CHAPTER-IV

Mononuclear Iron(III) Complexes with N_4-donor Ligands: Synthesis, Characterization and Catalytic Activity towards Oxygenation of Hydrocarbons

CHAPTER IV

Mononuclear Iron(III) Complexes with N_4-donor Ligands: Synthesis, Characterization and Catalytic Activity towards Oxygenation of Hydrocarbons

Abstract

Mononuclear iron(III) complexes $[Fe(L^1)Cl_2]Cl$ (**1**) and $[Fe(L^2)Cl_2]Cl$ (**2**), with N_4-donor ligands L^1 and L^2, where L^1= N,N′-bis(2-pyridylmethyl)-1,2-cyclohexanediamine and L^2= N,N′-bis(2-pyridylmethyl)ethane-1,2-diamine, have been synthesized. The synthesized complexes have been characterized by spectroscopic techniques and elemental analysis. The catalytic activities of the complexes towards oxygenation of hydrocarbons have been studied at room temperature using mild hydrogen peroxide (H_2O_2) and *tert*-butylhydroperoxide (*t*-BuOOH) as the terminal oxidants. Catalytic oxygenation of unactivated C-H bonds of saturated hydrocarbons has also been examined with *m*-chloroperbenzoic acid (*m*-CPBA) as the oxidant. Selective oxidation of alcohols to aldehydes or ketones with excellent yield has been achieved at room temperature by the monomeric complex **1** using environmentally benign hydrogen peroxide (H_2O_2) as the terminal oxidant. Kinetic analysis of the complex **1** catalyzed oxidation of 2,4,6-tri-*t*-butyl phenol (TTBP) by *m*-CPBA in acetonitrile exhibits the first order dependence of the rate on the concentration of catalyst as well as on that of the oxidant.

IV.1 Introduction

Hydrocarbons, especially saturated hydrocarbons are the main constituents of oil and natural gases. The functionalization of hydrocarbons under mild conditions constitutes an extremely important field of contemporary chemistry because of their great abundance in nature makes them a convenient chemical feedstock. Therefore, the development in this area is a key objective for the transformation of hydrocarbons to more valuable oxygen containing products such as alcohols, aldehydes, ketones, acids and epoxides. However, the inertness of saturated hydrocarbons makes their chemical transformation extremely challenging from the viewpoint of basic science. Hence, the oxyfunctionalization of a sp^3 C-H bond in a selective fashion under mild conditions remains a challenge of major interest in chemistry [1]. The high exothermicity of oxidation makes the formation of oxygen containing products from hydrocarbons and molecular oxygen a thermodynamically allowed process. However, this same exothermicity usually makes these processes uncontrollable. Thus, the selective oxygenation of hydrocarbons to valuable oxygenates represents a significant challenge, since initial oxidation products are susceptible to complete combustion to produce thermodynamically stable products such as water and carbon dioxide.

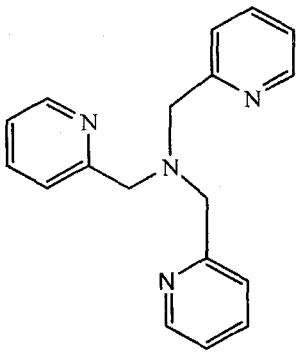
In spite of the inherent difficulty in achieving the selective oxygenation of C-H bonds of hydrocarbons, nature has evolved several iron-containing metalloenzymes to accomplish such transformations selectively under very mild conditions [1a, 2]. The group of enzymes, called monooxygenases, catalyzes the insertion of one oxygen atom from dioxygen into the C-H bond, while the second oxygen atom is reduced to form water. Cytochrome P-450, most extensively studied oxygen-activating enzymes, is capable of carry out the hydroxylation of aliphatic C-H bonds and the epoxidation of C-C double bonds (C=C bonds) with high regioselectivity and stereoselectivity [3]. Several other types of oxygen transfer reactions such as N-dealkylation, O-dealkyaltion and sulfoxidation are also catalyzed by this enzyme. The cytochrome P-450 catalyzed oxygen transfer reaction is proposed to proceed through an oxohaem catalytic intermediate [4]. Metalloporphyrins have always enjoyed a special preference as synthetic models for the reaction site of cytochrome P-450 [4d, 5]. The first oxidation system with synthetic metalloporphyrin as a catalyst was developed by Grooves and co-workers in 1979 [6]. Subsequently, numerous reports on metalloporphyrin-catalyzed oxidation systems have appeared in the literature [7-14]. Among the most extensively

studied systems are the epoxidation of alkenes and hydroxylation of alkanes catalyzed by iron, manganese and ruthenium porphyrins with different terminal oxidants.

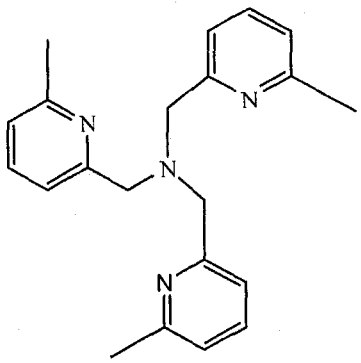
Apart from metalloporphyrins, metalloenzymes containing non-heme iron centers have been shown to promote novel oxidative chemistry [15]. In this context, methane monooxygenase [16] and Rieske dioxygenases [17] have received much attention. The iron containing active sites of these enzymes are supported by the "2-His-1-carboxylate facial triad" structural motif, leaving up to three *cis*-coordinating sites for oxygen/ or substrate binding. They catalyze an array of oxidative transformations even more diverse than those associated with the heme systems [18]. In view of the special capability of these iron-containing oxygenases in the hydrocarbon oxygenation process, the bio-inspired iron chemistry has attracted a great deal of interest [19].

A wide variety of multidentate N-based ligands have been designed and their mononuclear iron complexes have been synthesized for modelling the active site of iron enzymes exhibiting a catalytic function [15a, 18c]. A schematic representation of important polydentate ligands are given in Figure IV.1.

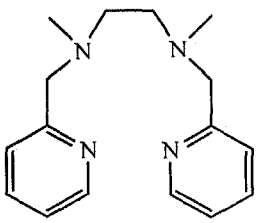
An interesting example of these non-heme iron catalysts was reported by Professor Que and his research group. They discovered a family of non-heme iron catalysts, represented by $[Fe(II)(tpa)(CH_3CN)_2]^{2+}$ **1** (tpa = tris(2-pyridylmethyl)amine), those are capable of stereospecific hydrocarbon oxidations using H_2O_2 as oxidant [20]. The oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane afforded tertiary alcohol products with 99% retention of stereochemistry and, furthermore, the system allowed oxygen insertion into olefins, affording only epoxide products with complete retention of stereochemistry [20]. Another iron(II) complex, $[Fe(II)(bpmen)(CH_3CN)_2]^{2+}$ **3** (bpmen = N,N′-dimethyl-N,N′-bis(2-pyridylmethyl)ethane-1,2-diamine), has been proven to be effective catalyst for alkane hydroxylation and alkene epoxidation with H_2O_2 [21]. Feringa and co-workers reported that the iron(II) complex containing pyridine-based pentadentate ligand (N4Py), $[Fe(N4Py)(CH_3CN)]^{2+}$ **4** (N4Py = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridylmethyl) amine), catalyzes the oxidation of alkanes with H_2O_2 [22]. Other mononuclear iron(II) complexes bearing N_5-pentadentate ligands, such as $[Fe(PMA)(CH_3CN)]^{2+}$ **5** (PMA=2-(2′,5′-diazapentyl)-5-bromopyrimidine-6-carboxylic acid N-[2-(4′-imidazolyl) ethyl]amide anion) [23] and $[Fe(PaPy_3)(CH_3CN)]^{2+}$ **6** ($PaPy_3H$ =N,N-bis(2-pyridylmethyl)amine-N-ethyl-2-pyridine-2-carboxamide, H is the dissociable carboxamido H atom) [19b] have been known to catalyze the oxidation of alkanes and alkenes with H_2O_2 or *t*-BuOOH as oxidant.



