Manganese corrole catalyzed oxygenation of hydrocarbons

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Dedicated to

My Grandmother

DECLARATION

I declare that the thesis entitled "**Manganese corrole catalyzed oxygenation of hydrocarbons**" has been prepared by me under the guidance of Dr. P. Bandyopadhyay, Associate Professor, Department of Chemistry, University of North Bengal & Dr. A. N. Biswas, Assistant Professor, Department of Chemistry, Siliguri College. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

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CERTIFICATE

We certify that Smt. SURANJANA BOSE has prepared the thesis entitled '**Manganese corrole catalyzed oxygenation of hydrocarbons**' for the award of Ph. D. degree of the University of North Bengal, under our guidance. She has carried out the work at the Department of Chemistry, University of North Bengal.

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ABSTRACT

The recent advances in the area of catalytic behavior of manganese complexes in oxidative processes have been described in Chapter I. Major emphasis has been given on catalytic oxygenation of hydrocarbons. The scope and purpose of the present investigation is cast against this background.

The synthesis and catalytic behavior of manganese(III) corrole complexes have been reported in Chapter II. At room temperature, manganese(III) corrole complexes efficiently catalyze the oxidations of alkenes with mild and benign *tert*-butylhydroperoxide (*t*-BuOOH). The oxygenations of alkanes and alkylbenzene like cyclohexane, adamantane and toluene have also been achieved with this catalytic system. A plausible reaction mechanism has been proposed on the basis of experimental evidences and kinetics measurements. Oxidation of hydrocarbons by the present catalytic system proceeds through a radical-chain mechanism in which the radicals are generated by oxidation and reduction of alkyl hydroperoxide. The participation of alkylperoxy ($ROO^{\bullet}$) radicals and organo-hydroperoxide (ROOH) has been confirmed. The main role of the catalyst is the activation of alkylhydroperoxide rather than oxygen atom transfer.

Oxidation of alkanes and alkylbenzenes at room temperature catalyzed by manganese(III) corrole complexes with *m*-chloroperbenzoic acid (*m*-CPBA) as the terminal oxidant constitutes the core area of Chapter III. The formation of high-valent oxomanganese(V) species from the manganese(III) corrole on treatment with *m*-CPBA has been confirmed by UV-visible spectroscopy in acetonitrile medium. It has been demonstrated that the high-valent oxomanganese(V) corroles are capable of oxygenating inert C-H bonds of alkanes and alkylbenzenes. The oxomanganese(V) corrole, despite having low redox potential, has been found to be capable of performing hydrogen atom transfer (HAT) reaction with 2,4,6-tri-*t*-butylphenol. Kinetic investigations with 2,4,6-tri-*t*-butylphenol (TTBP) reveal a first order rate dependence on the concentration of the catalyst as well as on that of the oxidant.

The chapter IV describes manganese(III) corroles catalyzed mild oxidation of alcohols to the corresponding carbonyl compounds with benign *tert*-butylhydroperoxide (*t*-BuOOH) at room temperature. The effect of substitution at the corrole ligands on the catalytic activity of manganese(III) corroles has been examined. It has been found that electron-withdrawing groups on the *meso*-phenyl rings of the corrole ligands enhance the catalytic activity of manganese corrole catalysts.

The manganese(III) corrole catalyzed selective epoxidation of olefins in ionic liquid medium forms the subject matter of Chapter V. The epoxidation of a series of conjugated and non-conjugated olefins has been undertaken in ionic liquid medium using different terminal oxidants such as *tert*-butylhydroperoxide (*t*-BuOOH), iodosylbenzene (PhIO) and sodium hypochlorite (NaOCl). The hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6] has been chosen as reaction medium. Remarkable improvement of product selectivity in ionic liquid medium for each oxidant has been observed over the corresponding ones in common organic solvents. The highest product yield has been achieved by a biphasic system involving ionic liquid with aqueous NaOCl as the terminal oxidant. The biphasic system provides easy recovery and recycling of the catalysts.

The chapter VI describes the synthesis of functionalized silica supported manganese corrole complex and its catalytic properties. The functionalized silica supported manganese corrole complex has been characterized using UV-visible, IR, AAS, powder XRD, SEM, and EDAX techniques. The catalytic activity of the supported manganese corrole complex has been studied for the oxidation of alkenes and alkanes with mild *tert*-butylhydroperoxide (*t*-BuOOH) and environmentally benign hydrogen peroxide (H_2O_2). The heterogeneous catalytic system exhibit excellent turnover numbers up to 3000 for alkene oxidation with *t*-BuOOH as the terminal oxidant. The heterogeneous catalytic system with hydrogen peroxide as terminal oxidant shows turnover numbers in the range of 400-800. The heterogeneous catalyst can be easily recovered from the reaction mixture.

PREFACE

The work in this thesis entitled 'Manganese corrole catalyzed oxygenation of hydrocarbons' was initiated in 2008 under the supervision of Dr. P. Bandyopadhyay and Dr. A. N. Biswas, in the Department of Chemistry, University of North Bengal.

This research work was realized within the framework of the Programme: 'UGC Research Fellowship in Science for Meritorious Students' and 'Senior Research Fellowship' awarded by CSIR. The work is an attempt to explore the catalytic activity of homogeneous and heterogeneous manganese corrole complexes for the oxygenation of hydrocarbons under ambient condition. Another perspective of the present work is to elucidate the mechanistic aspects of manganese corrole catalyzed hydrocarbon oxidation.

I was highly inspired by my listening and interaction with distinguished experts and scientists during the course of my research work through participation in several meets, workshops and national as well as international seminars across the country.

In keeping with general practice of reporting scientific observation, due acknowledgement has been made whenever the work described was based on the finding of other investigators. I must take the responsibility of any unintentional oversights and errors, which might have crept in spite of precautions.

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CONTENTS

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The inspiration, encouragement and whole-hearted cooperation that I received from my parents, family members and friends is most elegantly acknowledged.

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CHAPTER I

An overview of catalytic aspects of manganese complexes in oxidative processes

Abstract

A brief survey on catalytic aspects of manganese complexes in oxidative processes is reviewed with a special emphasis on catalytic oxygenation of hydrocarbons. Current challenges in the area have been discussed. In this background, the scope and purpose of the present work have been delineated.

