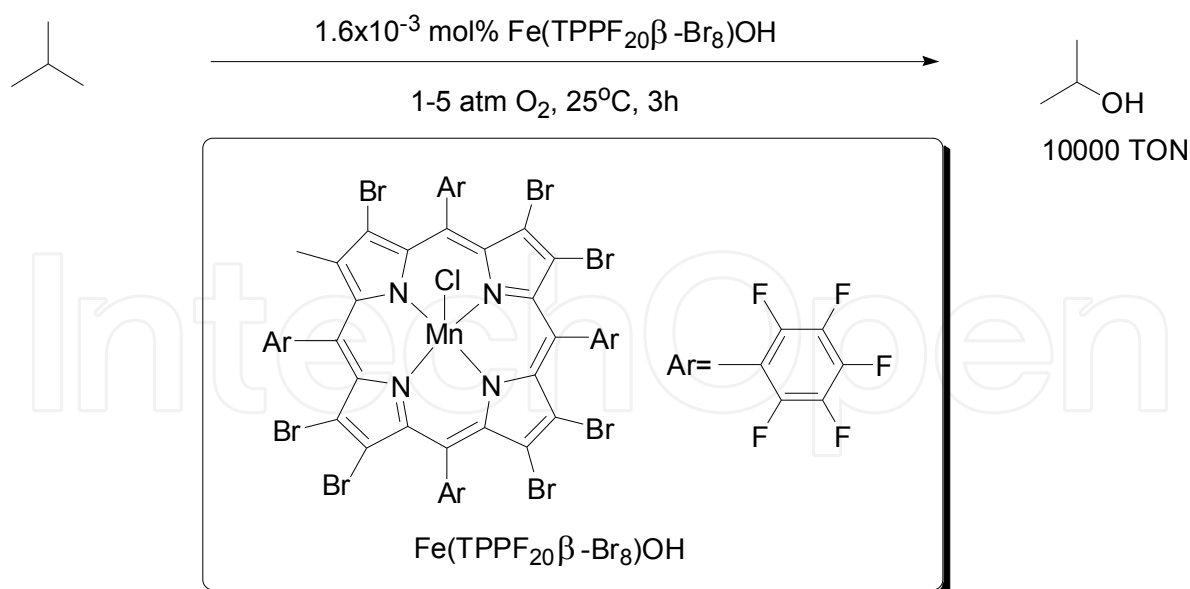
hydroxylation, epoxidation, N-oxidation and so on. An enormous range of oxidants have been used as oxygen atom transfer reagents to the metalloporphyrins in the oxidations. These include iodosylbenzenes, peroxyacids, hypochlorite, hydroperoxides, *N*-oxides, hydrogen peroxide, monoperoxyphthalate and potassium monopersulfate *et al.*²²⁻³⁷ However, the selective oxidation by green oxidants such as molecular oxygen or hydrogen peroxide is more attractive because of its cost-effectiveness and environmentally-friendly nature of the oxidant.³⁸⁻⁴²

The chapter will try to cover the biomimetic homogeneous oxidation of organic compounds catalyzed by metalloporphyrins with green oxidants based on our group's research works, in which the oxidized substrates include alkanes, olefins, alcohols, aldehydes, sulfides etc. Both practical and mechanistic point of view for the homogeneous oxidations of different substrates catalyzed by metalloporphyrins will be presented.

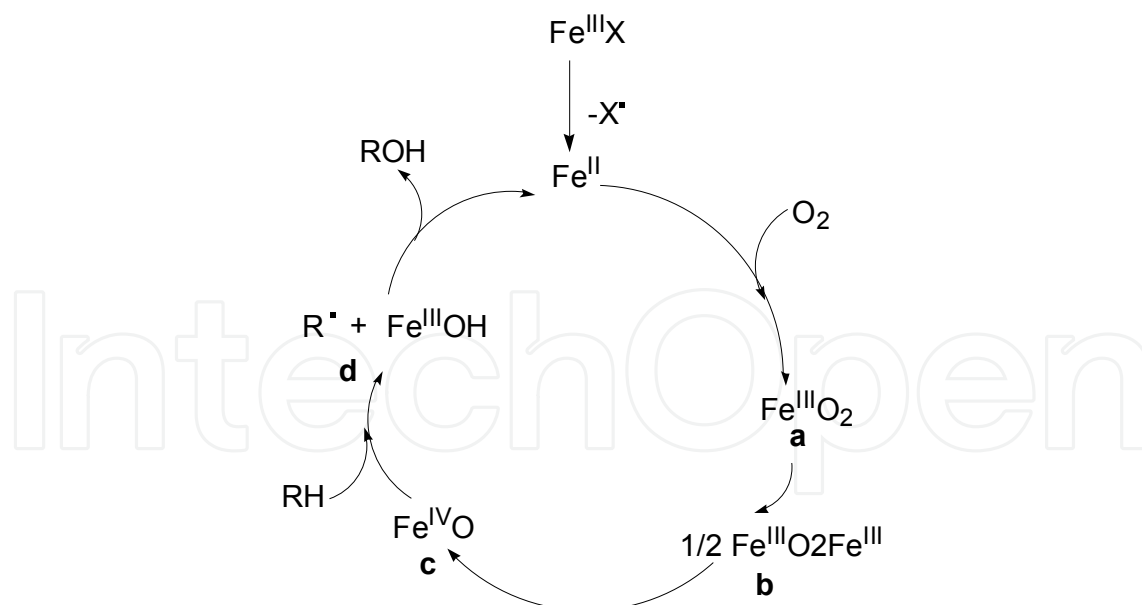
2. Hydroxylation of alkanes

The controlled and selective oxidation of saturated hydrocarbons under mild conditions is one of the most important technologies for the conversion of petroleum products to valuable commodity chemicals.⁴³ Often-used catalysts for the oxidation reactions at the industrial scale are transition metal complexes, for example, cobalt salt is used in cyclohexane oxidation. Their main drawback is the low reactivity.

In recent two decades, the catalysis of metalloporphyrins for alkane hydroxylation under mild conditions had widely received considerable attention.^{44, 45} Early reports indicated that manganese porphyrins or phthalocyanine can catalyze the oxidation of indoles or tryptophan with a product distribution different from that observed in a free-radical oxidation reaction.^{46, 47} Lyons and Ellis reported that chromium, manganese or iron complexes of *meso*-tetraphenylporphyrin with one azido as axial ligand were efficient catalysts for the oxidation of neat acyclic alkanes under molecular oxygen (1-5 atm).⁴⁸ Isobutane is oxidized to *tert*-butyl alcohol in 20000 TON in the presence of Fe(TPPF₂₀β-Br₈)OH [Fe(TPPF₂₀β-Br₈=tetrakis(pentafluorophenyl) β-octabromo) iron porphyrin] at 100°C. Although in this reaction the catalyst decomposition is a problem at somewhat elevated temperatures (>60°C), well over 10000 catalytic turnovers can be reached at ambient temperature with no decay of the catalyst (Scheme 2).

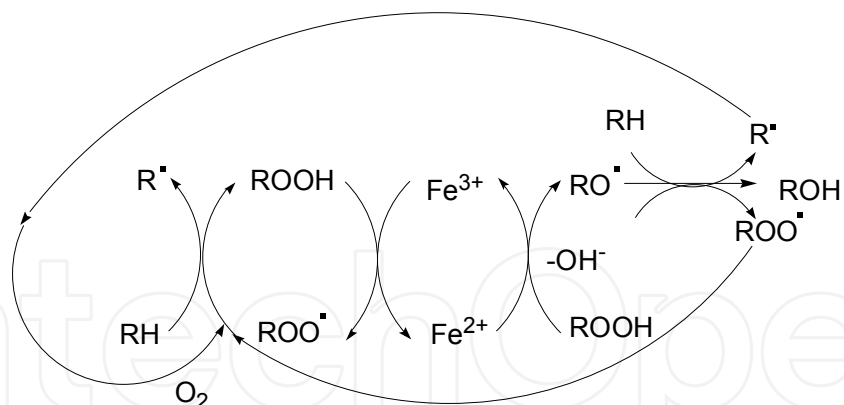
Scheme 2. Isobutane oxidation catalyzed by $\text{Fe(TPPF}_{20}\beta\text{-Br}_8\text{)OH}$

Similarly, the oxidation of propane to a 1:1.1 mixture of isopropyl alcohol and acetone is reported with 541 TON in the presence of $\text{Fe(TPPF}_{20}\beta\text{-Br}_8\text{)N}_3$ at 125°C . However, substituted alkanes such as 2-methylbutane, 3-methylpentane, 2,3-dimethylbutane, and 1,2,3-trimethylbutane are oxidized into a mixture of products due to oxidative cleavage of the carbon-carbon bond. The postulated mechanisms for these reactions are similar to those proposed for the biological oxidations by cytochrome P-450 (Scheme 3).⁴⁸



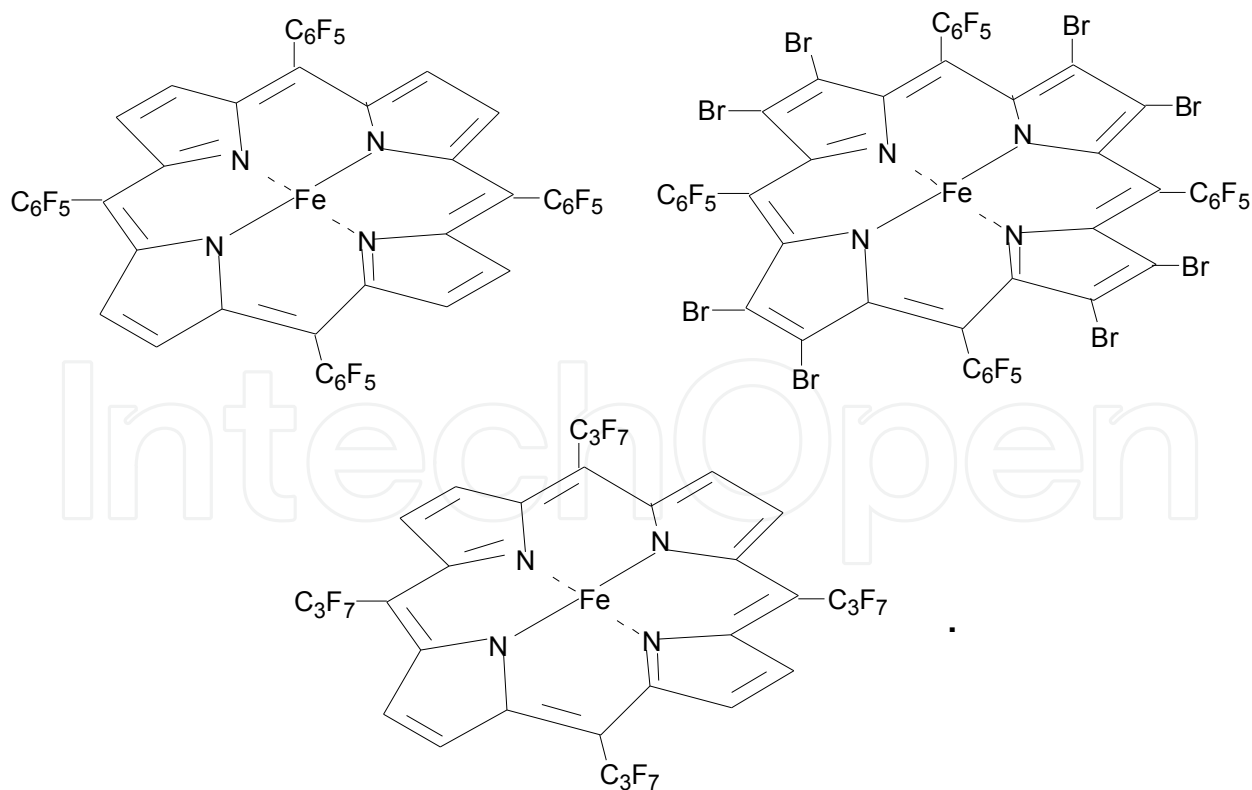
Scheme 3. Proposed mechanisms for alkane oxidation catalyzed by iron porphyrin