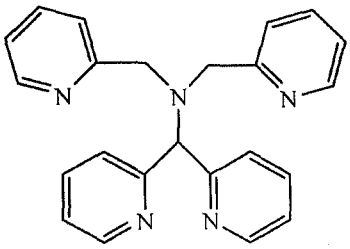
tpa
1: $[Fe^{II}(tpa)(NCCH_3)_2]^{2+}$



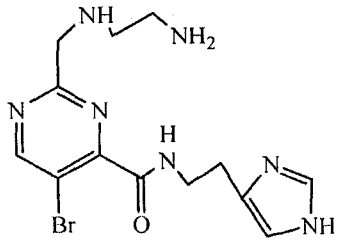
6-Me_3tpa
2: $[Fe^{II}(6\text{-}Me_3tpa)(NCCH_3)_2]^{2+}$



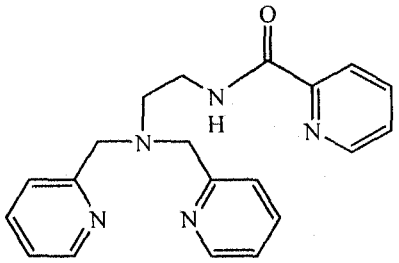
bpmen
3: $[Fe^{II}(bpmen)](NCMe)_2]^{2+}$



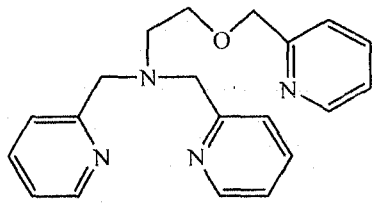
N4Py
4: $[Fe^{II}(N4Py)(NCCH_3)_2]^{2+}$



HPMA
5: $[Fe(PMA)(NCCH_3)_2]^{2+}$



$HPaPy_3$
6: $[Fe(PaPy_3)(NCCH_3)_2]^{2+}$



tpoen
7: $[Fe(tpoen)Cl]^{+}$

Figure IV.1 Structures of the polydentate ligands.

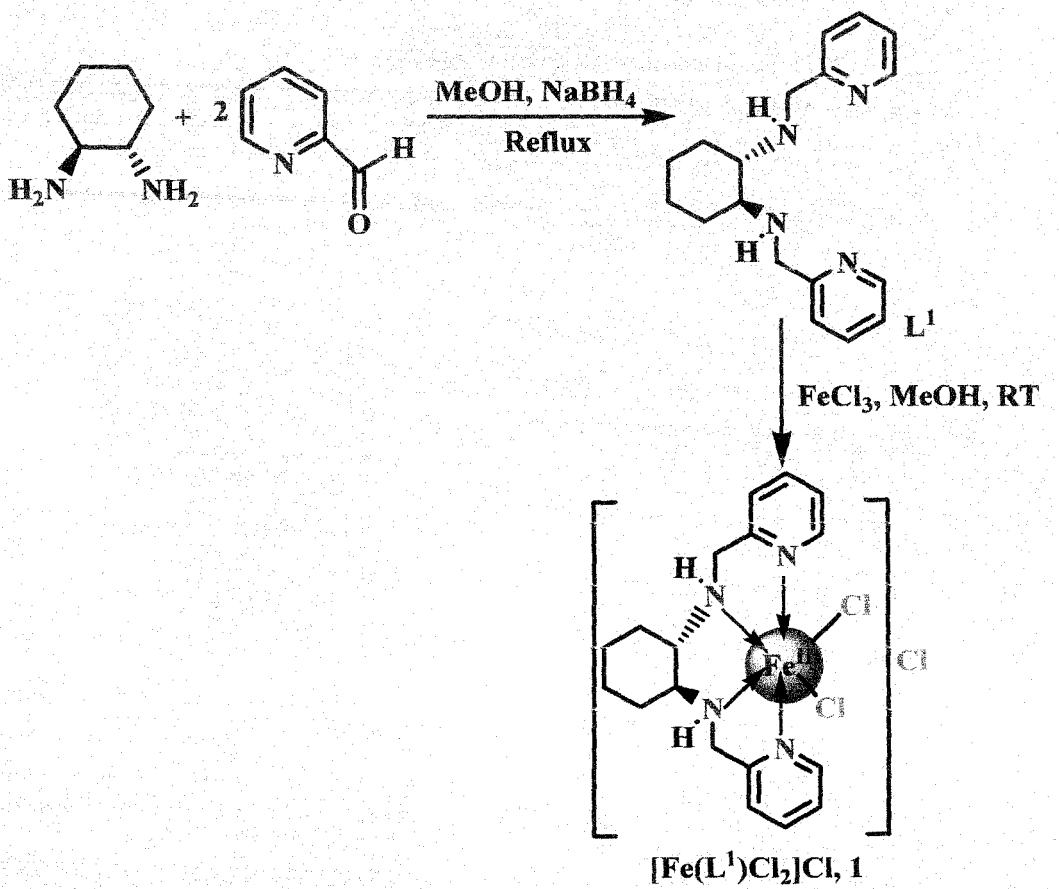
Three mononuclear iron complexes of tpoen ligand 7 (tpoen = N-(2-pyridylmethoxyethyl)-N,N'-bis(2-pyridylmethyl)amine), [Fe(tpoen)Cl].0.5(Fe_2OCl_6), [Fe(tpoen)Cl]PF_6 and Fe(tpoen)Cl_3 catalyze the oxidation of cyclohexane, adamantane and ethylbenzene with H_2O_2 and *m*-CPBA as oxidants [24]. In addition to this, a few mononuclear iron(III) biomimetic catalysts have also been reported containing deprotonated carboxamido-nitrogen based ligands that prevent the formation of hydroxo- or oxo-bridged polymeric species [19b, 25].

In the present chapter, we describe the synthesis and characterization of mononuclear iron(III) complexes $[Fe(L^1)Cl_2]Cl$ **1** and $[Fe(L^2)Cl_2]Cl$ **2**, where L^1 = N,N′-bis(2-pyridylmethyl)-1,2-cyclohexanediamine and L^2 = N,N′-bis(2-pyridylmethyl)ethane-1,2-diamine. The catalytic activities of the complexes in the oxygenation of hydrocarbons have been studied at room temperature using mild H_2O_2 and *t*-BuOOH as the terminal oxidants. Catalytic oxygenation of saturated hydrocarbons has also been described at room temperature with *m*-CPBA as the oxidant.

IV.2 Results and discussion

IV.2.1 *Synthesis*

The ligands L^1 and L^2 were synthesized according to a known two step procedure involving condensation of pyridine-2-carboxaldehyde and corresponding diamine to form a schiff base followed by reduction with $NaBH_4$ [26]. The synthesized ligands were characterized by various spectroscopic techniques (^1H NMR, IR and ESI-MS). The mononuclear iron(III) complex of L^1 with Cl^- as a counter anion was readily prepared by the reaction of equimolar amounts of L^1 and $FeCl_3$ in methanol medium (Scheme IV.1). On cooling, shinning crystals of complex **1** precipitated from the reaction mixture.



Scheme IV.1 Synthesis of complex, **1**.

IV.2.2 *Characterisation*

IV.2.2.1 IR spectra

The ligands L^1 and L^2 were characterized by infrared spectroscopy. The IR spectrum of N,N′-bis(2-pyridylmethylene)-1,2-cyclohexanediamine exhibits absorption at 1644 cm^{-1} characteristic of N=C bond [27], which is absent in the IR spectrum of N,N′-bis(2-pyridylmethyl)-1,2-cyclohexanediamine (L^1) and N,N′-bis(2-pyridylmethyl)ethane-1,2-diamine (L^2). Both the ligands exhibit absorption around 3300 cm^{-1} corresponds to N-H stretch [27].

IV.2.2.2 ^{1}H NMR spectra

The ligands L^1 and L^2 have been characterized by ^{1}H NMR spectroscopy. The spectral data of both the ligands are provided in the experimental section and the NMR spectrum of the ligand L^1 has been shown in Figure IV.2 as a representative case. The spectral data of the ligands are in good agreement with the reported data [28].