I. 1 Introduction

The functionalization of hydrocarbons under mild condition is an important scientific and economic goal [1] as saturated hydrocarbons are the main constituents of petroleum and natural gas, the feed-stock for chemical industry. The chemical transformation of C–H → C–OH of hydrocarbons, specially alkanes, is an energy intensive process reflected by inertness of alkanes toward chemical conversion and such transformation is extremely challenging from the viewpoint of basic science. However the biological world has evolved several enzymes to accomplish such transformation selectively under very mild conditions [2–5]. With an aim to model the selective oxygenation of hydrocarbons, different catalytic systems are being investigated to avail reaction path of lower activation energy during last few decades. Still, there is no unique catalytic route for selective and efficient functionalization of unactivated C-H bonds present in different types of hydrocarbons. The oxidative functionalization of saturated as well as olefinic, aromatic and acetylenic hydrocarbons for conversion to more valuable products such as alcohols, ketones, epoxides, acids *etc*. constitutes an important field in contemporary chemistry.

The catalytic systems for oxidative functionalization of hydocarbons reported so far, involve *d*-block metal complexes, which are well known for their catalytic activities due to the availability of *d*-orbitals, that can easily participate in the formation of activated complex as intermediate in the overall chemical process. The outermost *s*- and penultimate *d*-electrons of *d*-block transition metals can be easily disturbed by chemical reagents to different extent resulting in variable oxidation states. The complexes of first transition series metal ions have received more attention in comparison with other two series of *d*-block metals due to their commercial availability and relevance in biological systems. Manganese occupies unique position among the members of first transition series and is often recognized as the most versatile redox element due to its widest array of oxidation states (0 to VII), although other members are also known to contribute a lot as redox catalysts in both chemical and biological sciences. Moreover, manganese is a weak Lewis acid and needs a suitable ligand in order to adjust its redox potential. The catalytic behavior of manganese complexes in chemical and biological redox reactions is extremely attractive and versatile.

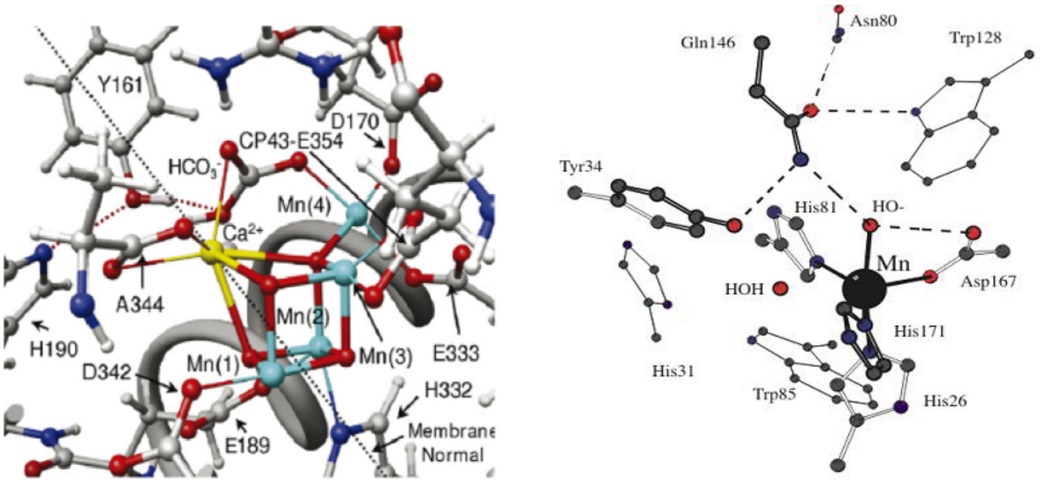
I. 2 Manganese in biological redox systems

Manganese is an essential trace nutrient in all forms of life [6]. Manganese plays important role in diverse types of biological redox reactions. Most significant one is oxygen evolution during photosynthesis at chloroplasts in plants. The oxygen-evolving complex (OEC), constituent of photosystem II, has a metalloenzyme core (Figure I.**1a**) containing four manganese centres, which catalyze the terminal photo-oxidation of water during the light reactions of photosynthesis (equation 1).

$$\mathbf{2H_2O \longrightarrow O_2 + 4H^+ + 4e^-} \tag{1}$$

The OEC water-splitting mechanism depends on the inorganic core of manganese centres along with the protein structure in which this cofactor is embedded. The OEC catalyzed water oxidation is responsible for the huge presence of dioxygen in the Earth's atmosphere.

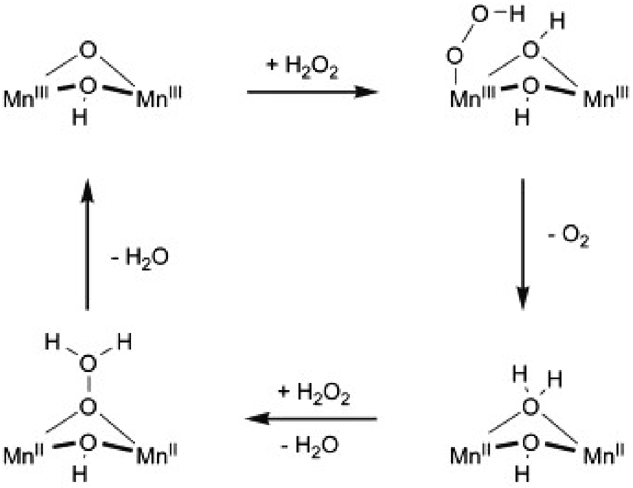
The manganese containing superoxide dismutase (Mn-SOD) [2] (Figure I.**1b**), another important group of manganese-enzymes, is found in eukaryotic mitochondria and also in most bacteria. Most of the organisms living in the presence of oxygen use Mn-SOD enzyme to deal with the toxic effects of superoxide, which is generated from one-electron reduction of dioxygen. Superoxide dismutases catalyze the dismutation of superoxide (O_2^-) to oxygen (O_2) and hydrogen peroxide (H_2O_2).



(**a**) (**b**)

Figure I. 1 (a) The oxygen-evolving complex (OEC) of photosystem II. [from ref. 3]; **(b)**The active site structure of Mn-SOD [from ref. 2].