Gray and co-workers studied the oxidation of 3-methylpentane to 3-hydroxy-3-methylpentane (>99% selectivity) using iron-haloporphyrins and molecular oxygen in benzene at 60°C .⁴⁹ The product selectivity and radical trap experiment suggest that this reaction takes place by an autoxidation process (Scheme 4).



Scheme 4. Mechanisms for the autoxidation of alkanes catalyzed by iron-haloporphyrins

A comprehensive study of (porphinato)iron [PFe]-catalyzed isobutane oxidation in which molecular oxygen is utilized as the sole oxidant was reported by Moore and co-workers.⁵⁰ Electron-deficient PFe catalysts were examined (Scheme 5). The nature and distribution of hydrocarbon oxidation products show that an autoxidation reaction pathway dominates the reaction kinetics, consistent with a radical chain process. Evidence was present for a radical chain autoxidation mechanism, in which (porphinato)iron(III)-OH (PFe-OH) species not only are responsible for the breakdown of the *tert*-butyl hydroperoxides generated in situ during the catalytic reaction, but also play the role of radical chain initiator in the autoxidation process.



Scheme 5. Electron-deficient (porphinato) iron structures

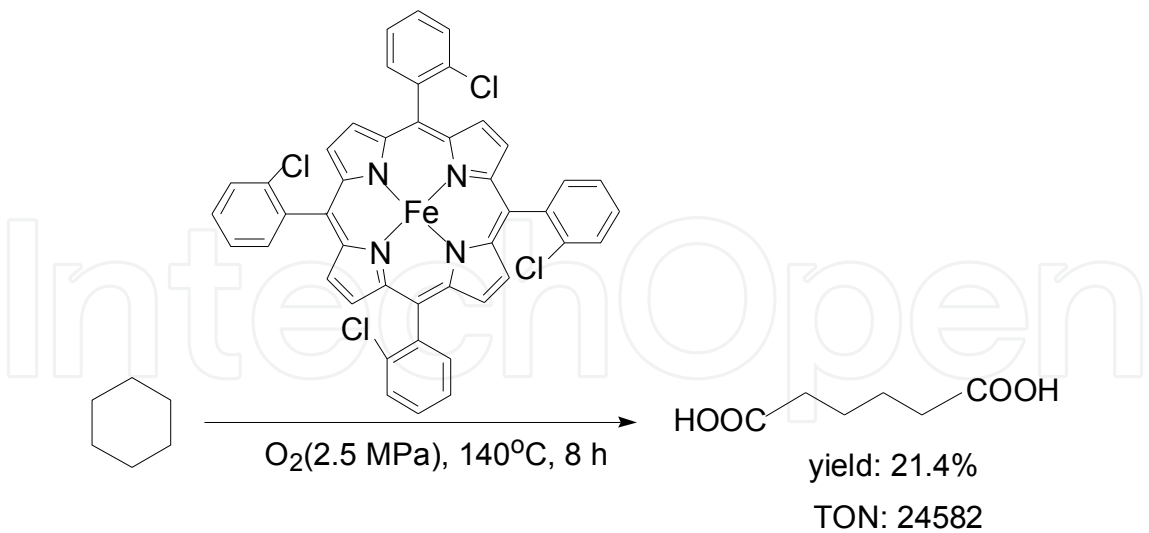
Oxidation of cyclohexane with air to cyclohexanol and cyclohexanone is a very important industrial process from both economical and environmental aspects. Simple iron, manganese and cobalt tetraphenylporphyrins were found to be the very effective catalysts for cyclohexane oxidation with air when the reaction temperature was higher than 100°C and pressure was greater than 0.4MPa.⁵¹ The cyclohexane conversion and the yields of alcohol and ketone catalyzed by cobalt porphyrin were more than that by manganese and iron porphyrins as shown in Table 1.

	TPP(Co)	TPP(Mn)	TPP(Fe)
Cyclohexane conversion (%)	15.0	11.9	8.54
Yields of alcohol and ketone (%)	75.6	73.4	65.1
Time until the yield maximum (H)	1.5	2.5	3.5
Ratios of alcohol to ketone	0.91	0.97	0.94
Catalyst mole turnover number	33937	26289	18866

C_{cat}=40ppm, V_{air}=3 l/min, P=0.6MPa, T=140°C.
Table 1. Effect of different metalloporphyrins on the oxidation reaction

For cyclohexane oxidation catalyzed by simple cobalt tetrapherylporphyrin, the conversion of cyclohexane was up to 16.2%, general yields of cyclohexanol and cyclohexanone was 82%, and the mole turnover numbers of the catalyst reached 400,000 under the optimum conditions of 0.6MPa and 140°C and 4 ppm cobalt porphyrin.

One-pot oxidation directly from cyclohexane to adipic acid with dioxygen as oxidant is gathering increasing interest. A novel one-pot oxidation of cyclohexane to adipic acid using molecular oxygen as an oxidant catalyzed by iron-porphyrins has been developed by our research group (Scheme 6).⁵²



Scheme 6. One-pot oxidation of cyclohexane to adipic acid catalyzed by iron-porphyrin

When the reaction temperature is 140°C, oxygen pressure is 2.5 MPa, concentration of catalyst is 1.33×10⁻⁵ mol %, and reaction time is 8 h, the yield of adipic acid reaches 21.4%. A turnover number of about 24582 is thus far the highest one among those reported for the direct oxidation from cyclohexane to adipic acid.

3. Epoxidation of olefins

Catalytic epoxidation of olefins has attracted much attention both in industry and in organic synthesis, for epoxides are among the most useful synthetic intermediates. Access to a variety of epoxides has largely been successful due to the remarkable catalytic activity of transition metal complexes, which have a unique ability to bring the alkene substrate and the oxygen source within the coordination sphere of the metal leaving to a facial transfer of oxygen atom to the carbon-carbon double bond.⁵³⁻⁵⁶

During the past two decades, metalloporphyrins have been widely applied for epoxidation of olefins to give epoxides with high regio-, shape- and stereoselectivity since the leading works of Groves and co-workers by using iodosylbenzene (PhIO) as oxygen atom donor.⁵⁷ The activation of the natural oxidant, O₂, with metalloporphyrins has also been realized.

In metalloporphyrin-catalyzed homogenous epoxidation of olefins with molecular oxygen, a stoichiometric amount of reducing reagent is usually used for the activation of dioxygen. Several model system using O₂ and reducing agents in the presence of Mn(III) porphyrins as catalyst have been described in the literature, in which including H₂/Pt,⁵⁸⁻⁶⁰ zinc powder,^{61, 62} or electrochemically on an electrode.^{63, 64}

Aldehyde is another effective reducing agent for the epoxidation of olefins with dioxygen as oxidant. Mukaiyama reported an efficient approach for epoxidation of olefins using dioxygen as oxidant under ambient conditions. The process involved use of β -diketonate complexes of Ni²⁺, Co²⁺, and Fe³⁺ as catalysts and an aldehyde as oxygen acceptor.⁶⁵⁻⁶⁷ Subsequently, many metal catalysts e.g. manganese complex, cobalt-containing molecular sieves and metalloporphyrins demonstrated highly catalytic performance for the aerobic oxidation in the presence of aldehyde.⁶⁸⁻⁷¹

Mandal and co-workers reported the epoxidation of various olefins using cobalt porphyrins in ambient molecular oxygen and 2-methylpropanal.⁷² Methyl styrene, stilbene were transformed to the corresponding epoxides in nearly quantitative yield (Table 2). It is noteworthy that trans-stilbene afforded the corresponding trans-epoxide. Limonene was readily transformed to a mixture of mono and diepoxide in 1:2.3 ratio in quantitative yield.

The simple structural metalloporphyrins has proven to be an excellent catalyst for the epoxidation of olefins in the presence of molecular oxygen and isobutylaldehyde. As a part of metalloporphyrins-catalyzed oxidations of our group works, the epoxidation of olefins catalyzed by very small amount of MnTPP (manganese *meso*-tetraphenyl porphyrin) was reported (Scheme 7), in which extremely high turnover number that could be comparable to most enzyme catalysis was obtained.⁷³