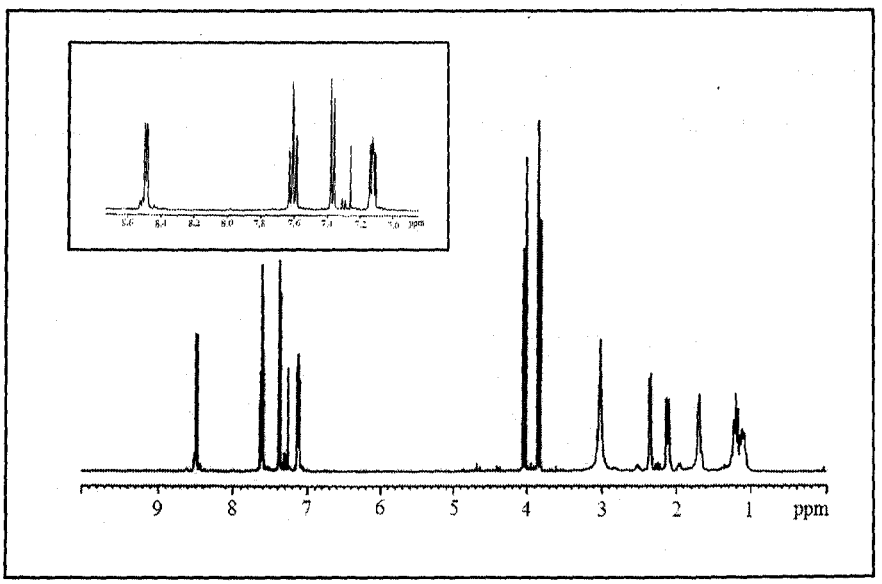


Figure IV.2 ^{1}H NMR spectra of the ligand L^1; Inset: Expanded aromatic region.

IV.2.2.3 Electronic spectra

The electronic spectral data of the mononuclear iron(III) complexes **1** and **2** are compiled in Table IV.1 and the overlay electronic absorption spectra of both the complexes are shown in Figure IV.3.

Table IV.1 Electronic spectral data for iron (III) complexes in acetonitrile.

Complex	$\lambda_{max.}$ (nm)	ε (M^{-1} cm^{-1})
1	252	22,100
	293(sh)	10,200
	358	6,000
2	253	9,300
	287(sh)	5,100
	353	2,700

In acetonitrile solution, both the complexes exhibit absorption bands in the region 250-400 nm. The intense band near 255 nm for both the complexes is due to the $\pi \rightarrow \pi^*$ transition within the pyridine moiety [24, 29]. The bands near 290 nm (sh) and a broad band near 360 nm for both the complexes are assigned to the chloro-to-iron(III) charge transfer transition [24, 30].

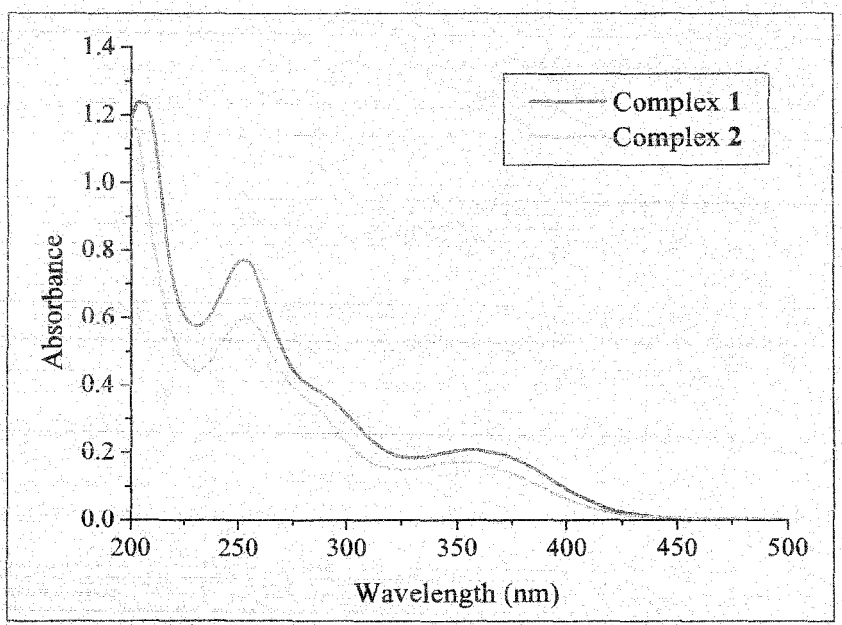


Figure IV.3 Electronic spectra of complexes **1** and **2** in acetonitrile.

IV.2.2.4 Magnetic property

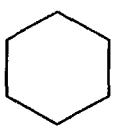
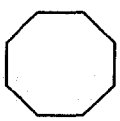
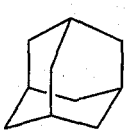
The magnetic susceptibility of the complexes **1** and **2** in solid state was determined at room temperature (298 K). Complex **1** exhibits a magnetic moment of 5.9 μ_B, which suggests the high spin configuration in mononuclear iron(III) [31]. Complex **2** shows effective magnetic moment of 5.4 μ_B, consistent with high spin mononuclear iron(III).

IV.2.3 *Catalytic properties*

IV.2.3.1 Oxygenation of saturated hydrocarbons

The catalytic activities of complexes **1** and **2** have been explored in the oxygenation of saturated hydocarbons (cyclohexane, cyclooctane and adamantane) with mild H_2O_2 and *t*-BuOOH under aerobic condition at room temperature. Detailed experimental procedures are given in the experimental section. The results are summarized in Table IV.2. Both the complexes catalyze the oxygenation of cyclohexane to cyclohexanol and cyclohexanone. When H_2O_2 is employed as an oxidant, complex **1** catalyzes the cyclohexane oxygenation with A/K ratio of 0.6. Total yield of the oxygenates is 16% (Table IV.2, entry 1). Under the same conditions, cyclohexane conversion decreases to 5% when *t*-BuOOH is used as oxidant. However, the A/K ratio (0.6) remains same as with H_2O_2 (Table IV.2, entry 2). Complex **2** catalyzes cyclohexane oxygenation with the same A/K ratio (0.6) using H_2O_2, but with a lower yield of oxygenates; however, with *t*-BuOOH, complex **2** fails to catalyze the oxygenation of cyclohexane (Table IV.2, entries 3, 4). Cyclooctane is oxidized to the corresponding alcohol and ketone with A/K ratio of 0.3-0.6 (Table IV.2, entries 5-8). The highest conversion (15%) has been achieved with **1**/ H_2O_2 system. However, control reactions performed in the absence of the iron(III) complex fail to effect the oxyfunctioanlization of alkanes.

Table IV.2 Catalytic oxygenation of alkanes by mild H_2O_2 and *t*-BuOOH at room temperature.

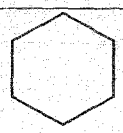
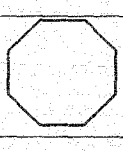
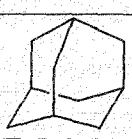
Entry	Substrate	Catalyst	Oxidant	Yield (%)[a]	Product Selectivity (%)[b]			Remarks[c]
					Ol	One		A/K
1		**1**	H_2O_2	16	38	62		0.6
2		**1**	*t*-BuOOH	5	40	60		0.6
3		**2**	H_2O_2	8	38	62		0.6
4		**2**	*t*-BuOOH	-	-	-		-
					Ol	One		A/K
5		**1**	H_2O_2	15	20	80		0.3
6		**1**	*t*-BuOOH	8	37	63		0.6
7		**2**	H_2O_2	3	-	100		-
8		**2**	*t*-BuOOH	3	33	67		0.5
					1-ol	2-ol	2-one	$3^\circ/2^\circ$
9		**1**	H_2O_2	14	72	14	14	7.5
10		**1**	*t*-BuOOH	12	66	17	17	6.0
11		**2**	H_2O_2	7	72	14	14	7.5
12		**2**	*t*-BuOOH	5	60	20	20	4.5

[a]Yields are based on oxidant concentration; [b]Selectivity is percentage expressed with respect to total yield; [c]A/K = alcohol/ketone, $3^\circ/2^\circ$ = (1-ol x 3)/ (2-ol + 2-one).