Manganese containing enzymes include catalases that decompose H_2O_2 into water and oxygen. X-ray crystallographic structure analysis elucidate that these catalases contain a binuclear manganese center [4]. During the catalytic process the dinuclear manganese active site cycles between the Mn_2^{II} and Mn_2^{III} oxidation states [5]. The proposed catalase mechanism is depicted in Scheme I. 1. Hydrogen peroxide decomposition is initiated by binding of H_2O_2 to Mn^{III}-Mn^{III} binuclear centre, followed by reduction to the Mn^{II}-Mn^{II} intermediate and subsequent oxidation of the peroxide to O_2. The catalytic cycle closes *via* binding of a second molecule of H_2O_2 to the Mn^{II}-Mn^{II} species which effects the reduction of H_2O_2 to H_2O and results in the oxidation of Mn^{II}-Mn^{II} species to the Mn^{III}-Mn^{III} binuclear complex.

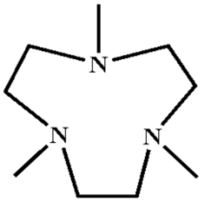


Scheme I. 1 The proposed mechanism for the decomposition of H_2O_2 by binuclear manganese containing catalases [from ref. 5].

In spite of very rich redox chemistry of manganese in biological systems, manganese enzyme catalyzed oxyfunctionalization of hydrocarbons is not known.

I. 3 Oxygenation of hydrocarbons catalyzed by manganese complexes of flexible and redox innocent ligands

Manganese complexes of the tridentate macrocycle ligand 1,4,7-triazacyclononane (tacn) and in particular complexes of 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) (**1**) have been studied extensively in oxidation chemistry. In 1996, De Vos and Bein reported a series of manganese complexes generated *in situ* with substituted 1,4,7-triazacyclononanes (**2 & 3**) and examined their catalytic behavior in the epoxidation reaction [7].



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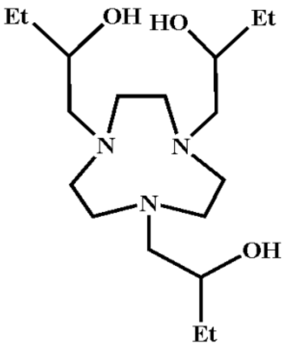

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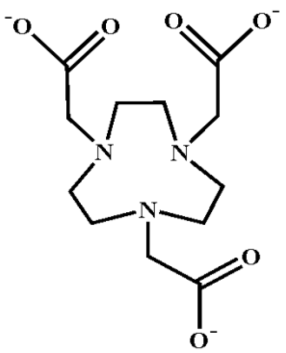

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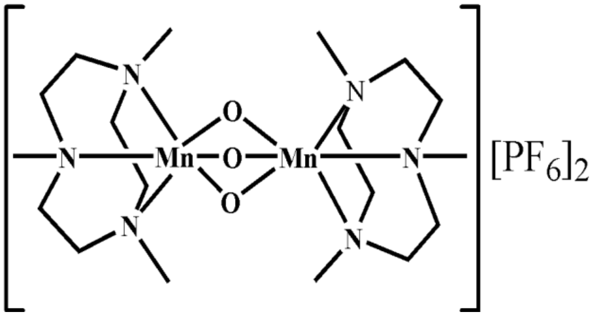
Binuclear manganese(IV) complex [(Me$_3$tacn)Mn(O)$_3$Mn(Me$_3$tacn)](PF$_6$)$_2$ (**4**), which was first synthesized by Wieghardt and co-workers [8] is a highly active and selective epoxidation catalyst in combination with H_2O_2 [9]. In the year 1998, Shul'pin and Lindsay Smith reported an efficient oxygenation of alkanes with H_2O_2 in the presence of complex **4**. The use of additive (acetic acid) was essential; propionic and trifluoroacetic acid were also used instead of acetic acid. In absence of carboxylic acids only decomposition of H_2O_2 was detected. The reactions demonstrated high turnover numbers (up to 1350 for hexane oxidation) and alcohol/ketone ratios about 1.3–1.4.



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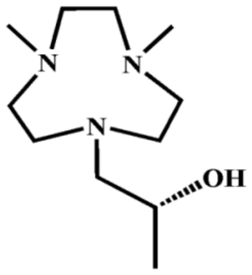
Srinivas and co-workers examined the benzylic oxidations of several alkylarenes in the presence of a manganese complex prepared *in situ* from Me$_3$tacn and MnSO$_4$ in the presence of carboxylate buffers. Ethylbenzene oxidations with H_2O_2 proceeded with good ketone selectivities [10]. Kim and co-workers tested the reactivity of the Mn-Me$_3$tacn/H_2O_2 system towards cyclohexane oxidation in aqueous acetone in the presence of several carboxylic acids and their sodium salts [11].

Süss-Fink and co-workers prepared binuclear manganese complex with chiral derivative **5** and studied oxidation reactions of various alkanes [12]. Beller and Bolm reported the first asymmetric epoxidation reaction catalyzed by *in situ* prepared manganese catalyst from chiral tacn ligands. The chirality was introduced *via* alkylation of the secondary amine moieties to generate the C_3-symmetric ligands **6** and **7**.



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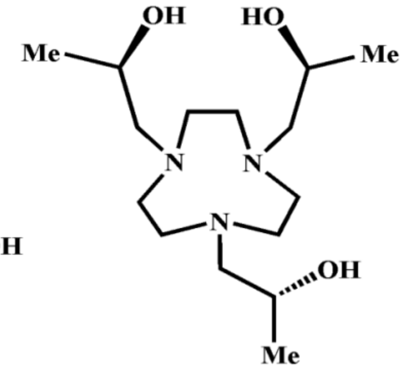

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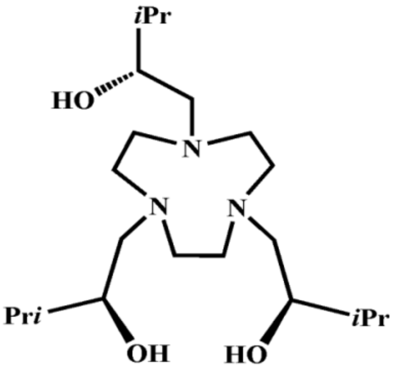

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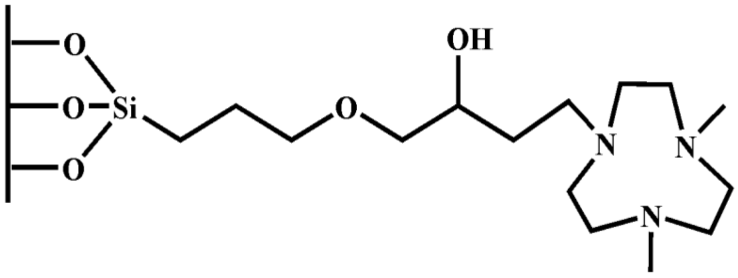
In 2000, Jacobs *et al.* reported manganese complex of the ligand 1,4-dimethyl-1,4,7-triazacyclononane (dmtacn) covalently anchored to a functionalized silica (**8**) that can catalyze the epoxidation of olefins with H_2O_2 [13].