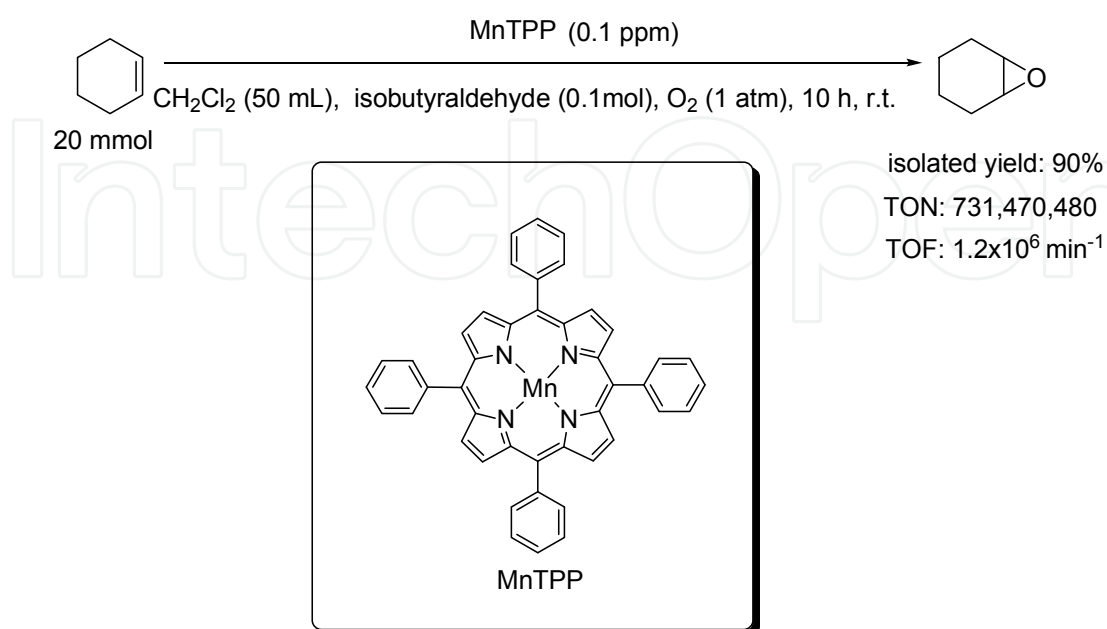
When the amount of manganese *meso*-tetraphenylporphyrin catalyst was 2.5×10^{-8} mmol, the cyclohexene oxide could be obtained with the isolated yield of 90%. It should be mentioned that the turnover number of the present catalyst could reach 731,470,480. Since commonly, TOF is used to express the catalytic efficiency of enzyme with the definition as converted substrate (mol) per enzyme (mol) per minute. The TOF of most enzymes is about 1000 min^{-1} or more. For example, the TOF of catalase is $6 \times 10^6 \text{ min}^{-1}$, and the TOF of β -galactosidase is $1.25 \times 10^4 \text{ min}^{-1}$. In the present manganese *meso*-tetraphenylporphyrin catalyzed system, the TOF reaches up to $1.2 \times 10^6 \text{ min}^{-1}$, which is the range for enzyme activity.

Entry	Substrate	Product ^b	Yield (%) ^a
1			94
2			100
3			80
4			100 ^c
5			83
6			51

^a Isolated yield. ^b Yield determined from ¹H-NMR of the crude reaction mixture.

^c Obtained as a mixture of syn-anti diastereomers

Table 2. Co(II) porphyrin catalyzed oxidation of olefins using 2-methylpropanal and dioxygen



Scheme 7. Manganese *meso*-tetraphenylporphyrin catalyzed epoxidation of olefins

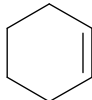
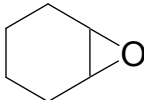
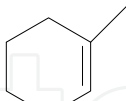
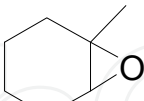
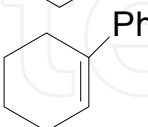
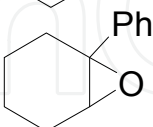
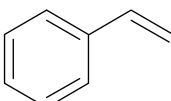
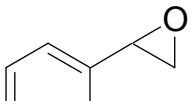
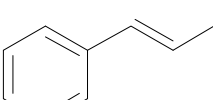
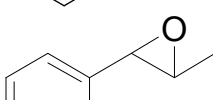
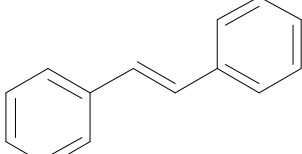
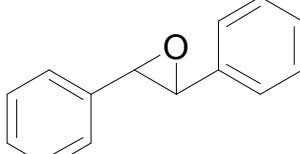
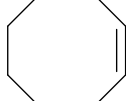
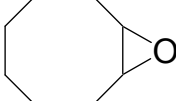

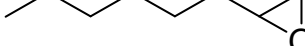

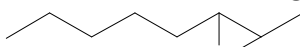
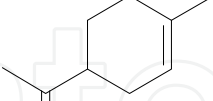
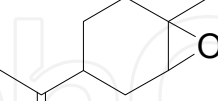
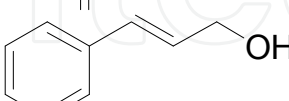
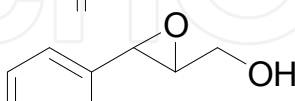
Also, various olefins could be smoothly converted to the corresponding epoxides in the catalytic system under ambient conditions. As shown in Table 3, it seems that the efficiency of epoxidation in this catalytic system is very dependent on the steric structure of substrates. The influence of steric effects could further be found when styrene and its derivatives were oxidized, the conversion rates of styrene, *trans*- β -methylstyrene and *trans*-stilbene were 95%, 89% and 86% after reacting for 4.5, 7.0 and 8.0 h, again demonstrating a steric effect (entries 4-6).

Similarly, in the epoxidation of other cycloolefin *e.g.* cyclooctene, the reaction system exhibits high catalytic performance with 93% yield of cyclooctene epoxide (entry 7). Epoxidation of linear chains *e.g.* 1-octene and *trans*-2-octene smoothly proceeded with high conversion and yield, and similar catalytic activities for the two substrates show the located position of C=C bond on linear chain alkenes could hardly influence their catalytic performance (entries 8-9).

Despite of the high efficiency of the catalyst system, another salient feature of the present epoxidation is its high regioselectivity (entry 10). In addition, the catalyst system exhibits specific selective oxidation performance towards C=C bond and hydroxyl group activation. C=C bond was preferentially activated and the corresponding epoxide as the only product with 90% yield could be obtained for the cinnamyl alcohol oxidation, and no products from hydroxyl group oxidation could be detected (entry 11).

A mechanism for the epoxidation of olefins by dioxygen in the presence of metalloporphyrins and isobutyraldehyde has been proposed from the experimental results, as shown in Figure 3.

Based on the proposed mechanism, the manganese porphyrin reacts with the aldehyde to generate an acyl radical (a) at first. The acyl radical then reacts with dioxygen to give an acylperoxy radical (b). The acylperoxy radical is assumed to play two roles. Firstly, it reacts with olefins to yield epoxides directly accompanying the generation of carboxyl radical (c), which reacts with aldehyde to generate another acyl radical and carboxylic acid (pathway A). Secondly, in pathway B, the acylperoxy radical acts as a carrier by reacting with another aldehyde molecule to give peroxyacid (d), thereby generating another acyl radical. Formation of epoxide is assumed by active high-valent Mn porphyrin intermediates (e), which are formed by the reaction of the peroxyacid with the manganese porphyrin. The evidence described above suggests that pathway B is usually superior over pathway A.

Entry	Substrate	Product	Reaction time (h)	Conv. (%)	Yield (%)
1			4.5	97	95
2			5.0	93	90
3			6.0	83	72
4			4.5	95	93
5			7.0	89	87
6			8.0	86	85
7			5.0	95	93
8			5.0	94	93
9			5.0	93	89
10			5.0	92	91
11			6.0	92	90

^asubstrate (2 mmol), isobutyraldehyde (0.01mol), CH₂Cl₂ (5 mL), O₂ bubbling, r.t.
Table 3. Epoxidation of alkenes catalyzed by manganese *meso*-tetraphenylporphyrin in the presence of molecular oxygen and isobutyraldehyde ^a

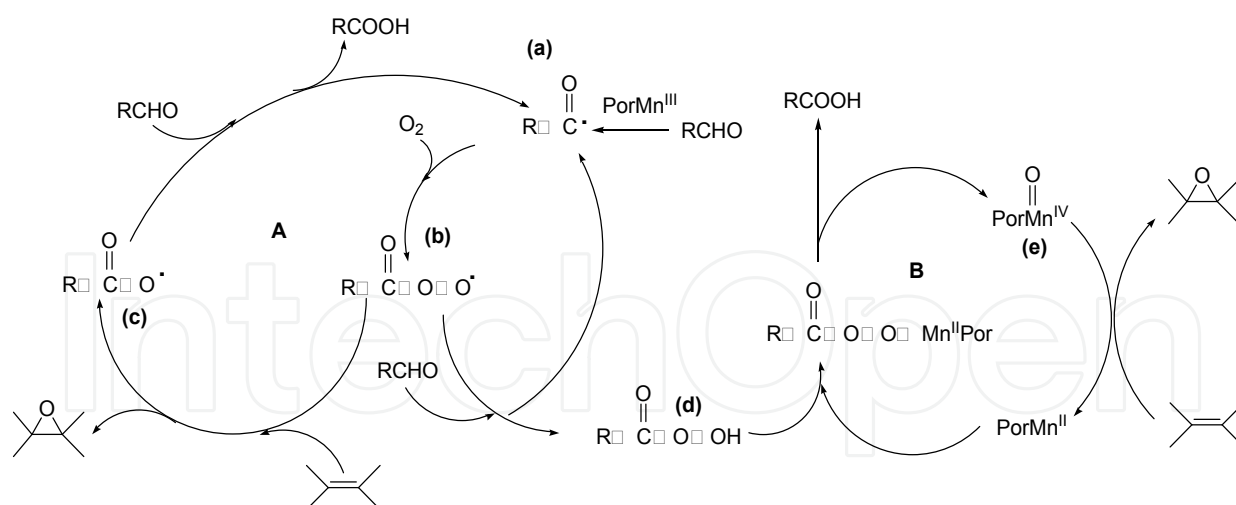
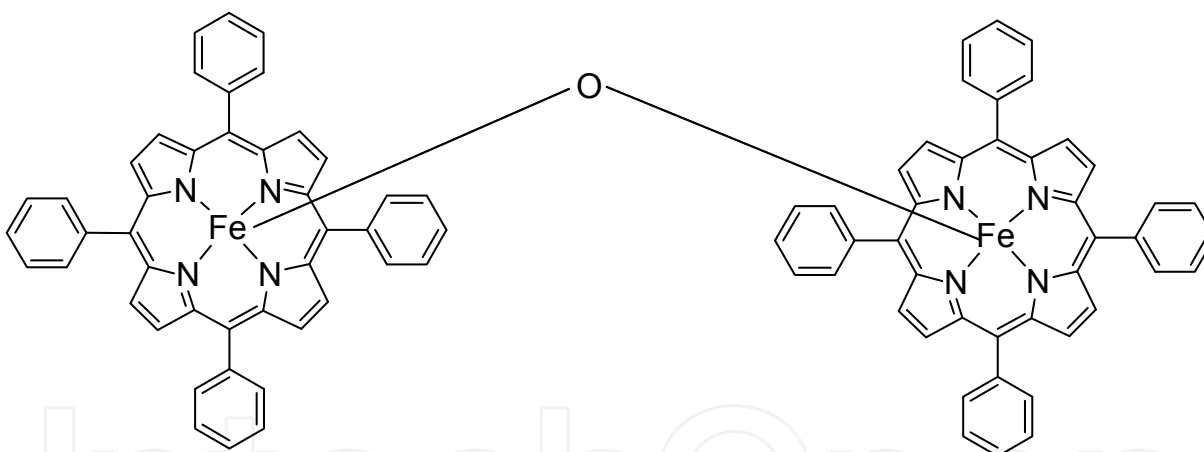