The catalytic activities of complexes **1** and **2** have also been examined in the oxygenation of adamantane with H_2O_2 and *t*-BuOOH as oxidants. The oxygenation of adamantane affords mainly 1-adamantanol along with 2-adamantanol and 2-adamantanone as minor products. The total yield of oxygenates is 12-14% with $3^\circ/2^\circ$ ratio of 6.0-7.5 catalyzed by **1** using both the oxidants (Table IV.2, entries 9, 10). Complex **2** diminishes the conversions to 5-7% with $3^\circ/2^\circ$ ratio of 4.5-7.5 (Table IV.2, entries 11, 12). Thus, at room temperature, **1**/oxidant emerges as a better catalytic system than **2**/oxidant towards the oxyfunctionalization of saturated hydrocarbons in presence of both the oxidants.

Oxygenation of saturated hydrocarbons has also been studied at room temperature using *m*-CPBA as oxidant with the present catalytic system. The results are summarized in Table IV.3.

Table IV.3 Oxygenation of alkanes by *m*-CPBA at room temperature.

Entry	Substrate	Catalyst	Yield (%)[a]	Product Selectivity (%)[b]			Remarks[c]
				Ol	One		A/K
1		**1**	6	67	33		2.0
2		**2**	5	60	40		1.5
				Ol	One		A/K
3		**1**	6	67	33		2.0
4		**2**	5	60	40		1.5
				1-ol	2-ol	2-one	$3^\circ/2^\circ$
5		**1**	11	82	9	9	13.6
6		**2**	7	79	14	7	11.3

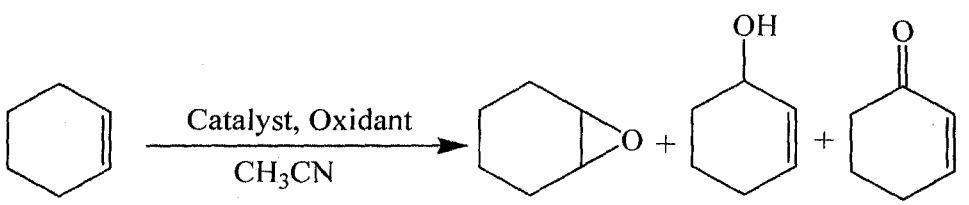
[a]Yields are based on oxidant concentration; [b]Selectivity is percentage expressed with respect to total yield; [c]A/K = alcohol/ketone, $3^\circ/2^\circ$ = (1-ol x 3)/ (2-ol + 2-one).

The selectivity of alkane oxygenation increases in presence of *m*-CPBA. For instance, in case of cyclohexane and cyclooctane oxygenation, A/K ratio of 1.5-2.0 has been obtained with the yield of 5-6% (Table IV.3, entries 1-4). In case of adamantane oxygenation, the regioselectivity has been enhanced with $3^\circ/2^\circ$ ratio of 11.3-13.6 in presence of *m*-CPBA (Table IV.3, entries 5, 6). For comparison, $3^\circ/2^\circ$ ratios of 2.7 found for Gif-type oxidations, about 2 for the oxidation of alkanes by hydroxyl radicals [32] and values of 3.1-3.3 for $[Fe(N4Py)(CH_3CN)](ClO_4)_2$ [22, 33]. A $3^\circ/2^\circ$ ratio of 9.5-10.0 has been observed for $[Fe_2O(bpy)_4(H_2O)_2](ClO_4)_4$ or $[Fe(tpa)Cl_2]ClO_4$ [34, 35] and 11-48 for oxidation with PhIO catalyzed by P450 mimics [35b, 36].

The low A/K ratios (0.3-0.6) in the oxygenation of cyclohexane and cyclooctane and the poor regioselectivity with $3^{\circ}/2^{\circ}$ ratios in the range of 4.5-7.5 in adamantane oxidation with H_2O_2 and *t*-BuOOH as oxidants suggest the involvement of radical based reaction pathway [15a, 20a, 37]. In contrast, enhanced selectivity in the oxyfunctionalization of alkanes with *m*-CPBA indicates the involvement of a metal-based intermediate [15b, 33]. The radical character of the oxygenation reactions with H_2O_2 or *t*-BuOOH has been confirmed by conducting the reactions in presence of "radical scavenger" 2,4,6-tri-*t*-butylphenol (TTBP). In case of cyclohexane oxygenation, addition of TTBP prior to H_2O_2 addition resulted in total quenching of the oxygenation reaction. This observation suggests the possible involvement of typical radical based reaction mechanism in the oxygenation reactions with H_2O_2 or *t*-BuOOH as oxidant [38].

IV.2.3.2 Oxygenation of alkenes

The catalytic properties of mononuclear iron(III) complexes have also been examined in the oxygenation of alkenes at room temperature using environmentally benign H_2O_2 and *t*-BuOOH as oxidants in acetonitrile medium under argon atmosphere. In case of oxygenation of cyclohexene catalyzed by **1** and **2** (Scheme IV.2), allylic oxidation is preferred over epoxidation affording cyclohexene-1-one as the major product with the selectivity of 73-75% in presence of H_2O_2 (Table IV.4, entries 1, 2).



Scheme IV.2 Oxygenation of cyclohexene.

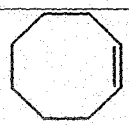
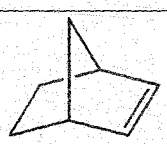
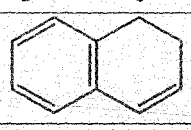
Table IV.4 Oxygenation of cyclohexene at room temperature.

Entry	Catalyst	Oxidant	Yield (%)[a]	Product Selectivity (%)[b]		
				Epoxide	Cyclohexene-1-ol	Cyclohexene-1-one
1	**1**	H_2O_2	30	7	20	73
2	**2**	H_2O_2	20	10	15	75
3	**1**	*t*-BuOOH	41	-	17	83
4	**2**	*t*-BuOOH	42	-	19	81

[a]Yields are based on oxidant concentration; [b]Selectivity is percentage expressed with respect to total yield.

The oxygenation of other alkenes (cyclooctene, 1-octene, norbornene and dihydronaphthalene) has also been studied with the present catalytic system. The results are given in Table IV.5. It has been found that **1**/oxidant emerges as the better catalytic system than **2**/oxidant towards oxygenation of alkenes at room temperature.

Table IV.5 Oxygenation of alkenes by mild H_2O_2 and *t*-BuOOH at room temperature.

Entry	Substrate	Catalyst	Product	Yield (%)[a]	
				H_2O_2	*t*-BuOOH
1		**1**	Cyclooctene oxide	13	6
2		**2**		7	3
3		**1**	1,2-epoxyoctane	16	19
4		**2**		17	18
5		**1**	Exo-epoxide	55	25
6		**2**		39	35
7		**1**	Oxide	65	60
8		**2**		36	29

[a]Yields are based on oxidant concentration.

IV.2.3.3 Oxidation of alcohols

The selective oxidation of primary and secondary alcohols to aldehydes and ketones, respectively, is one of the most vital functional group transformations in organic synthesis [40]. The carbonyl compounds represent an important group of products and intermediates in the fine chemicals [41]. Several methods have been explored to accomplish selective oxidation of alcohols to more valuable carbonyl compound [42]. These methods involve the use of expensive reagents, long reaction times, strongly acidic condition and tedious work-up procedure leading to the generation of a large amount of toxic waste [43]. Considering these facts, much attention has been paid to the development of selective oxidation using safe, economic and environmentally benign agents [44]. The aim of this work is to study the catalytic behavior of mononuclear non-heme iron(III) metal complexes towards oxidation of various alcohols to their corresponding carbonyl compounds by mild H_2O_2 at room temperature. The results of alcohol oxidation by **1**/H_2O_2 system have been compiled in Table IV.6.

Table IV.6 Oxidation of alcohols by $1/H_2O_2$ system at room temperature.