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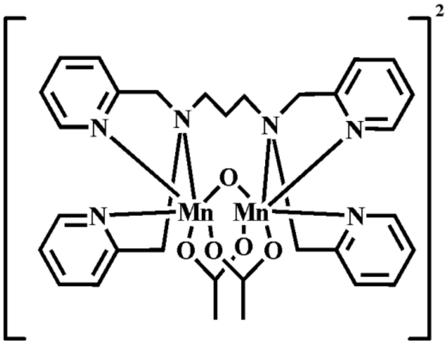
The synthesis of 1,4,7-triazacyclononane (tacn) derivatives involves multiple steps with low yields and their manganese complexes are often catalytically inactive [14].

Recently, high epoxidation activity was found for manganese complexes based on the binuclear ligand N,N, N',N'-tetrkis(2-pyridylmethyl)-1,3-propanediamine (tptn) [15]. The ligand contains a three carbon-spacer between the three N-donor sets. This type of ligand is readily accessible and easy modification of the ligand structure can be achieved. Feringa and co-workers reported that the manganese complex [$Mn_2O(OAc)_2$tptn] (**9**) is able to catalyze epoxidation of various alkenes with good yields, high selectivity and turnover of up to 870. However, manganese complex of tpen [N,N, N',N'-tetrkis(2-pyridylmethyl)-1,2-

ethanediamine] featuring a two-carbon spacer between three N-donor sets in the ligand (**10**) fails to catalyze epoxidation reaction [15].



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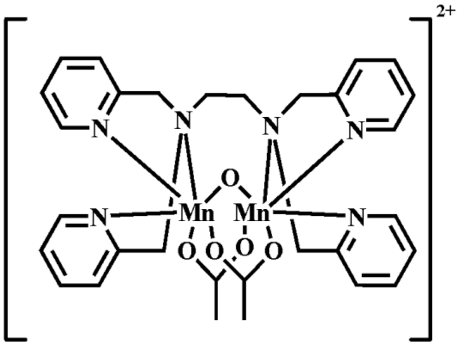

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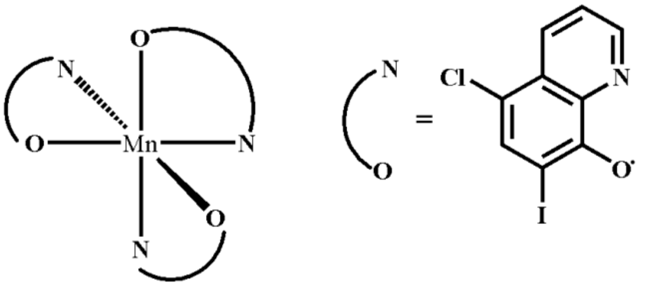
Fu and Xie with co-workers reported a 5-chloro-7-iodo-8-quinolinolatomanganese(III) complex (**11**) which catalyzes epoxidation of various alkenes with H_2O_2 with good efficiency (up to 50 turnovers) and selectivity (up to 67–98%) in an acetone/water media [16]. The epoxidation is pH dependent and best results have been obtained with $NH_4OAc/HOAc$ buffer.



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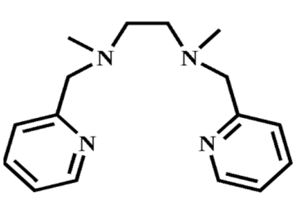
In 2003, Stack with co-workers reported an efficient catalytic system for the epoxidation of alkenes with commercial peracetic acid, based on manganese(II) complexes with ligands bpmen [N,N’-dimethyl-N,N’-bis(2-pyridylmethyl)-ethane-1,2-diamine] (**12**) and bpmcn [N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-trans-1,2-diaminocyclohexane] (**13**) [17]. In 2007, Nam and co-workers reported mononuclear manganese(II) complex of bqen [N,N’-dimethyl-N,N’-bis(8-quinolyl)ethane-1,2-diamine] (**14**) and studied its catalytic efficiency for the epoxidation of olefins by PhIO and oxidation of olefins, alcohols and alkanes by CH_3CO_3H with high stereo and regioselectivity [18].



bpmen

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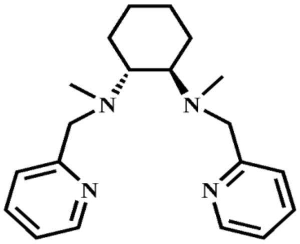

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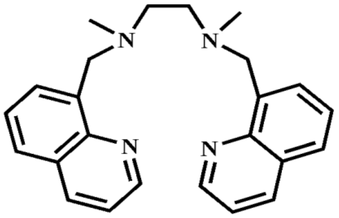


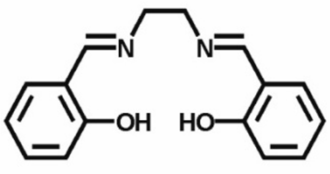
bqen

14

In contrast to numerous iron catalysts with flexible ligand frames, very few related manganese complexes are known. Manganese systems have been more successful in catalytic epoxidations rather than C-H bond oxidations [14]. For non-asymmetric epoxidation reactions, complexes with stable ligands framework, such as 1,4,7-triazacyclononane derivatives and the pyridine-derived ligands are more suitable. These complexes are very stable, versatile and tunable catalysts [14].

I. 4 Oxygenation of hydrocarbons by manganese salens and Schiff base complexes

The condensation between an aldehyde and a primary amine leading to a Schiff base, first reported by Hugo Schiff in 1864 [19]. Schiff base ligands are able to coordinate metals through imine nitrogen and another donor group, usually linked to the aldehyde.