Fig. 3. Plausible mechanism of olefin epoxidation catalyzed by Mn(III) porphyrins in the presence of molecular oxygen and isobutyraldehyde

Compared with mono-metallporphyrins as catalyst, remarkable enhancement of reactivity was obtained for μ -oxo-bisiron(III) porphyrin-catalyzed olefin epoxidation system (Scheme 8), in which the turnover number (TON) of the catalyst has doubled from about 700 million to 1,400 million.⁷⁴

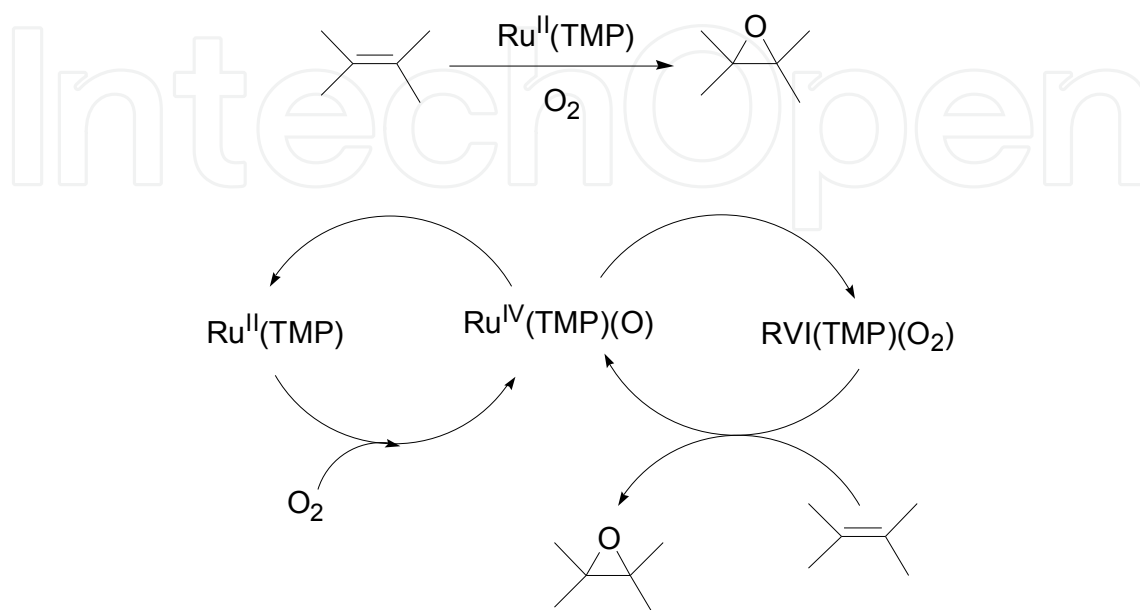


Scheme 8. Structure of μ -oxo-bisiron(III) porphyrin

It is usually considered that μ -oxo dimeric metalloporphyrins could easily form monometalloporphyrins during the catalytic process. In fact, whether the dinuclear intermediate or the mononuclear intermediate is the active species remains controversial for the oxygenation of hydrocarbons by using μ -oxo dimeric metalloporphyrins as catalyst. The results of in situ UV-vis spectra indicate that both the dinuclear and the mononuclear high-valent intermediate exist in the catalytic system. Probably two kinds of oxo-iron intermediates, that is $\text{O}=\text{VFe}-\text{O}-\text{Fe}^{\text{V}}=\text{O}$ and $\text{Fe}^{\text{V}}=\text{O}$ were formed by series of free radical processes.

Few examples on the metalloporphyrins-catalyzed epoxidation by dioxygen in the absence of a co-reductant could be found. It is worthy mentioning that $\text{Ru}^{\text{VI}}(\text{TMP})(\text{O})_2$ catalyzes olefin epoxidation with O_2 without the requirement a sacrificial reductant reported by

Groves group.^{75, 76} The proposed mechanism is shown in Scheme 9. The active oxidant $\text{Ru}^{\text{VI}}(\text{TMP})(\text{O})_2$ reacts with an olefin to afford the epoxide and $\text{Ru}^{\text{IV}}(\text{TMP})(\text{O})$, and the disproportionation of the latter generates $\text{Ru}^{\text{II}}(\text{TMP})$ and the active oxidant $\text{Ru}^{\text{VI}}(\text{TMP})(\text{O})_2$. The $\text{Ru}^{\text{II}}(\text{TMP})$ re-enters the catalytic cycle after being oxidized by dioxygen to $\text{Ru}^{\text{IV}}(\text{TMP})(\text{O})$.



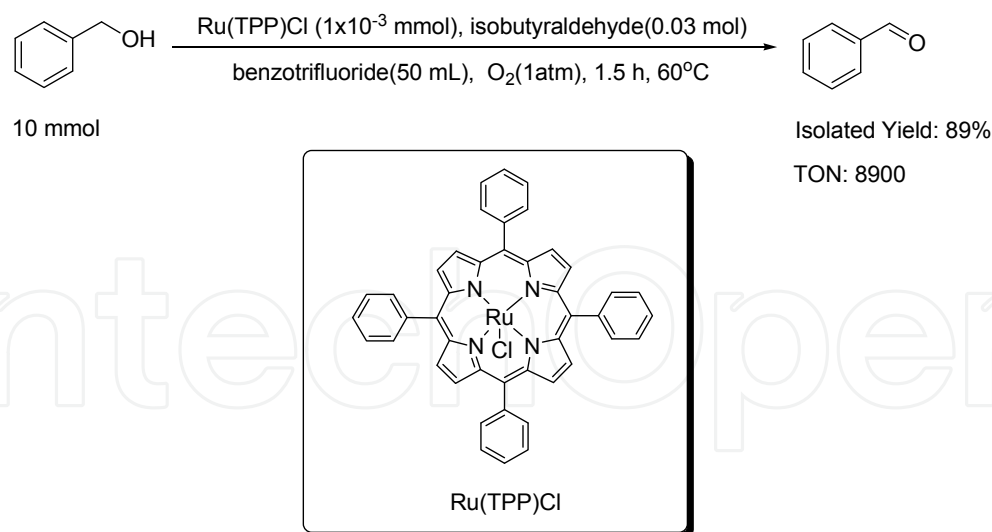
Scheme 9. Ru(TMP)-catalyzed olefins epoxidation with dioxygen

4. Oxidation of alcohols

Oxidation of alcohols to the corresponding carbonyl compounds is a very important step for organic synthesis.⁴¹ From an environmental and cost effective viewpoint, catalytic oxidation processes with molecular oxygen or air are extremely valuable and particularly attractive. Accordingly, variety of transition metal based catalysts (mainly cobalt, vanadium, ruthenium and palladium) has been intensively investigated for aerobic oxidation of alcohols so far.⁷⁷⁻⁸⁰

Although metalloporphyrins have been used to catalyze the oxidation of alcohols with PhIO , $t\text{-BuOOH}$, KHSO_5 and $m\text{-CPBA}$ (m -chloroperbenzoic acid) as oxidants,⁸¹⁻⁸⁴ few studies on metalloporphyrins-catalyzed oxidation of alcohols by molecular oxygen were reported. For examples, Woo and co-authors ever reported the aerobic homogeneous oxidation of benzyl alcohol with oxotitanium porphyrin ($\text{TTP})\text{Ti}=\text{O}$ ($\text{TTP}=\text{meso-tetra-}p\text{-tolylporphyrin}$), which gave benzaldehyde in modest yields (48%) after 94 hours in refluxing chlorobenzene.⁸⁵

Ruthenium-porphyrin has been proved to be efficient for oxidation of alcohols with high yields for carbonyl compounds under mild conditions (Scheme 10).⁸⁶ Alcohols including benzylic alcohols, secondary alcohols and primary alcohols were efficiently converted to the corresponding carbonyl compounds in the catalytic system by atmospheric dioxygen (Table 4).



Scheme 10. Oxidation of alcohols catalyzed by ruthenium (III) *meso*-tetraphenylporphyrin chloride in the presence of molecular oxygen and isobutyraldehyde

Entry	Alcohol	Product	Time (h)	Conv. (%)	Yield (%)
1	<chem>c1ccccc1CO</chem>	<chem>c1ccccc1C=O</chem>	0.5	>99	>99
2	<chem>COc1ccc(CO)cc1</chem>	<chem>COc1ccc(C=O)cc1</chem>	1.0	35	35
3	<chem>Clc1ccc(CO)cc1</chem>	<chem>Clc1ccc(C=O)cc1</chem>	0.5	91	91
4	<chem>c1ccc(CO)cn1</chem>	<chem>c1ccc(C=O)cn1</chem>	1.0	17	17
5	<chem>CC(O)c1ccccc1</chem>	<chem>CC(=O)c1ccccc1</chem>	0.5	94	94
6	<chem>Oc1ccccc1C(O)c2ccccc2</chem>	<chem>O=C1C(=O)c2ccccc2C1c3ccccc3</chem>	1.5	93	93
7	<chem>Oc1ccccc1C1CCCCC1</chem>	<chem>O=C1C(=O)c2ccccc2C1</chem>	1.0	94	94
8	<chem>Oc1c2ccccc2C1</chem>	<chem>O=C1C(=O)c2ccccc2C1</chem>	0.5	91	72
9	<chem>CCCCCCCCCO</chem>	<chem>CCCCCCCCC(=O)O</chem>	1.0	93	71

^aBenzyl alcohol (1mmol), Ru(TPP)Cl (1×10⁻³ mmol), isobutyraldehyde (3mmol), benzotrifluoride (5mL), O₂ bubbling (1 atm), 60°C, 0.5 h
^btoluene (5 mL) as solvent
Table 4. Oxidation of various alcohols by molecular oxygen in the presence of Ru(TPP)Cl ^a

As shown in Table 4, it seems that the catalytic activity is dependent on the electronic property of substrates (entries 2-4). Secondary alcohols could be easily converted to the corresponding ketones in high yield (entries 5-8). In the case of 2-adamantanol, the catalytic system shows high activity, which gave ketone yield of 72% when the reaction continued for 30 min despite the hindrance. In the cases of saturated primary aliphatic alcohols e.g. 1-octanol and 1-hexanol, further oxidation of aldehydes to the corresponding carboxylic acids was observed under the same reaction conditions (entries 9).

A mechanism for the epoxidation of olefins by dioxygen in the presence of metalloporphyrins and isobutyraldehyde has been proposed from the experimental results, as shown in Figure 4.