Entry	Substrate	Product	Yield (%)[a]
1	Benzyl alcohol	Benzaldehyde	77
2	4-Hydroxybenzyl alcohol	4-Hydroxybenzaldehyde	100
3	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	99
4	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	76
5	Cyclohexene-1-ol	Cyclohexene-1-one	100
6	Adamantane-2-ol	Adamantane-2-one	37

[a]Yields are based on oxidant concentration.

The oxidation of benzyl alcohol afforded benzaldehyde with 77% yield based on H_2O_2 (Table IV.6, entry 1). The substituted benzylic alcohols have also been converted to the corresponding aldehydes by $1/H_2O_2$ system in high yields (Table IV.6, entries 2-4). The data shown in Table IV.6 clearly suggest that the carbonyl compound is the only product obtained in comparatively high yields. No over oxidation of the primary alcohols to the corresponding acids was observed. Complex **1** has also been found effective in oxidizing the secondary alcohols with H_2O_2 at room temperature (Table IV.6, entries 5, 6). Cyclohexen-1-ol is converted to the corresponding ketone quantitatively, but the conversion decreases to 37% when adamantane-2-ol is used as substrate.

IV.2.3.4 TTBP oxidation

The rate of catalyst oxidation with the oxo-transfer reagent has been studied by monitoring the oxidation of 2,4,6-tri-*t*-butyl phenol (TTBP). The choice of this particular substrate was due to its oxidized product namely 2,4,6-tri-*t*-butylphenoxy radical (TTBP•) which absorbs at 630 nm (ε = 385 mol^{-1} cm^{-1}) and provides a simpler tool to monitor its generation by UV-visible spectroscopy [45]. The catalytic oxidation of TTBP is very slow in presence of H_2O_2. Thus we shifted our attention to measure the rate of catalyst oxidation by *m*-CPBA using 2,4,6-tri-*t*-butylphenol (TTBP) under argon atmosphere. The detailed regarding kinetic procedure is given in the experimental section.

Now in order to predict the reaction pathway of TTBP oxidation, the absorbance increase at 630 nm due to the formation of TTBP• has been measured. One representative kinetic plot of absorbance increase at 630 nm vs. time is shown in Figure IV.4.

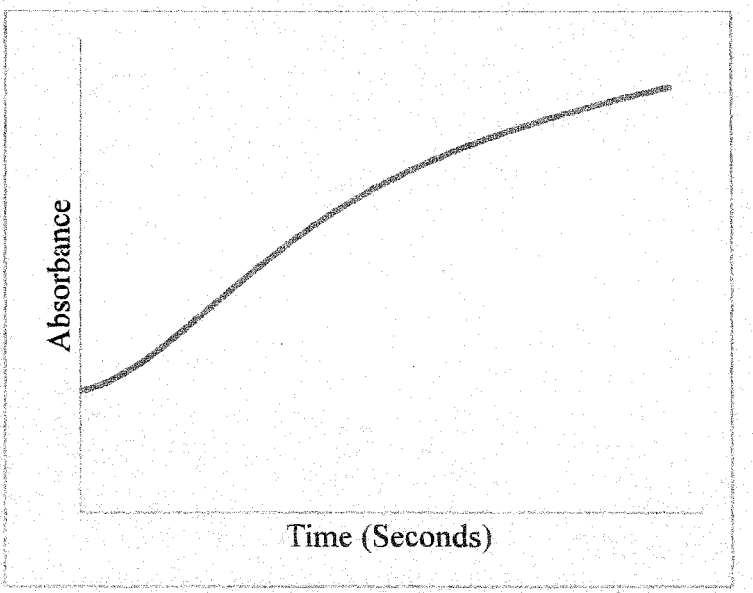


Figure IV.4 Absorbance vs. time plot of 2,4,6-tri-*t*-butylphenoxy radical formation in acetonitrile at 25±1 °C. TTBP= 54.6 mM, Catalyst= 0.7 mM, *m*-CPBA= 4 mM.

The absorbance vs. time plot shows that the increase in absorbance does not fit with a simple first or second order kinetic patterns. Therefore, the data obtained were analyzed by "initial rate" method [46]. The values of $(dA/dt)_0$ at varying initial concentrations of the reaction components, *m*-CPBA, catalyst and substrate are compiled in Table IV.7.

Table IV.7 Complex **1** catalysed oxidation of TTBP by *m*-CPBA in acetonitrile at 25±1 °C.

Entry	TTBP (mM)	Catalyst (mM)	Oxidant (mM)	$(dA/dt)_0$ $M\ s^{-1} \times 10^5$	Yield (%)[a]
1	14.5	0.7	1	3.7579	12
2	27.3	0.7	1	4.7034	17
3	41.6	0.7	1	5.6979	23
4	58.4	0.7	1	6.1893	26
5	80.7	0.7	1	9.0673	25
6	112.4	0.7	1	8.2847	28
7	54.4	0.7	1	7.3230	28
8	54.4	0.7	2	16.563	28
9	54.4	0.7	3	31.09	18
10	54.6	0.7	4	47.277	17
11	54.8	0.7	5	55.794	15
12	54.4	1.0	1	11.951	17
13	54.0	1.2	1	17.821	20
14	54.2	1.5	1	25.358	26
15	54.0	2.0	1	32.644	22

[a]Yields are based on the amount of *m*-CPBA used.

All runs were carried out in twice and the values of $(dA/dt)_0$ given in Table IV.7 are the average of the runs. It has been found that with increasing the TTBP concentration, $(dA/dt)_0$ increases, but the best yields are obtained in the range of 40 mM to 110 mM

TTBP concentrations (Table IV.7, entries 3-8). The plot of $(dA/dt)_0$ vs. [*m*-CPBA] at constant catalyst concentration and $(dA/dt)_0$ vs. [Catalyst] at constant *m*-CPBA concentration are shown in Figure IV.5 and Figure IV.6 respectively. Despite small deviations of the points in the figures, it is clear that the data are best fitted by a first order dependence of $(dA/dt)_0$ on the concentration of *m*-CPBA as well as on the concentration of catalyst.

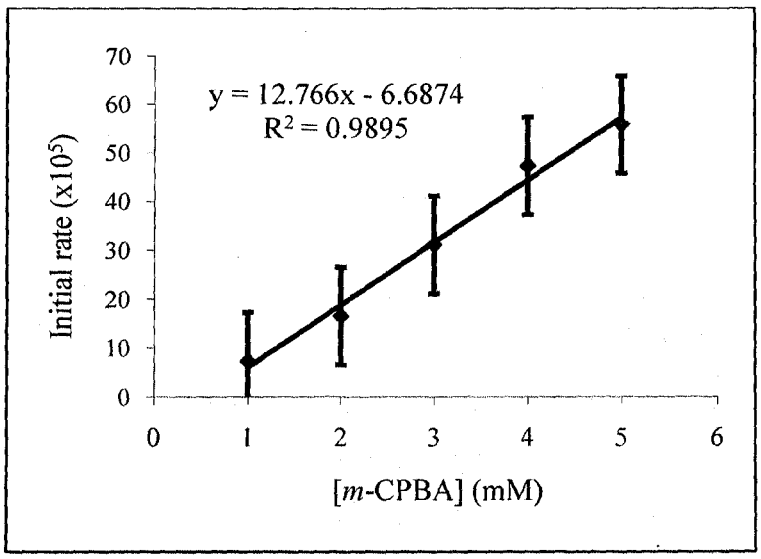


Figure IV.5 Plot of $(dA/dt)_0$ vs. [*m*-CPBA].