Salen

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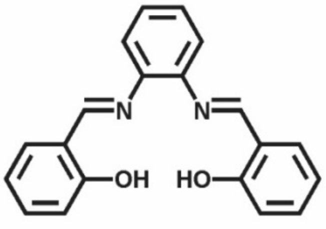

Salophen

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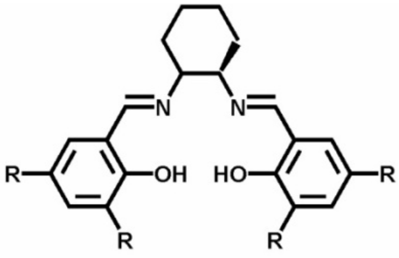

Chiral Salen

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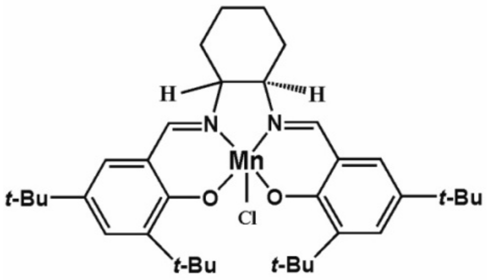
The term Salen was used originally only to describe the tetradentate Schiff bases (**15**) derived from ethylenediamine and salicylaldehyde, the more general term Salen-type is used in the literature to describe the class of [O,N,N,O] tetradentate Schiff base ligands (**16** & **17**) [20]. The Salen ligands, with four coordinating sites and two axial sites open to ancillary ligands, are very much like porphyrins, but their preparation is considerably simple [20.(c)].

The metallosalen derivatives, most notably those of manganese [21, 22] have emerged as efficient catalysts in various reactions. Several chiral manganese salen complexes, reported by Jacobsen [21] and Katsuki [22] have been known to be efficient catalysts for the asymmetric epoxidation of *cis*-olefins with oxidants like iodosylarenes, NaOCl, H_2O_2, $NaIO_4$, peracids and also molecular oxygen in combination with aldehyde.



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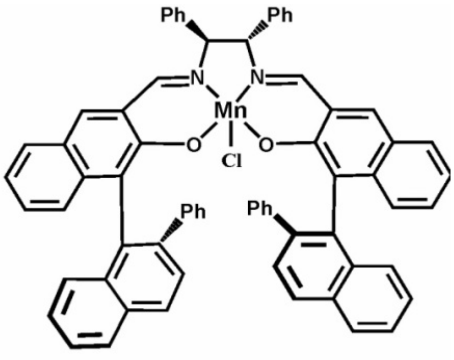

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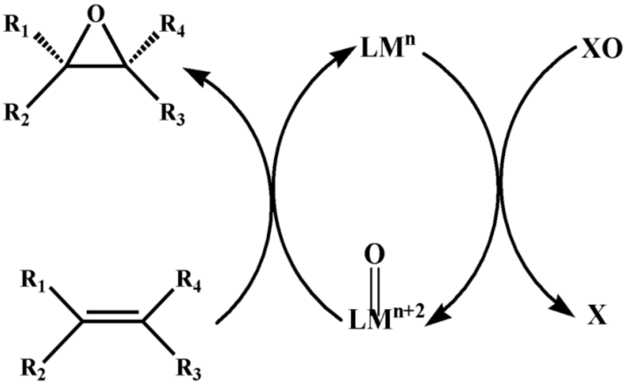
Infact, the Jacobsen-Katsuki reaction is universally recognized as one of the most powerful methods for the epoxidation of unfunctionalized prochiral olefins. Chiral Mn(III)(salen)Cl **18** can easily be prepared using accessible methods developed by Jacobsen. The ligand introduced by Jacobsen is now commercially available, while the ligand described by Katsuki is obtained from binol (binol = 1,1'-bi-2-naphthol) following several synthetic steps. Katsuki's Mn(Salen) complex (**19**) gave higher turnover numbers with respect to Jacobsen's ligand, but its application in catalytic enantioselective reactions has only been reported on a small scale [21, 22].

In 1990 Jacobsen and Katsuki independently reported Mn(salen) catalyzed asymmetric epoxidation of unfunctionalized alkenes using iodosylarenes (ArIO) as stoichiometric oxidants [21.(a), 22.(a)]. Highly enantioselective Mn(salen) catalysts have been developed for the asymmetric epoxidation of a wide variety of alkenes [21, 22]. Commercially available Jacobsen's catalyst has been demonstrated to be very effective for a broad range of conjugated alkenes even for small-scale use. The second-generation Mn(salen) catalysts introduced by Katsuki and coworkers have surpassed Jacobsen's catalyst in terms of selectivity and activity, but their applications are limited due to commercial non-availability. The *trans*-epoxides can be accessed in high ee from *cis*-alkenes using Jacobsen's catalyst or from *trans*-alkenes using specific second-generation Mn-(salen) catalysts. Access to variety of epoxides has largely been successful due to the remarkable catalytic activity of manganese salen 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 [20.(c)-(e)].

The electronic effects of the substituents, on the salicylidene ligands towards the reactivity of the Mn(III)(salen) complexes were studied in the 1980's by Kochi *et al.* [23]. They showed that the presence of electron withdrawing groups, suchs as -Cl or -NO_2, enhance the catalytic activity of the complex. Jacobsen *et al.* have unequivocally shown that the electronic nature of the substituent also strongly influences enantioselectivity [21]. Complexes with electron-donating substituents show higher enantioselectivity than complexes possessing electron withdrawing substituents.

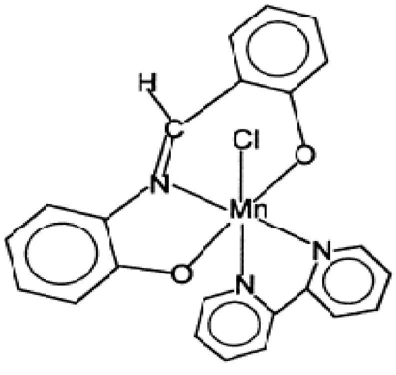


Scheme I. 2 Manganese(salen) catalyzed asymmetric epoxidation of alkenes by oxygen rebound. LM= manganese complex (L= Salen), XO= oxygen atom donor (e.g. NaOCl, PhIO, O_2/reductant, H_2O_2).