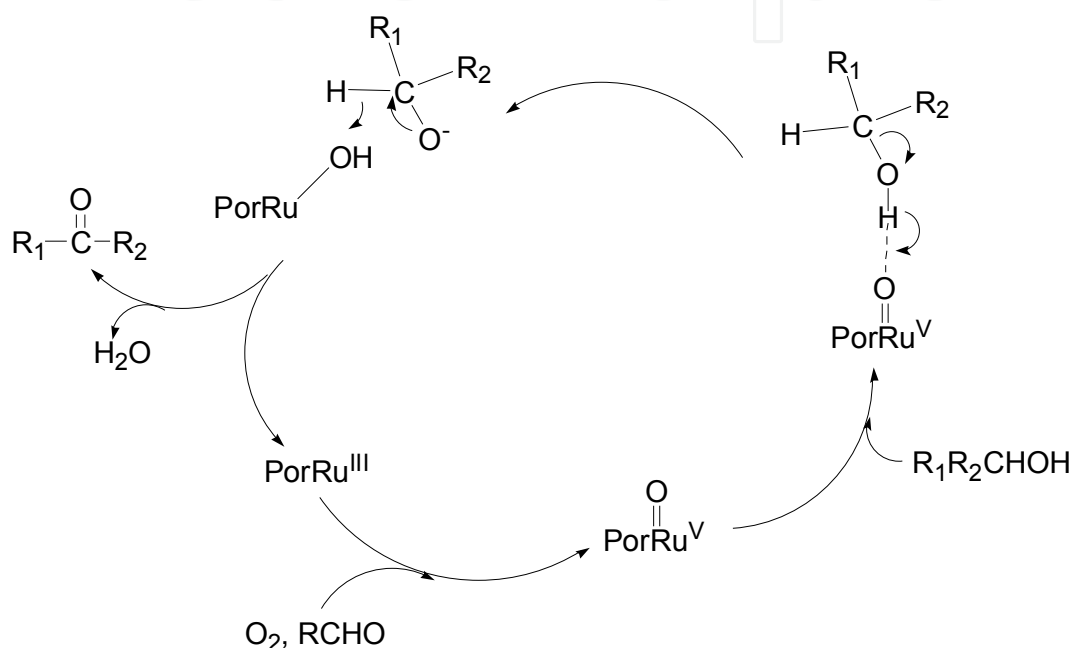
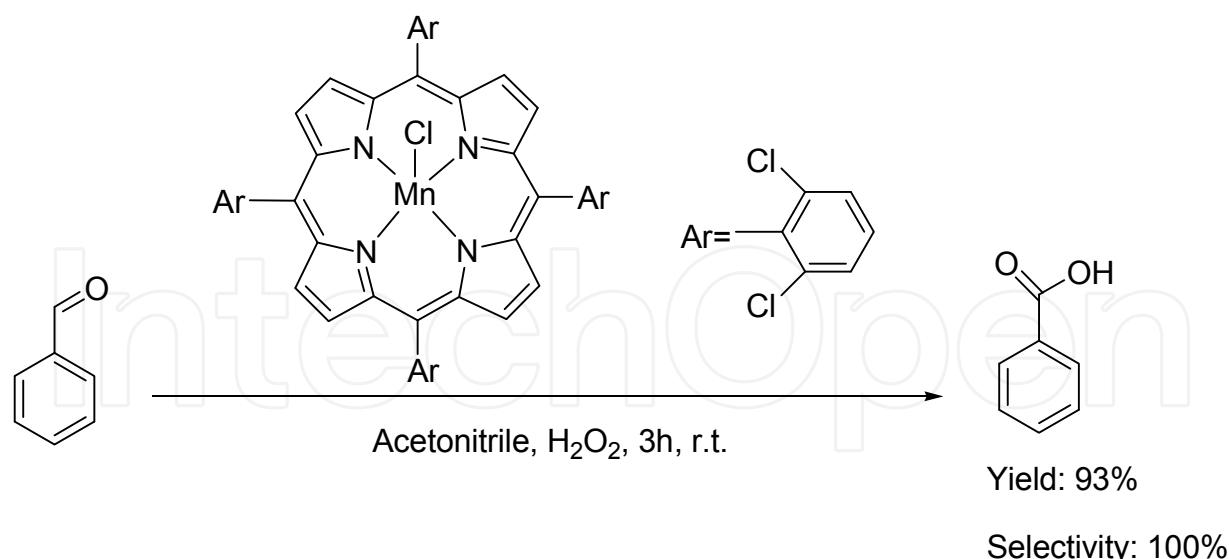


Fig. 4. Proposed mechanisms for the aerobic oxidation of alcohols catalyzed by ruthenium-porphyrin

5. Oxidation of aldehydes

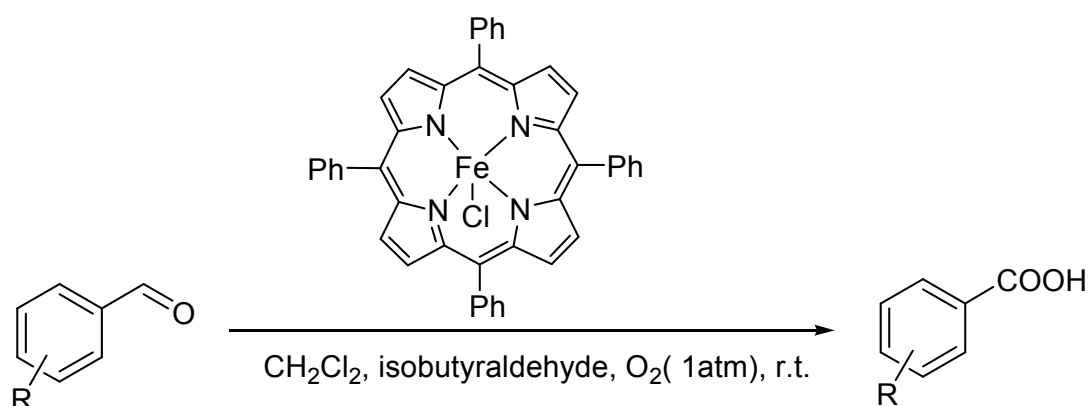
Oxidation of aldehydes to the corresponding carboxylic acids is one of the important methods in organic synthesis as carboxylic acids are versatile intermediates in a variety of synthetic transformations.⁸⁷ Few reports were found on the oxidation of aldehydes catalyzed by metalloporphyrins with hydrogen peroxide or molecular oxygen.

Rebello reported the oxidation of benzaldehyde with hydrogen peroxide in Mn(III) porphyrin/ammouium acetate system, which can give 93% yield of benzoic acid by conducting the reaction for 3 h (Scheme 11).⁸⁸



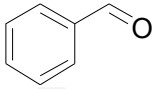
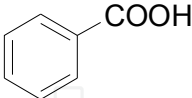
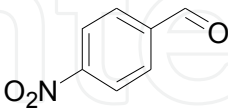
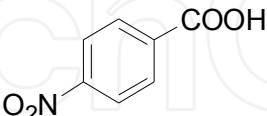
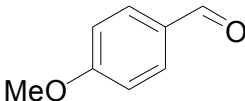
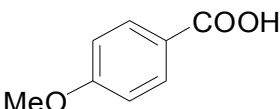
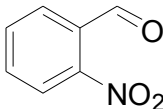
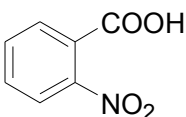
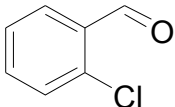
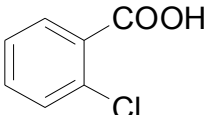
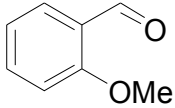
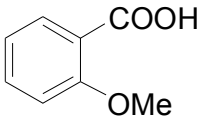
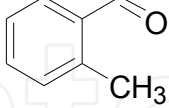
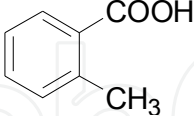
Scheme 11. Oxidation of benzaldehyde catalyzed by manganese-porphyrin with H_2O_2

First example of metalloporphyrins-catalyzed benzylic aldehyde oxidation using molecular oxygen as a sole oxidant at room temperature was developed previously by our research group (Scheme 12).⁸⁹



Scheme 12. Benzylic aldehydes aerobic oxidation catalyzed by $\text{Fe}(\text{TPP})\text{Cl}$

Various benzylic aldehydes were oxidized at room temperature in the presence of molecular oxygen and isobutyraldehyde as shown in Table 5. Most benzylic benzaldehydes could be smoothly converted to benzylic acids with high conversions by using $\text{Fe}(\text{TPP})\text{Cl}$ as a catalyst and molecular oxygen as a sole oxidant. The influence of steric effects could be clearly found for those *ortho*-position substituted substrates in comparison with those *para*-position substituted ones. For example, the oxidation of 4-methoxy-benzaldehyde for 2 h gave 93% yield of the corresponding acid; whereas only 75% yield of the corresponding acid could be obtained from the oxidation of 2-methoxy-benzaldehyde for 4 h (entries 3 and 6).

Entry	Substrate	Product	Time/h	Conv.(%)	Yield(%)
1			2.0	95	95
2			3.0	87	87
3			2.0	93	93
4			4.0	82	82
5			3.0	90	90
6			4.0	75	75
7			3.0	85	85