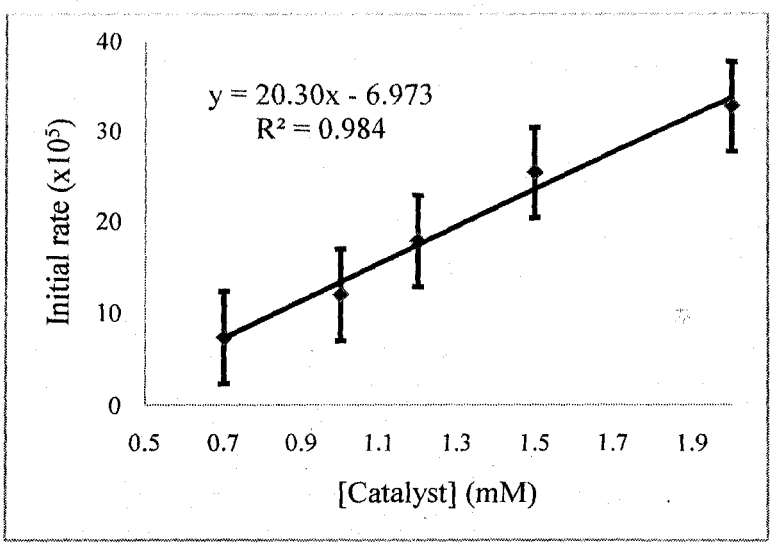


Figure IV.6 Plot of $(dA/dt)_0$ vs. [Catalyst].

Since substrate has always been taken excess, the dependence of $(dA/dt)_0$ on substrate concentration has been ignored and overall we propose that dA/dt is given by eqn. (1).

$$dA/dt \propto [m\text{-CPBA}]\,[\text{Catalyst}] \quad \ldots\ldots\ldots\ldots\ldots (1)$$

From the slope of the $(dA/dt)_0$ vs. [*m*-CPBA] at constant catalyst concentration, second order rate constant 1.82 x 10^4 dm^3 mol^{-1} was obtained while the $(dA/dt)_0$ vs. [Catalyst] plot gives a value of 2.03 x 10^4 dm^3 mol^{-1}.

IV.3 Conclusion

1. Mononuclear iron(III) complexes with N_4-donor ligands, **1** and **2**, have been synthesized and characterized. Oxygenation of various types of hydrocarbons has been achieved at room temperature by both the complexes with mild and benign hydrogen peroxide (H_2O_2) and *tert*-butylhydroperoxide (*t*-BuOOH) as the terminal oxidants.

2. Complex **1** exhibits moderate selectivities and moderate activities in the oxygenation of hydrocarbons. Complex **2** is found to be less efficient towards the catalytic oxygenation reactions.

3. The product profiles of **1** and **2** catalyzed oxygenation reactions with H_2O_2 or *t*-BuOOH suggest radical based reaction pathway. The low A/K ratio and predominately allylic oxidation of cyclohexene indicate the presence of radical intermediates. Finally, total quenching of oxygenation process in presence of "radical scavenger" 2,4,6-tri-*t*-butylphenol (TTBP) confirms the involvement of radicals during catalytic cycles.

4. The oxygenation of saturated hydrocarbons by *m*-CPBA suggests the involvement of metal-oxo intermediates.

5. Mononuclear iron(III) complexes efficiently catalyze an important oxidative transformation of alcohols to the corresponding carbonyl compounds selectively at room temperature with soft H_2O_2.

6. The kinetic data of the catalytic oxidation of TTBP by *m*-CPBA have been interpreted using the "initial rate" approach. The kinetic investigations reveal a first order dependence of reaction rate on the concentration of *m*-CPBA as well as on the concentration of catalyst.

IV.4 Experimental section

IV.4.1 *Materials*

Pyridine-2-carboxaldehyde, *trans*-1,2-diaminocyclohexane, ethylenediamine, sodium borohydride, anhydrous $FeCl_3$ and all other reagents were purchased from Sigma Aldrich and were used as received. Cyclohexene was distilled under argon and passed through a silica gel column prior to reaction. The active oxygen contents of the oxidants, H_2O_2 (as ~30% solution in water), *t*-BuOOH (as ~70% solution in water) and *m*-CPBA were determined iodometrically prior to use. 2,4,6-tri-*t*-butylphenol (TTBP) was obtained from Aldrich, purified by recrystallising several times from 95% ethanol (until the

ethanol solution was colourless). The solvents used for the catalytic experiments were distilled under argon and stored over molecular sieves (4 Å).

IV.4.2 ***Instrumental analyses***

UV-visible spectral measurements were done with JASCO V-530 spectrophotometer. The infrared spectra were recorded on KBr disc in a JASCO 5300 FT-IR spectrophotometer. The ^{1}H NMR analyses were undertaken on a Bruker spectrometer operating at 400 MHz. ESI-MS spectra were obtained on Agilent 6520 Q-TOF mass spectrometer. Magnetic susceptibility measurements were carried out using MSB mk1-Sherwood magnetic susceptibility balance. Elemental microanalyses (C, H and N) were done by Perkin-Elmer (Model 240C) or Heraeus Carlo Erba 1108 elemental analyzer. The product analyses were done by Perkin Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column).

IV.4.3 ***Synthesis of the ligands***

IV.4.3.1 *Synthesis of N,N'-bis(2-pyridylmethyl)-1,2-cyclohexanediamine* (L^1)

The ligand was synthesized according to the literature procedure [26].

Pyridine-2-carboxaldehyde (1.9879 g, 18.56 mmol) was added to a solution of *trans*-1,2-diaminocyclohexane (1.0580 g, 9.26 mmol) in 20 mL of dry methanol. The reaction mixture was stirred at 60 °C for 2 h, at which point sodium borohydride (2.1242 g, 55.9 mmol) was added as a solid. The resultant mixture was heated at reflux for 16 h and then cooled to ambient temperature. The solvent was removed under reduced pressure, yielding crude N,N'-bis(2-pyridylmethyl)-1,2-cyclohexanediamine. The crude material was dissolved in distilled H_2O, at which point the precursor was extracted with CH_2Cl_2. The extracts were dried over Na_2SO_4. Removal of the CH_2Cl_2 under reduced pressure yielded the purified N,N'-bis(2-pyridylmethyl)-1,2-cyclohexanediamine as a yellow oil. Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, 2H, Py, J = 4 Hz), 7.61 (m, 2H, Py), 7.37 (d, 2H, Py, J = 8 Hz), 7.2 (m, 2H, Py), 4.04 and 3.84 (d, 2 x 2H, J = 16 Hz), 3.03 (s, 2H, NH), 2.35 (m, 2H, CyH), 2.12 (m, 2H, CyH), 1.7 (m, 2H, CyH), 1.2 (m, 4H, CyH). ESI-MS: m/z 297.2 $[M+H]^+$.

IV.4.3.2 *Synthesis of N,N'-bis(2-pyridylmethyl)ethane-1,2-diamine* (L^2)

The procedure employed for L^1 was also used for the preparation of L^2. Ethylenediamine was used in the place of *trans*-1,2-diaminocyclohexane.

Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, 2H, Py, J = 4 Hz), 7.7 (m, 2H, Py), 7.41 (d, 2H, Py, J = 8 Hz), 7.23 (m, 2H, Py), 4.12 (s, 4H), 3.36 (s, 2H, NH), 3.13 (s, 4H). ESI-MS: m/z 243.1 $[M+H]^+$.

IV.4.4 ***Synthesis of the catalysts***

IV.4.4.1 *Synthesis of* $[Fe(L^1)Cl_2]Cl$ (**1**)

A methanolic solution (5 mL) of anhydrous $FeCl_3$ (0.1624 g, 1 mmol) was added to a solution of L^1 (0.296 g, 1 mmol) in methanol (10 mL) with stirring at room temperature. After stirring for 1 h, the solution was cooled. The yellow precipitate obtained was filtered off, washed with diethylether and then dried. The complex was recrystallized from acetonitrile as shining crystals.

Yield: 70%. Anal. Calc. for $C_{18}H_{24}Cl_3FeN_4.2H_2O$: C, 43.71; H, 5.71; N, 11.33. Found: C, 43.38; H, 5.41; N, 11.15%.

IV.4.4.2 *Synthesis of* $[Fe(L^2)Cl_2]Cl$ (**2**)

This compound was prepared according to the literature procedure [31].

To an aqueous solution (8 mL) of $L^2.4HCl$ (0.388 g, 1 mmol) was added $FeCl_3.6H_2O$ (0.270 g, 1 mmol) with stirring. After 10 min, sodium acetate (0.408 g, 3 mmol) was added to the yellow solution. The yellow solid that precipitated was filtered off and air dried. The complex was recrystallized from acetonitrile as yellow needles.