A wide variety of oxidants can be used with Mn(salen) catalysts, but sodium hypochlorite is most commonly used. This has the advantage of being relatively inexpensive and, once reduced, environmentally benign [21, 22]. Iodosylbenzene and sodium hypochlorite are considered to oxidize manganese(III)(salen) complexes directly to oxo manganese species (Scheme I. 2) [21, 22]. When hydrogen peroxide is used as an oxidant addition of a donor ligand is indispensable probably because the coordination of an axial ligand is crucial to the O-O bond cleavage of the intermediate hydroperoxide species [HO-O-Mn(III)]. When hydrogen peroxide is used as an oxidant addition of donor ligands such as pyridine-*N*-oxide can have dramatic effects on asymmetric epoxidations catalyzed by manganese salen complexes [21, 22, 24]. The epoxidation using a combination of molecular oxygen and aldehyde is also accelerated by the addition of donor ligand [25]. Coordination of these additives to the metal center is the principal way in which they exert their influences. In the case of Mn(salen)-catalyzed asymmetric epoxidation with NaOCl as oxidant there is an additional role of these additives as phase-transfer catalysts [21, 22, 24]. Chiral non racemic donor ligands can induce good ee with achiral Mn(salen) catalysts. The choice of oxidant can affect the yield, specificity and ee [21-25].

Recently, Rezaeifard and Jafarpour with co-workers reported the catalytic efficiency and excellent selectivity of tetradentate manganese(III) Schiff base complexes in the oxidation of alcohols to the corresponding aldehydes and ketones using *tetra*-n-butylammonium peroxomonosulfate (Bu_4NHSO_5) under mild conditions. The presence of an electron donating group on the phenyl ring of the benzyl alcohol increased the reactivity of the substrate, while electron-withdrawing and bulky groups on the Schiff-base ligands enhanced the catalytic activity of the manganese catalyst. The simple catalytic system is applicable to a wide variety of primary and secondary benzylic, allylic, and also saturated cyclic and alicyclic alcohols with excellent selectivity, combined with high turnover rates [26].

Chatterjee and co-workers synthesized mononuclear manganese(III) complex $[Mn^{III}(amp)(bipy)(Cl)]$ (H_2amp: *N*-(hydroxyphenyl)salicyldimine; bipy: 2,2'-bipyridyl) (**20**) and $[Mn^{III}(app)(bipy)\text{-}(Cl)]^+$ (H_2app: *N*-hydroxyphenyl)pyridine-2- carboxaldimine; bipy: 2,2'-bipyridyl) (**21**) and studied their catalytic activities in the oxidation of both saturated and unsaturated hydrocarbons using *tert*-butylhydroperoxide (*t*-BuOOH) [27].



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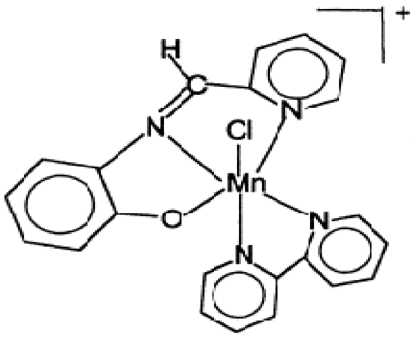

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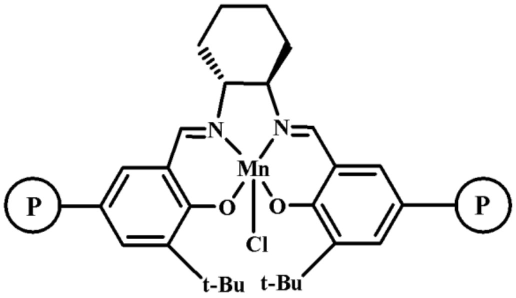
The synthesis of the first polymer-supported chiral manganese(salen) complexes along with their application as recyclable asymmetric catalysts was independently reported by

Sivaram *et al.* [28] and Minutolo *et al.* [29]. Monomeric Jacobsen-type units (containing two polymerisable vinyl groups) were copolymerised with styrene and divinylbenzene to yield the corresponding crosslinked polymers **22–24.** The insoluble Jacobsen's catalyst **22** epoxidized unfunctionalized alkenes in good yields (65–72%), but with low enantioselectivity (1–26% ee), the heterogeneous catalysts containing a spacer arm between the active site and the polymeric backbone **23** and **24** induced better enantioselectivity (14–62% ee). In all cases, reactions were performed with an excess of iodosylbenzene as the oxygen source and without additives.



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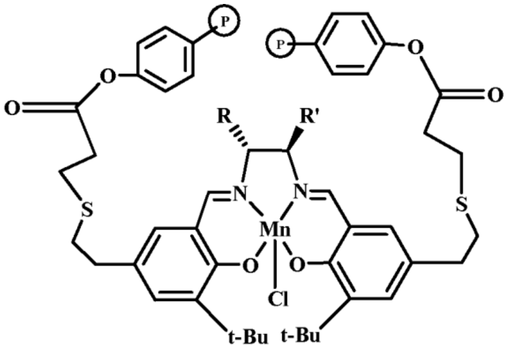
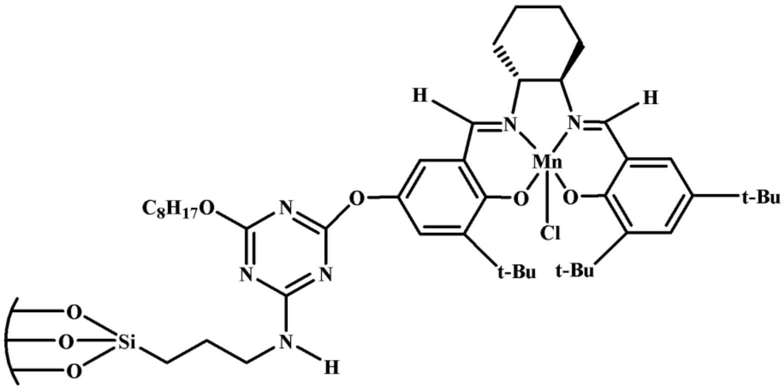


23 R and R' = -$(CH_2)_4$-

24 R = R' = Ph

Bein reported the encapsulation of Mn(salen) complex into zeolite. These heterogeneous catalysts generated good asymmetric inductions with up to 88% ee for *cis*-β-methylstyrene. The group also proved that the epoxidation took place inside the cage of the zeolite [30].

Bigi and coworkers achieved high enantioselectivity (ee up to 84%) in heterogeneous asymmetric epoxidation using a silica-bound unsymmetrical manganese(III)(salen) complex **25** [31].