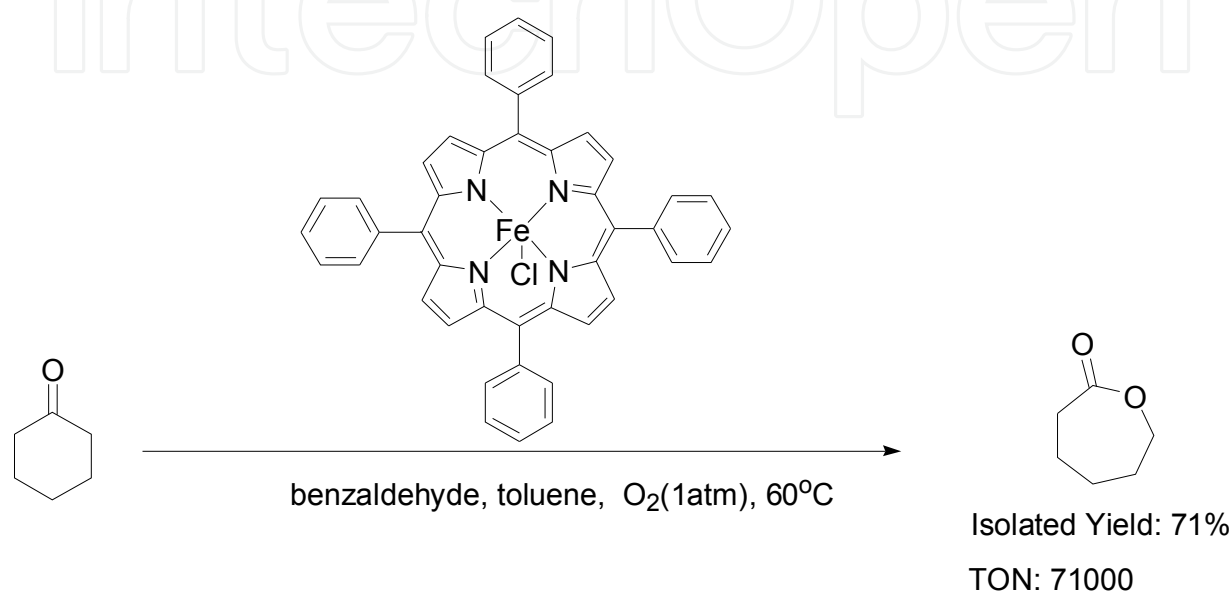
^aSubstrate =1.5 mmol, substrate/isobutyraldehyde (molar ratio)=1/5, catalyst(FeTPPCL, 1.5×10⁻³ mmol), r.t.; O₂ bubbling (1atm), 5mL CH₂Cl₂ solvent
Table 5. Oxidation of various benzylic aldehydes catalyzed by Fe(TPP)Cl in the presence of molecular oxygen^a

6. Oxidation of ketones

In 1899 Adolf Baeyer and Victor Villiger reported the oxidation of menthone to the corresponding lactone using a mixture of sodium persulfate and concentrated sulfuric acid.⁹⁰ The persulfuric acid was subsequently replaced by organic peracids such as persulfuric acid, *m*-CPBA, trifluoroperacetic acid and perbenzoic acid, then the

Baeyer-Villiger (B-V) reaction became one of the most well-known and widely applied reactions in organic synthesis.⁹¹ A combination of molecular oxygen and aldehydes under heterogeneous catalyst such as silica-supported nickel complex, iron(III)-containing mesoporous silica have been extensively studied.⁹²

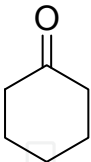
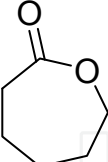
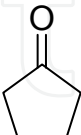
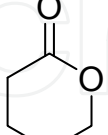
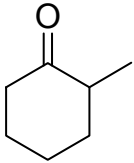
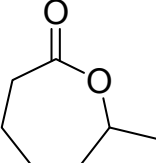
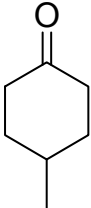
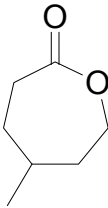
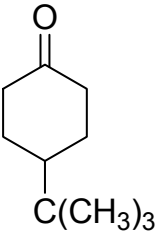
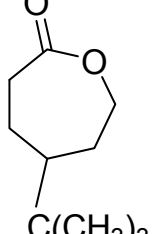
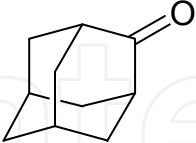
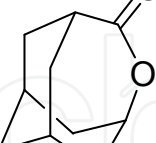
One example of B-V reaction catalyzed by metalloporphyrins with dioxygen has been developed by our group. Iron (III) *meso*-tetraphenylporphyrin chloride (Fe(TPP)Cl) was efficient for the B-V reaction of ketones to lactones in the presence of molecular oxygen and benzaldehyde (Scheme 13).



Scheme 13. Aerobic oxidation of ketones to lactone catalyzed by iron-porphyrins

The scope of substrates for the B-V reaction catalyzed by the Fe(TPP)Cl was examined and the typical results are shown in Table 6.

The oxidations of various cyclic ketones occurred smoothly to afford selectively the corresponding lactones by atmospheric dioxygen in the presence of Fe(TPP)Cl under mild conditions. It seems that cyclic ketones were more efficiently oxidized than acyclic ketones. Moreover among the cyclic ketones, six-membered cyclic ketones could be most efficiently oxidized to the corresponding lactones. For example only 32% cyclopentanone (entry 3) was converted to the corresponding lactone (entry 2) under the same reaction conditions. It might be that only those substrates with suitable steric configuration favored the conversion owing to the existence of the large ring of the metalloporphyrin catalyst in the present system. Furthermore, the substituent on the six-membered cyclic ketones was also investigated (entries 3~5), and the alkyl substitution to the ring of cyclic ketones caused no retardation of the oxidation, 96% conversion of 4-*tert*-butylcyclohexanone was obtained even increasing bulkiness of the substituent (entry 5).

Entry	Ketones	Product	Time (h)	Conv. (%)	Yield (%)
1			5	96	96
2			5	32	32
3			5	98	98
4			6	94	94
5			5	96	96
6			8	84	84

^aFe(TPP)Cl (0.2×10⁻³ M), substrate (1 mmol), toluene (5 mL), benzaldehyde (15 mmol), O₂ bubbling, 60°C
Table 6. Oxidation of various ketones by molecular oxygen in the presence of Fe(TPP)Cl^a

The possible presence of iron-oxo porphyrin was confirmed by UV-vis spectra from the oxidation of cyclohexanone, as show in Figure 5. Curves a and b show the spectra of cyclohexanone oxidation catalyzed Fe(TPP)Cl at the beginning and the point after the reaction for 30 min. A shift from 409 to 416 nm was observed, which is indicative of the existence of an active oxidation species expected as the iron high-valent intermediate.

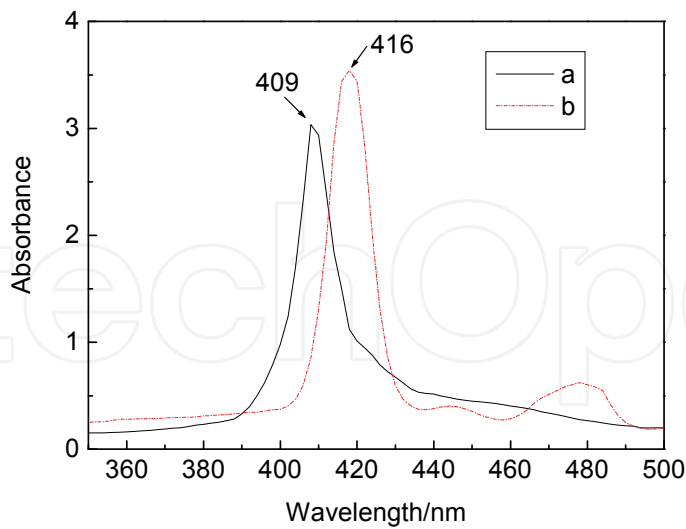


Fig. 5. UV-vis spectra of cyclohexanone oxidation by molecular oxygen in the presence of benzaldehyde and Fe(TPP)Cl. Cyclohexanone(1 mmol), Fe(TPP)Cl (0.2×10^{-3} M), benzaldehyde (15 mmol), toluene (5 mL), (a) initial point of reaction, (b) 30 min after reaction.

The reaction mechanism might be as shown in Figure 5. Based on the proposed mechanism, the iron porphyrin reacts with the benzaldehyde to generate an acyl radical at first. The acyl radical then reacts with dioxygen to give an acylperoxy radical. The acylperoxy radical acts as a carrier in a chain mechanism by reaction with another benzaldehyde molecule to give the peroxybenzoic acid, and generating another acyl radical as well. The peroxybenzoic acid is assumed to play two roles. Firstly, it reacts with another iron porphyrin molecule to generate high-valent Fe porphyrin intermediate, which combines cyclohexanone to accomplish oxygen transfer step and to generate ϵ -caprolactone (pathway A). Secondly, the peroxybenzoic acid attacks activated ketone to form a Criegee adduct, followed by protolysis to afford the lactone together with benzoic acid (pathway B).

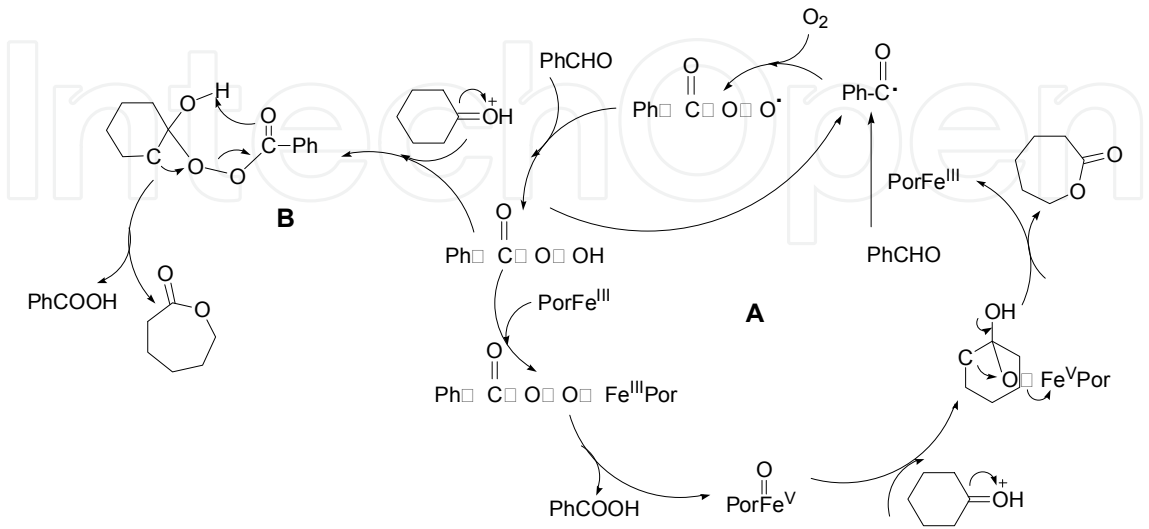


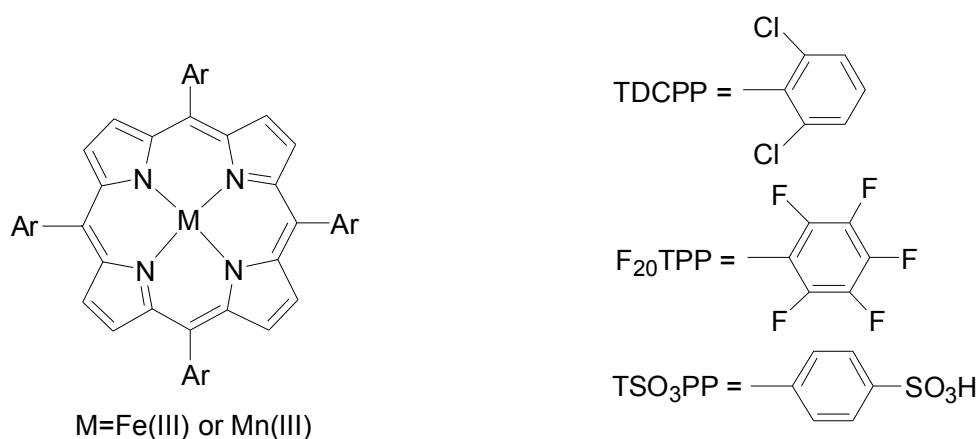
Fig. 6. Plausible mechanism of cyclohexanone oxidation in the presence of Fe(TPP)Cl and molecular oxygen