Yield: 74%. Anal. Calc. for $C_{14}H_{18}Cl_3FeN_4$: C, 41.57; H, 4.49; N, 13.85. Found: C, 41.14; H, 4.48; N 13.65%.

IV.4.5 ***Catalytic oxygenation of hydrocarbons***

Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction, 0.7 mM of catalyst and 700 mM of substrate were dissolved in 2 mL acetonitrile (argon saturated in case of anaerobic condition). In case of adamantane oxidation, mixture of acetonitrile and dichloromethane (1:1, *v/v*) was used due to solubility constrain. The oxygenation reaction was initiated by adding 7 mM of oxidant (2 mM in case of *m*-CPBA) and the contents were magnetically stirred at room temperature for 3 h (or 1 h in case of oxygenation reaction with *m*-CPBA). In case of alcohol oxidation, 0.7 mM of catalyst and 100 mM of substrate were dissolved in 2mL of acetonitrile and the oxidation reaction was initiated by adding 2 mM of H_2O_2 and the contents were magnetically stirred. The product analysis was done by injecting 1μL aliquot from the reaction vial into a capillary column of a preheated GC after addition of pentafluoroiodobenzene (PFIB) as internal standard. The identification and quantification of the products were done from the response factors of standard product samples.

IV.4.6 *Kinetic experiment of TTBP oxidation*

In a typical kinetic experiment, 2,4,6-tri-*t*-butylphenol (TTBP) (54 mM) and catalyst (0.7 mM) were taken in a cuvette fitted with silicon rubber septa. The cuvette was degassed by blowing argon over it for 15 minutes. Acetonitrile was taken in a 5 mL gas-tight syringe and was degassed by bubbling argon through the solvent for 15 minutes. This degassed acetonitrile (2 mL) was used to dissolve the TTBP and catalyst in the cuvette. In a small screw capped vial, a solution of *m*-CPBA was prepared in degassed acetonitrile. An aliquot volume of this stock solution of *m*-CPBA was added to the cuvette to initiate the reaction such that final concentration of *m*-CPBA becomes 1 mM. The cell was vigorously shaken and was placed immediately in a thermostated cell holder in a spectrophotometer and the absorbance data at 630 nm were collected at 10 s intervals.

References

1. (a) A. L. Feig, S. J. Lippard, *Chem. Rev.*, 1994, **94**, 759; (b) *Handbook of C-H Transformations*, Vol. 1-2, (Ed., G. Dyker), Wiley-VCH, Weinheim, 2005; (c) C. -L. Sun, B. -J. Li, Z. -J. Shi, *Chem. Rev.*, 2011, **111**, 1293; (d) T. Newhouse, P. S. Baran, *Angew. Chem. Int. Ed.*, 2011, **50**, 3362.

2. (a) L. Que, Jr., R. Y. N. Ho, *Chem. Rev.*, 1996, **96**, 2607; (b) B. J. Wallar, J. D. Lipscomb, *Chem. Rev.*, 1996, **96**, 2625.

3. I. G. Denisov, T. M. Makris, S. G. Sligar, I. Schlichting, *Chem. Rev.*, 2005, **105**, 2253.

4. (a) B. Meunier, Ed; *Biomimetic Oxidation Catalyzed by Transition Metal Complexes*, Imperial College Press; River Edge, NJ, 2000; (b) P. R. Ortiz de Montellano (Ed.), *Cytochrome P-450: Structure, Mechanism and Biochemistry*, Plenum, New York, 1976; (c) R. A. Sheldon, J. K. Kochi (Eds.) *Metal-Catalyzed Oxidations of Organic Compounds*, Academic, New York, 1981; (d) I. D. Cunningham, T. N. Danks, J. N. Hay, I. Hamertson, S. Gunathilagan, C. Janczak, *J. Mol. Catal. A: Chem.*, 2002, **185**, 25.

5. (a) V. Maraval, J. E. Ancel, B. Meunier, *J. Catal.*, 2002, **206**, 349; (b) R. F. Parton, I. F. J. Vankelecom, M. J. A. Casselman, C. P. Bezoukhanova, J. B. Uytterhoeven, P. A. Jacob, *Nature*, 1994, **370**, 541; (c) I. L. V. Rosa, C. M. C. P. Manso, A. A. Serra, Y. Iamamoto, *J. Mol. Catal. A: Chem.*, 2000, **160**, 199; (d) M. S. Niassary, F. Farzaneh, M. Ghandi, L. Turkian, *J. Mol. Catal. A: Chem.*, 2000, **157**, 183.

6. J. T. Grooves, T. E. Nemo, R. S. Myers, *J. Am. Chem. Soc.*, 1979, **101**, 1032.

7. (a) I. Tabushi, *Coord. Chem. Rev.*, 1988, **86**, 1; (b) P. E. Ellis Jr., J. E. Lyons, *Coord. Chem. Rev.*, 1990, **105**, 181; (c) M. J. Gunter, P. Turner, *Coord. Chem. Rev.*, 1991, **108**, 115; (d) D. Mansuy, *Coord. Chem. Rev.*, 1993, **125**, 129.

8. (a) B. Meunier, *Chem. Rev.*, 1992, **92**, 1411; (b) B. Meunier, A. Robert, G. Pratviel, J. Bernadou, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith, R. Guilard, Academic Press, San Diego, 2000, Vol. **4**, p. 119; (c) B. Meunier, J. Bernadou, *Top. Catal.*, 2002, **21**, 47.

9. J. Bernadou, B. Meunier, *Adv. Synth. Catal.*, 2004, **346**, 171.

10. J. P. Collman, X. Zhang, V. J. Lee, E. S. Uffelman, J. I. Brauman, *Science*, 1993, **261**, 1404.

11. K. S. Suslick, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith, R. Guilard, Academic Press, San Diego, 2000, vol. **4**, p. 41.

12. M. B. Ezhova, B. R. James, in *Advances in Catalytic Activation of Dioxygen by Metal Complexes*, ed. L. I. Simándi, Kluwer Academic Publishers, London, 2003, p. 1.

13. W. Nam, *Acc. Chem. Res.*, 2007, **40**, 522.

14. J. Leroy, A. Bondon, *Eur. J. Org. Chem.*, 2008, 417.

15. (a) M. Costas, K. Chen, L. Que, Jr., *Coord. Chem. Rev.*, 2000, **200–202**, 517; (b) S. V. Kryatov, E. V. Rybak-Akimova, S. Schindler, *Chem. Rev.*, 2005, **105**, 2175; (c) A. Gunay, K. H. Theopold, *Chem. Rev.*, 2010, **110**, 1060; (d) M. Fontecave, S. Menage, C. Duboc-Toia, *Coord. Chem. Rev.*, 1998, **178–180**, 1555.

16. (a) M. Merkx, D. A. Kopp, M. H. Sazinsky, J. L. Blazyk, J. Muller, S. J. Lippard, *Angew. Chem. Int. Ed.*, 2001, **40**, 2782; (b) S. C. Pulver, W. A. Froland, J. D. Lipscomb, E. I. Solomon, *J. Am. Chem. Soc.*, 1997, **119**, 387.

17. (a) M. D. Wolfe, J. V. Parales, D. T. Gibson, J. D. Lipscomb, *J. Biological Chem.*, 2001, **276**, 1945; (b) A. Karlsson, J. V. Parales, R. E. Parales, D. T. Gibson, H. Eklund, S. Ramaswamy, *Science*, 2003, **299**, 1039.