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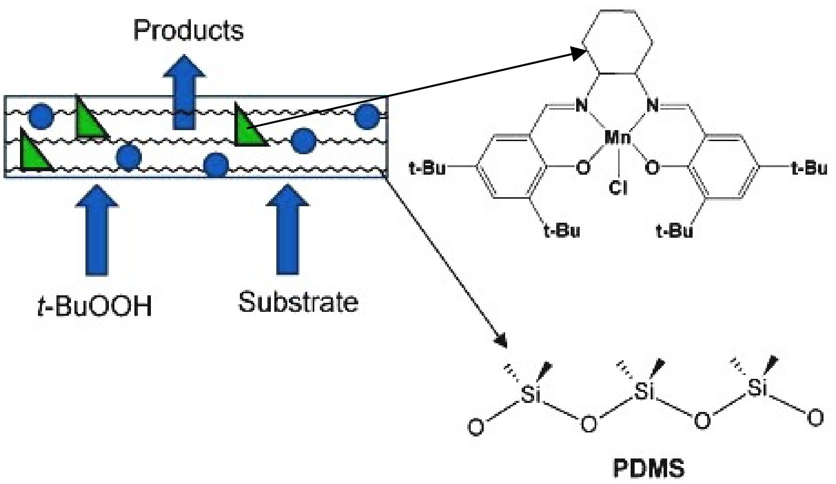
Heterogeneous chiral Mn(salen) catalysts axially immobilized on mesoporous materials *via* phenyl sulfonic groups result in remarkably high ee values (up to 95%) for asymmetric epoxidation of unfunctionalized olefins [32].

Homogeneous and heterogeneous manganese(salen) complexes have been extensively studied for the asymmetric epoxidation of various types of olefins but reports of C-H bond activation catalyzed by manganese(salen) complexes are very few. Recently, Assis and co-workers reported mild oxidation of linear (n-pentane, n-hexane, n-heptane and n-octane) and cyclic (1,2-dimethylcyclohexane) alkanes to the corresponding secondary alcohols and ketones, as well as of toluene to benzaldehyde, catalyzed by homogeneous and immobilized {(R,R)-N,N-bis(3,5-di-tert-butylsalicylidenato)-1,2-cyclohexanediamine(2-)} chloro manganese(III) complex on a polydimethylsiloxane (PDMS) based membrane with mild *t*-BuOOH (Scheme I. 3). These oxidations are markedly promoted by the addition of various acids, namely nitric, pyrazine-2-carboxylic, acetic, benzoic and oxalic acids [33].



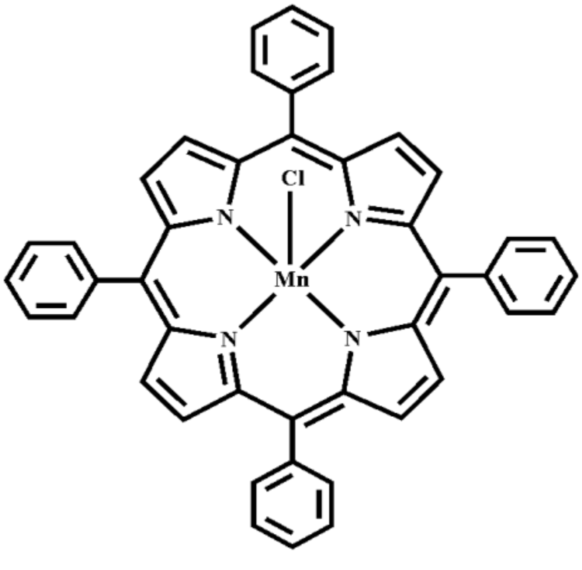
Scheme I. 3 Hydrocarbon oxidation catalyzed by manganese salen complex immobilized on polydimethylsiloxane (PDMS) based membrane with mild *t*-BuOOH (from ref. 33).

I. 5 Manganese porphyrins as oxidation catalysts

Metalloporphyrins are most extensively studied because of their unique nature, coordination chemistry and also relevance as biological models [34]. Although a large number of metalloporphyrins have been examined, manganese porphyrins are of considerable interest for several reasons [35]. The unique absorption spectrum of the manganese complexes is presumably diagnostic of an unusual electronic structure. A thorough understanding of manganese porphyrins would be valuable in sorting out the closely related and biologically import iron system, as well as for the general understanding of metalloporphyrin spectra and structure.

A manganese porphyrin complex was first reported by Zalesky in 1904 [36]. Fifty years later Calvin and co-workers published a series of papers relating the preparation and properties of manganese porphyrin complexes [37]. The most common oxidation states of manganese are Mn^{II}, Mn^{III} and Mn^{IV}. Although all these oxidation states appear to be accessible by the porphyrin complexes, the stable complexes are those of Mn^{III}. The lower and higher oxidation states can be generated by the appropriate reduction and oxidation of manganese(III) porphyrins [38].

For more than a decade, oxidations of manganese porphyrin complexes by sodium hypochlorite were carried out in order to understand the mechanism of water oxidation in photosynthesis. In 1979, Tabushi reported oxidation of benzylic alcohol to benzaldehyde catalyzed by Mn(TPP)Cl (TPP = tetraphenyl porphyrin) (**25)** with NaOCl as the terminal oxidant [39]. At the same period, Meunier *et al.* found that porphyrin ligands are more suitable than Schiff base macrocycles in catalyzing olefin epoxidation reaction using NaOCl as oxygen atom source [40]. In this case very small amounts of manganese porphyrin catalyst have been used (catalyst/olefin molar ratio range from 0.025% to 2.5%). The catalytic oxygen-transfer reaction takes place in the organic phase, and the phase-



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transfer agent is present simply to transfer $OC1^{-}$ as ammonium salt into the dichloromethane solution (equation 2).

$$\mathbf{PhHC{=}CH_2 + NaOCl \xrightarrow[R_4N^+Cl^-/H_2O/CH_2Cl_2]{Mn(TPP)Cl} PhCH(O)CH_2 + NaCl} \qquad (2)$$