7. Oxidation of sulfides

7.1 Oxidation of sulfides to sulfones

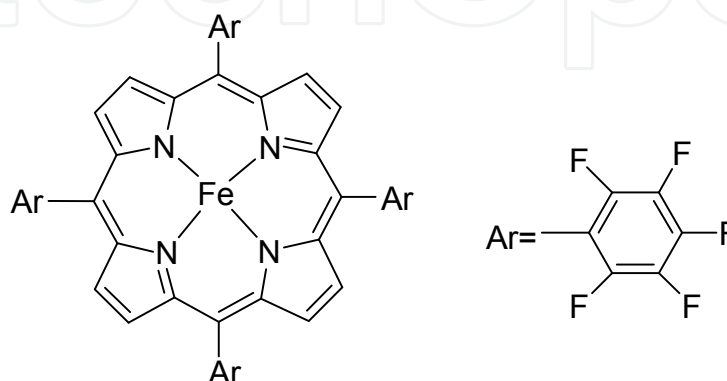
Oxidation of sulfide to sulfone has been the subject of extensive studies, since both products are useful organic intermediates for construction of various chemically and biologically significant molecules.⁹³ Hydrogen peroxide has been frequently applied to sulfoxidation system as an environmentally benign oxidant.

Sulfoxidation of sulfides catalyzed by cytochrome P-450 and peroxidase is a subject of current interest since the pioneering work of Oae and co-workers.⁹⁴ Recently, the practical application of sulfoxidation catalyzed by metalloporphyrins has been concerned increasingly. Marques reported a new approach of mustard oxidation in a protic solvent with H_2O_2 as an oxidant.⁹⁵ The results show that catalysis by Fe(III)- and Mn-(III)-tetraarylporphyrins (Scheme 14) can provide an interesting route to the transformation of mustard and related sulfides into sulfones. Differences in the behavior of Mn- and Fe-porphyrins for the efficiency in sulfide oxidation were also observed.



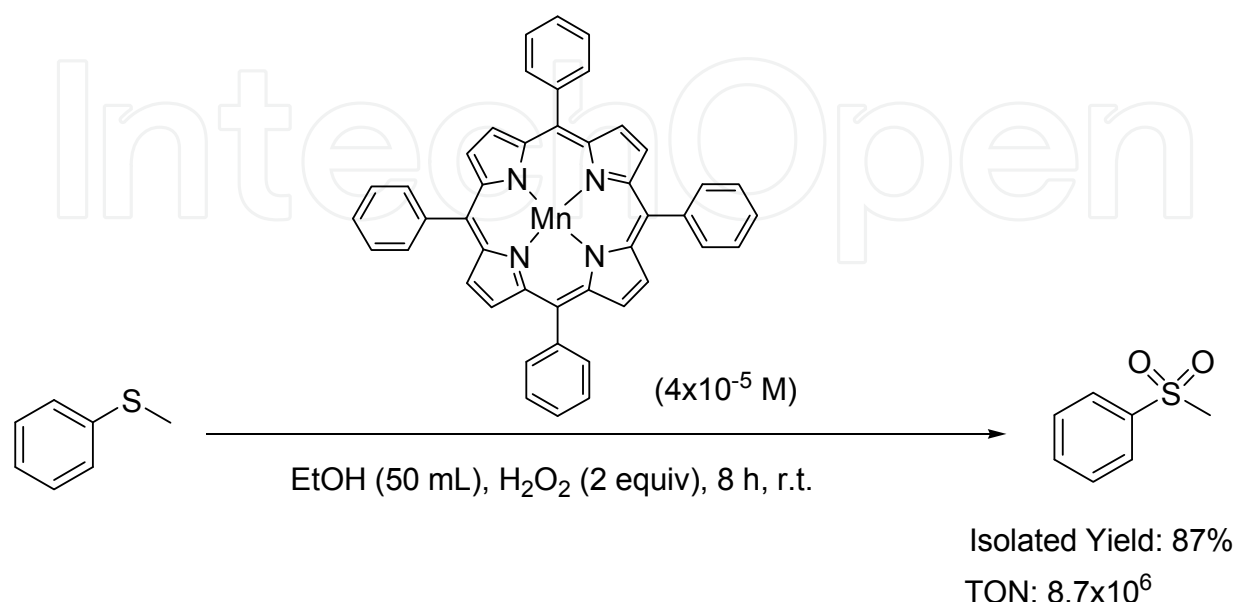
Scheme 14. Structures of metalloporphyrins used in the oxidation of mustard

Baciacchi and co-workers presented an efficient and chemically selective process for sulfide oxidation by hydrogen peroxide in the presence of complicated structural iron metalloporphyrins (tetrakis-pentafluorophenyl porphyrin, Scheme 15).⁹⁶ With a catalyst concentration between 0.09% and 0.25% of that of substrate, sulfones are obtained in almost quantitative yield and high chemoselectivity with both aromatic and aliphatic sulfides.



Scheme 15. Structures of tetrakis-pentafluorophenyl porphyrin

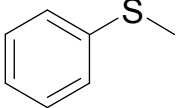
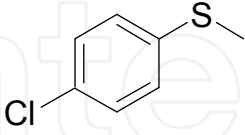
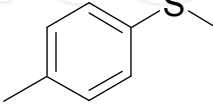
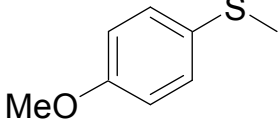
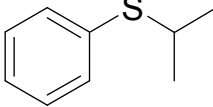
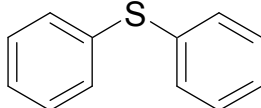
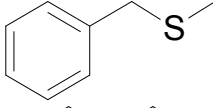


Simple structural metalloporphyrins has also been proved to be effective in the oxidation of sulfides to sulfones. As a part of our works, manganese *meso*-tetraphenyl porphyrin (MnTPP) was used for highly efficient selective oxidation of sulfide to sulfone by hydrogen peroxide at room temperature (Scheme 16).⁹⁷



Scheme 16. Oxidation of sulfide to sulfone catalyzed by manganese-porphyrin with H₂O₂

Various sulfides could be smoothly converted to the corresponding sulfones directly with high yields at room temperature as shown in Table 7. It could also be observed that the electronic property of substrate affected the conversion to some extent. Lower conversion rates could be obtained for electron-withdrawing substrates with longer reaction time (entry 2) than those substrates containing electron donating substituents that require shorter reaction time (entries 3-4).

The steric effects could be observed from the oxidation of diphenyl sulfide and isopropyl phenyl sulfide. The conversion rates of diphenyl sulfide and isopropyl phenyl sulfide were 89% and 83% after 2.0 and 3.0 h, respectively (entries 5-6). Compared with thioanisole, methyl benzyl sulfide presents similar catalytic behavior, and could be stoichiometrically converted at room temperature (entry 7). Sulfoxidation of the linear chain *di-n*-butyl sulfide smoothly proceeded with a high conversion rate and an excellent yield of sulfone in a shorter reaction time (entry 8).

Entry	Substrate	Time (h)	Conv.(%)	Select.(%)	
				sulfoxide	Sulfone
1		1.0	>99	<1	>99
2		3.0	94	7	93
3		1.5	98	9	91
4		1.5	98	7	93
5		2.0	89	<1	>99
6		3.0	83	<1	>99
7		1.5	>99	<1	>99
8		1.0	>99	3	97
9		2.0	95	12	88

^aReaction conditions: substrate (2 mmol), 30% H₂O₂(2 equiv), 5 mL of ethanol solvent, catalyst(4×10⁻⁵ M), r.t.,

Table 7. Oxidation of sulfide catalyzed by Mn(TPP) using hydrogen peroxide as oxidant^a

Besides high efficiency of the present catalyst system, another salient feature of the present sulfoxidation is its high chemical selectivity. Sulfone can be conveniently synthesized from sulfide containing hydroxyl group without carbonyl compound byproduct (entry 9). The profile of thioanisole oxidation in the presence of H₂O₂ and Mn(TPP) is shown in Figure 7, demonstrating that the reaction proceeded *via* two steps: the first step was the oxidation of sulfide to sulfoxide, and the second step was the oxidation of sulfoxide to sulfone. The sulfoxide was the reaction immediate.

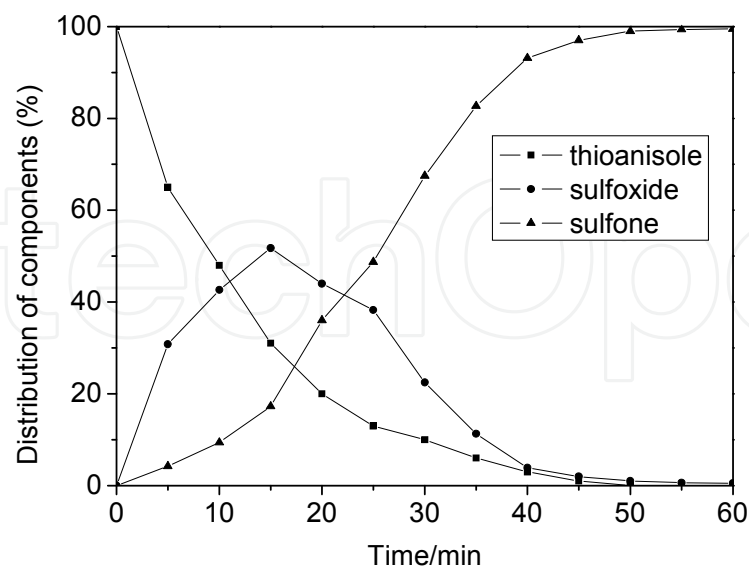


Fig. 7. Reaction profile for the oxidation of thioanisole in the presence of H₂O₂ and Mn(TPP) (4×10⁻⁵ M) in ethanol (5mL) at room temperature

Direct oxygen transfer from metal-oxo porphyrin radical cation to the sulfide is generally accepted to be the mechanism for sulfide oxidation in the presence of H₂O₂ and metalloporphyrins. The possible presence of metal-oxo porphyrin was confirmed by in situ UV-Vis spectrum from the thioanisole oxidation system, as shown in Figure 8.