18. (a) M. M. Abu-Omar, A. Loaiza, N. Hontzeas, *Chem. Rev.*, 2005, **105**, 2227; (b) P. C. A. Bruijnincx, G. van Koten, R. J. M. Klein Gebbink, *Chem. Soc. Rev.*, 2008, **37**, 2716. (c) M. Costas, M. P. Mehn, M. P. Jensen, L. Que, Jr., *Chem. Rev.*, 2004, **104**, 939; (d) I. Prat, A. Company, V. Postils, X. Ribas, L. Que, Jr., J. M. Luis, M. Costas, *Chem. Eur. J.*, 2013, **19**, 6724

19. (a) C. P. Horwitz, D. R. Fooksman, L. D. Vuocolo, S. W. Gordon-Wylie, N. J. Cox, J. T. Collins, *J. Am. Chem. Soc.*, 1998, **120**, 4867; (b) J. M. Rowland, M. Olmstead, P. K. Mascharak, *Inorg. Chem.*, 2001, **40**, 2810; (c) F. G. Gelalcha, G. Anilkumar, M. K. Tse, A. Bruckner, M. Beller, *Chem. Eur. J.*, 2008, **14**, 7687; (d) E. P. Talsi, K. P. Bryliakov, *Coord. Chem. Rev.*, 2012, **256**, 1418.

20. (a) J. Kim, R. G. Harrison, C. Kim, L. Que, Jr., *J. Am. Chem. Soc.*, 1996, **118**, 4373; (b) C. Kim, K. Chen, J. Kim, L. Que, Jr., *J. Am. Chem. Soc.*, 1997, **119**, 5964; (c) K. Chen, L. Que, Jr., *J. Am. Chem. Soc.*, 2001, **123**, 6327.

21. (a) K. Chen, L. Que, Jr., *Chem. Commun.*, 1999, 1375; (b) M. Costas, A. K. Tipton, K. Chen, D. H. Jo, L. Que, Jr., *J. Am. Chem. Soc.*, 2001, **123**, 6722; (c) M. C. White, A. G. Doyle, E. N. Jacobsen, *J. Am. Chem. Soc.*, 2001, **123**, 7194; (d) J. Y. Ryu, J. Kim, M. Costas, K. Chen, W. Nam, L. Que, Jr., *Chem. Commun.*, 2002, 1288.

22. G. Roelfes, M. Lubben, R. Hage, L. Que, Jr., B. L. Feringa, *Chem. Eur. J.*, 2000, **6**, 2152.

23. C. Nguyen, R. J. Guajardo, P. K. Mascharak, *Inorg. Chem.*, 1996, **35**, 6273.

24. F. Li, M. Wang, C. Ma, A. Gao, H. Chen, L. Sun, *Dalton Trans.*, 2006, 2427.

25. X. Wang, S. Wang, L. Li, E. B. Sundberg, G. P. Gacho, *Inorg. Chem.*, 2003, **42**, 7799.

26. Y. He, J. D. Gorden, C. R. Goldsmith, *Inorg. Chem.*, 2011, **50**, 12651.

27. Y. Zhang, L. Xiang, Q. Wang, X. F. Duan, G. Zi, *Inorganica Chimica Acta.*, 2008, **361**, 1246.

28. T. Soundiressane, S. Selvakumar, S. Menage, O. Hamelin, M. Fontecave, A. P. Singh, *J. Mol. Catal. A: Chem.*, 2007, **270**, 132.

29. M. C. Esmelindro, E. G. Oestreicher, H. M. Alvarez, C. Dariva, S. M. S. Egues, C. Fernandes, A. J. Bortoluzzi, V. Drago, O. A. C. Antunes, *J. Inorg. Biochem.*, 2005, **99**, 2054.

30. V. Balland, F. Banse, E. A. Mallart, M. Ghiladi, T. A. Mattioli, C. Philouze, G. Blondin, J. J. Girerd, *Inorg. Chem.*, 2003, **42**, 2470.

31. N. Arulsamy, D. J. Hodgson, *Inorganica Chimica Acta.*, 1993, **209**, 61.

32. B. Singh, J. R. Long, F. F. de Biani, D. Gatteschi, P. Stavropoulos, *J. Am. Chem. Soc.*, 1997, **119**, 7030.

33. T. A. van den Berg, J. W. de Boer, W. R. Browne, G. Roefles, B. N. Feringa, *Chem. Commun.*, 2004, 2550.

34. (a) S. Menage, J. -M. Vincent, C. Lambeaux, G. Chottard, A. Grand, M. Fontecave, *Inorg. Chem.*, 1993, **32**, 4766; (b) S. Menage, J. -M. Vincent, C. Lambeaux, M. Fontecave, *J. Mol. Catal. A: Chem.*, 1996, **113**, 61.

35. (a) T. Kojima, R. A. Leising, S. Yan, L. Que, Jr., *J. Am. Chem. Soc.*, 1993, **115**, 11328; (b) J. T. Groves, T. E. Nemo, *J. Am. Chem. Soc.*, 1983, **105**, 6243.

36. N. Kitajima, H. Fukui, Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1988, 485.

37. (a) P. A. Macfaul, K. U. Ingold, D. D. M. Wayner, L. Que, Jr., *J. Am. Chem. Soc.*, 1997, **119**, 10594; (b) P. A. Macfaul, I. W. C. E. Arends, K. U. Ingold, D. D. M. Wayner, *J. Chem. Soc., Perkin Trans. 2*, 1997, 135.

38. G. L. Tembe, P. A. Ganeshpure, React. *Kinet. Catal. Lett.*, 1999, **67**, 83.

39. W. Nam, R. Ho, J. S. Valentine, *J. Am. Chem. Soc.*, 1991, **113**, 7052.

40. (a) R. A. Sheldon, J. K. Kochi, *Metal-catalyzed Oxidation of Organic Compounds*, Academic Press, New York, 1981; (b) R. A. Sheldon, I. C. W. E. Arends, A. Dijksman, *Catal. Today*, 2000, **57**, 157; (c) J. E. Backvall, *Modern Oxidation Methods*, Wiley-VCH, Weinheim, 2004.

41. A. Kockritz, M. Sebek, A. Dittmar, J. Radnik, A. Bruckner, U. Bentrup, M. M. Pohl, H. Hugl, W. Magerlein, *J. Mol. Catal. A: Chem.*, 2006, **246**, 85.

42. (a) W. J. Mijs, C. R. H. I. De Jonge (Eds.), *Organic Synthesis by Oxidation with Metal Compounds*, Plenum, New York, 1986; (b) J. March, *Advanced Organic Chemistry,* 4th edn., Wiley, New York, 1992, p 1167; (c) R. J. Highet, W. C. Wildman, *J. Am. Chem. Soc.*, 1955, **77**, 4399; (d) D. G. Lee, U. A. Spitzer, *J. Org. Chem.*, 1970, **35**, 3589; (e) R. V. Stevens, K. T. Chapman, H. N. Weller, *J. Org. Chem.*, 1980, **45**, 2030; (f) F. M. Menger, C. Lee, *J. Org. Chem.*, 1979, **44**, 3446.

43. (a) S. Zhang, L. Xu, M. L. Trudell, *Synthesis*, 2005, **11**, 1757; (b) B. Z. Zhan, M. A. White, T. K. Sham, J. A. Pincock, R. J. Doucet, K. V. R. Rao, K. N. Robertson, T. S. Cameron, *J. Am. Chem. Soc.*, 2003, **125**, 2195; (c) J. N. Moorthy, N. Singhal, P. Venkatakrishnan, *Tetrahedron Lett.*, 2004, **45**, 5419.

44. (a) R. A. Sheldon, I. W. C. E. Arends, G. -J. Ten Brink, A. Dijksman, *Acc. Chem. Res.*, 2002, **35**, 774; (b) T. Mallat, A. Baiker, *Chem. Rev.*, 2004, **104**, 3037.

45. (a) A. Agarwala, V. Bagchi, D. Bandyopadhyay, *J. Chem. Sci.*, 2005, **117**, 187; (b) T. G. Traylor, W. A. Lee, D. V. Stynes, *J. Am. Chem. Soc.*, 1984, **106**, 755.

46. (a) D. G. Lee, E. J. Lee, W. D. Chandler, *J. Org. Chem.*, 1985, **50**, 4306; (b) I. D. Cunningham, T. N. Danks, K. T. A. O'Connell, P. W. Scott, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2133; (c) B. G. Cox, *Modern Liquid Phase Kinetics*, Oxford University Press, Oxford, 1994.