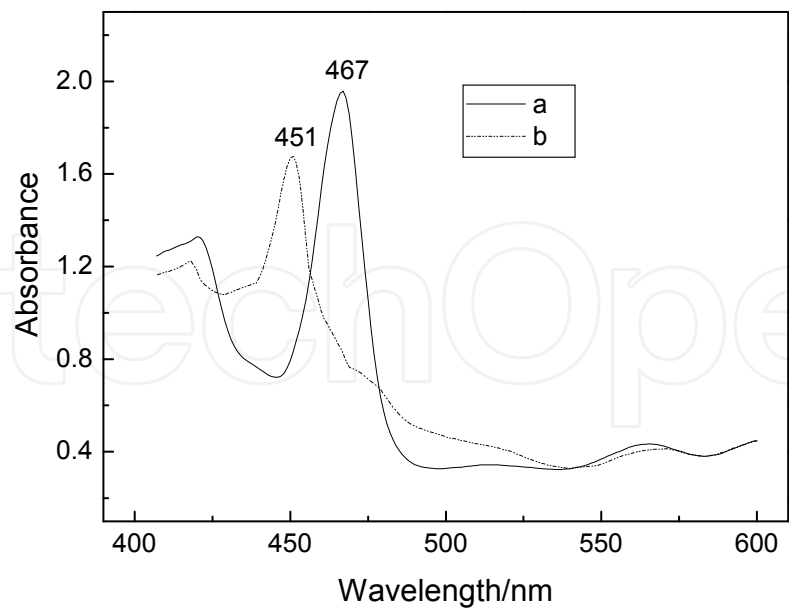


Fig. 8. In situ UV-Vis spectra of thioanisole oxidation catalyzed by Mn(TPP) in the presence of hydrogen peroxide, thioanisole (2mmol), 30% H₂O₂(2 equiv), 5 mL of ethanol solvent, Mn(TPP) catalyst(4×10⁻⁵ M), r.t., a: initial point of reaction, b: 15 min after reaction

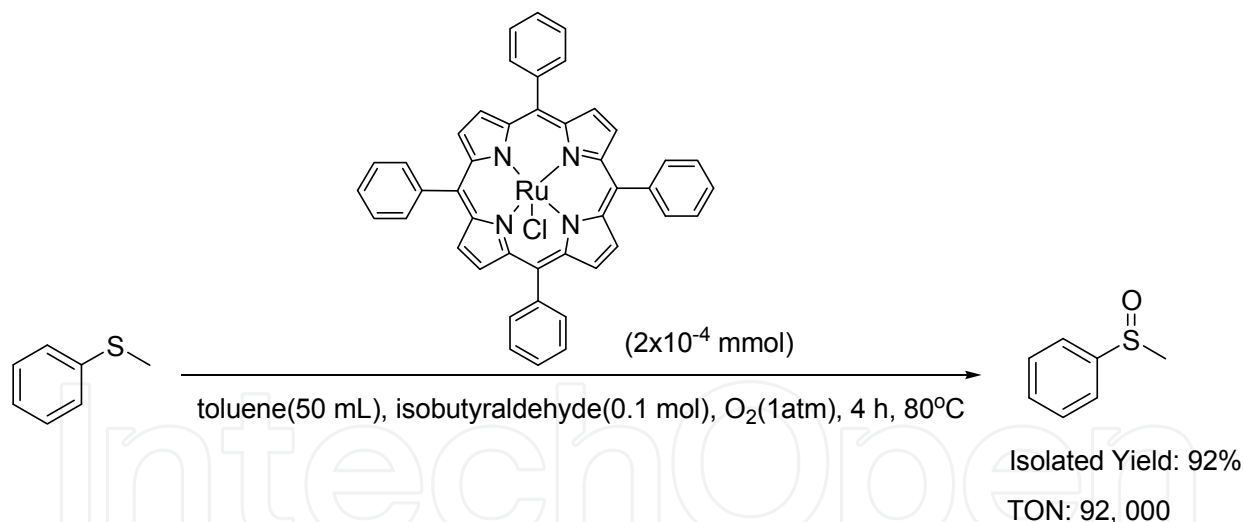
In Figure 8, a and b show the spectra of thioanisole oxidation catalyzed by Mn(TPP) at the beginning and the point after the reaction for 15 min. A shift from 467 to 451 nm with a small loss of intensity was observed. The GC control of the reaction revealed the formation of the sulfoxide and sulfone, which is indicative of the existence of an active oxidation species expected as the Mn(IV) porphyrin.

7.2 Oxidation of sulfides to sulfoxides

Selective oxidation of sulfides to the corresponding sulfoxides remains a challenge and is interesting because of the importance of sulfoxides as synthetic intermediates in organic synthesis.⁹⁸⁻¹⁰⁰ Although selective oxidation by molecular oxygen is more attractive because of its cost-effectiveness and environmentally-friendly nature of the oxidant, few reports were found for such oxidation of sulfides catalyzed by metalloporphyrins.

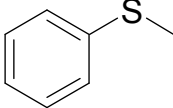
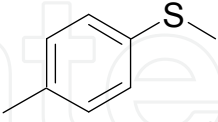
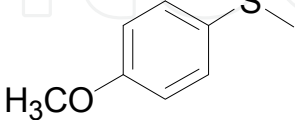
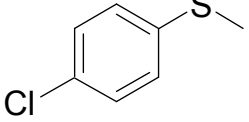
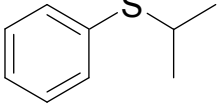
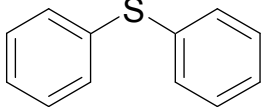
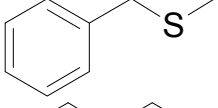
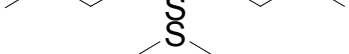
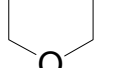
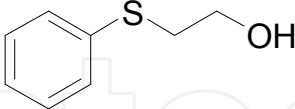
Mansuy ever reported selective aerobic oxidation of di-n-butylsulfide to the corresponding sulfoxide in 68% yield in the presence of Mn(TPP)Cl catalysts, zinc powder and CH₃COOH.¹⁰¹

Highly efficient selective oxidation of sulfides to sulfoxides by molecular oxygen catalyzed by ruthenium (III) *meso*-tetraphenylporphyrin chloride (Ru(TPP)Cl) with isobutyraldehyde as oxygen acceptor has been reported by our group.¹⁰² In large-scale experiment of thioanisole oxidation, the isolated yield of sulfoxide of 92% was obtained and the turnover number reached up to 92000 (Scheme 17).



Scheme 17. Ruthenium *meso*-tetraphenylporphyrin chloride catalyzed sulfoxidation

Different substrates could be smoothly converted to sulfoxides with high conversion rates, and excellent selectivities were obtained by Ru(TPP)Cl catalyst and molecular oxygen as the sole oxidant.

Entry	Substrate	Time (min)	Conv.(%)	Selectivity (%)	
				sulfoxide	sulfone
1		30	99	>99	<1
2		30	97	96	4
3		30	98	95	5
4		45	96	95	5
5		45	93	96	4
6		60	98	92	8
7		30	>99	>99	<1
8		20	>99	>99	<1
9		60	94	97	3
10		45	>99	90	<1

^aReaction conditions: substrate (2 mmol), molar ratio of substrate/isobutylaldehyde (1/5), molar ratio of catalyst/substrate (1/10000), toluene (5 mL), O₂(bubbling), 80°C
Table 8. Oxidation of various sulfides by molecular oxygen catalyzed by Ru(TPP)Cl ^a

It can be observed that the electronic property of substrate affects the reaction rate (entries 1~4). It required a slightly longer reaction time for substrate with electron-withdrawing groups (entry 4). The influence of steric effects could further be found from the oxidation of diphenyl sulfide and isopropyl phenyl sulfide. The conversion rates of diphenyl sulfide and isopropyl phenyl sulfide were 98%, 93% after much longer reactions time (entries 5-6). Compared with thianisole, methyl benzyl sulfide presents the similar reaction behavior, and it could be stoichiometrically converted at the same conditions (entry 7). Sulfoxidation of the linear chain di-n-butyl sulfide smoothly proceeded in less reaction time with high conversion and yields (entry 8). Cyclic sulfide, *i.e.* 1,4-thioxane could also be efficiently

sulfoxidated to the corresponding sulfoxide with 94% conversion and 97% selectivity (entry 9).

Despite of high efficiency, another salient feature of the present sulfoxidation system is its high chemoselectivity. For oxidation of hydroxyl group-containing sulfide e.g. 2-(phenylthio) ethanol (entry 10), sulfide can be entirely converted and the yields of sulfoxide could reach 90%, and 10% yield of the corresponding aldehyde was found in products. It demonstrates that the sulfide functional group is highly active, but hydroxyl group could hardly be activated under such reaction conditions.

It should be mentioned that the present reaction system was highly selective. Sulfoxides could be nearly stoichiometrically produced, and the generation of the corresponding sulfones was well controlled, which makes this process be a good alternative for sulfoxides production.

8. Conclusion

The foregoing sections have clearly demonstrated the impressive progress made in the area of metalloporphyrins-catalyzed aerobic oxidations. It is convincing that metalloporphyrins are very versatile oxidation catalysts which can be used in many different oxidation reactions (alkane hydroxylations, epoxidations of olefin, oxidation of compounds containing oxygen, sulfur and nitrogen, etc.). Meanwhile, many articles are dealing with mechanism studies on oxidations catalyzed by metalloporphyrins, attempting to learn the exact nature of the active species.

As described above, remarkable progress in mimicking the action of cytochrome P-450 enzymes has been made over the past decades. And this field is still seems to be achieved much attention. Biomimetic catalysis of metalloporphyrins is now a meeting for chemistry, chemical engineering, catalysis and biology. Combined efforts in such an interdisciplinary area will probably produce new applications of metalloporphyrins chemistry. Metalloporphyrins catalyzed oxidation of organic substrates with molecular oxygen is becoming an important and highly rewarding protocol for important feedstock for petrochemical and fine chemical industries. Initial successes in this area is promising and forecasts future growth in accessing oxidized organic molecules using molecular oxygen and metalloporphyrins catalysts. The efforts in this area will clearly culminate in tackling the major issues pertaining to environmentally acceptable technologies for future.

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Nature's evolution has led to the introduction of highly efficient biological mechanisms. Imitating these mechanisms offers an enormous potential for the improvement of our day to day life. Ideally, by bio-inspiration we can get a better view of nature's capability while studying its models and adapting it for our benefit. This book takes us into the interesting world of biomimetics and describes various arenas where the technology is applied. The 25 chapters covered in this book disclose recent advances and new ideas in promoting the mechanism and applications of biomimetics.

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