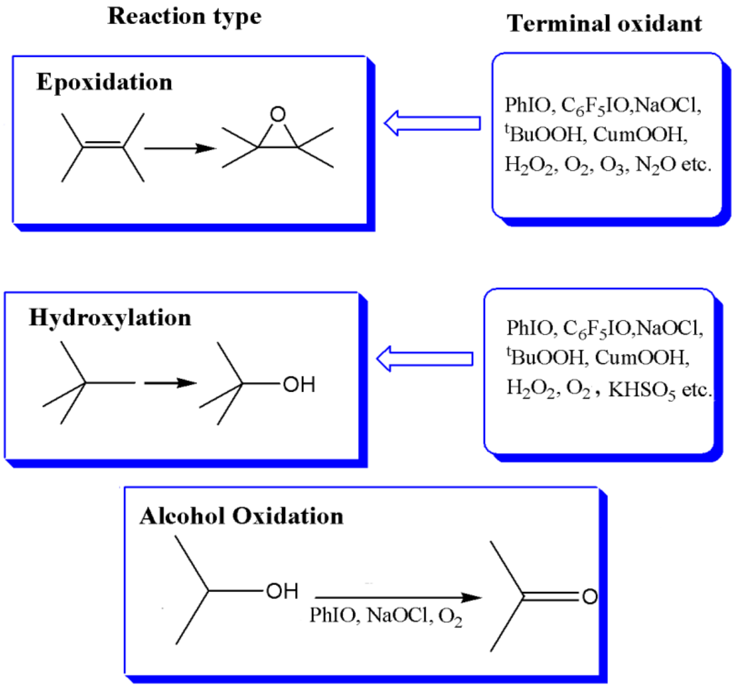
Manganese porphyrins with a trimethylammonium substituent on the *para* position of one of the phenyl rings have been used as catalysts in the absence of a tetraalkylammonium salt [41].

The most striking features of these catalytic epoxidations with manganese porphyrins are the remarkable improvement of the rate, chemo- and stereoselectivity of the reaction by addition of pyridine derivatives in the reaction mixture [42]. Because of improved chemoselectivity, a large number of different olefins have been epoxidized with NaOCl in good yields, *e.g.*, terpenes, steroid olefins [43]. Dienes have been epoxidized to the corresponding monoepoxides [42.(a), 43.(b)]. Pyridine could be replaced by imidazole derivatives, but these axial ligands are less robust with respect to oxidation than pyridine derivatives. A variety of oxidants such as iodosylarenes, alkylhydroperoxides, peracids, hydrogen peroxide and molecular oxygen have been employed in epoxidation of alkenes [39-43].

Manganese porphyrins have been studied extensively as catalysts in hydroxylation of alkanes. The first report of an alkane hydroxylation with NaOCl as oxidant was published by Tabushi in 1979, using Mn(TPP)Cl (**25**) as catalyst [39]. However, it was found that NaOCl is a poor oxygen atom donor in manganese porphyrin catalyzed hydroxylation reactions. The first attempt to mimic cytochrome P-450 mediated epoxidation reactions was reported by Tabushi in the same year. Cyclohexene is oxidized to cyclohexanol and 2-cyclohexen-1-o1 (ratio = 80/20) in the presence of dioxygen, sodium borohydride, and a catalytic amount of **25** [44]. A series of manganese porphyrins with sterically protected ligands have been studied by Suslick *et al.* for the alkane hydroxylation with iodosylbenzene as oxidant [45]. Hydrogenperoxide as terminal oxidant in combination with manganese porphyrin catalysts give high conversions of alkanes to alcohols and ketones in the presence of imidazole [46]. The manganese porphyrin catalyzed hydroxylation is strongly accelerated by addition of small amounts of a carboxylic acid such as benzoic acid along with a nitrogen base still being present [47]. Although this base could be a 4-substituted pyridine and not necessarily an imidazole derivative.

Alkyl hydroperoxides and potassium monopersulfate have also been utilized as terminal oxidant in manganese corrole catalyzed hydroxylation reactions [48].

The early manganese porphyrin catalysts (often called first generation catalysts) suffered from rapid deactivation due to oxidative degradation of the ligand. Spectacular improvements in robustness and activity of catalysts were obtained after the introduction of electron withdrawing substituents into *meso*-aryl positions (second generation catalysts) and also into *β*-pyrrolic positions (third generation catalyst) of porphyrin ligand [49]. For example, the second generation manganese complex of *meso*-tetrakis(2,6-dinitropheny1)porphyrin is an efficient catalyst for alkane hydroxylation [50]. The third generation of porphyrin catalysts with chlorine or bromine atoms at the *β*-pyrrolic positions of the macrocycle is highly efficient in hydroxylation of linear alkanes or norbornane derivatives [51].

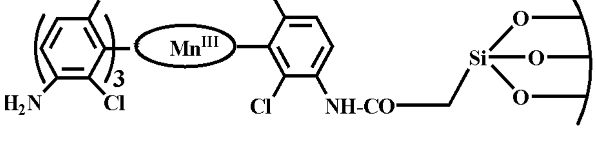


Scheme I. 4 A brief outline of manganese porphyrin catalyzed oxygenation of hydrocarbons.

A variety of oxidants such as iodosylarenes, alkylhydroperoxides, peracids, hypochlorite and hydrogen peroxide were employed in manganese porphyrin catalyzed oxygenation of hydrocarbons. A brief outline of the manganese porphyrin catalyzed oxidation systems previously reviewed in literature is shown in Scheme I. 4.

Attachment of metalloporphyrins to supports can be classified as either chemical or physical. Reports have appeared in the eighties about porphyrins successfully attached to organic and inorganic supports *via* coordinative anchorage [52, 53], electrostatic interactions [54-57] and covalent binding [58-62]. Several supported manganese porphyrins have been prepared by encapsulation in a polymer or inorganic material such as zeolite, montmorillonite K_{10}, LDH or immobilized *via* coordinative binding between the metal centre and a nitrogenous axial ligand, which is covalently anchored to a support such as polyvinylpyridines (PVP), polystyrene with imidazole group, functionalized silica *etc.* Electrostatic interactions between an ionic metalloporphyrin and a counterionic group situated on the support have been shown to be stronger than the coordinative ones [63].

In the year 1989, Mansuy and co-workers prepared a supported manganese porphyrin catalyst by strong adsorption of the tetracationic manganese [meso-*tetra*(4-*N*-*m*ethyl pyridiniumyl) porphyrin] chloride on silica, and was found very efficient for cyclooctene epoxidation and for alkane hydroxylation with iodosylbenzene [64]. In 1992 Meunier reported the use of robust sulfonated manganese porphyrins supported on poly(vinylpyridinium) polymers as catalysts in olefin epoxidation and alkane hydroxylation by iodosylbenzen [65]. Mansuy *et al.* reported meso-tetrakis-(2,6-dichlorophenyl) porphyrin derivatives bearing -NH_2 or -SO_3H functions on their meso-aryl rings covalently bound to either silica (**26**) or montmorillonite K_{10} (**27**). All these supported manganese porphyrins efficiently catalyze the epoxidation of alkenes with PhIO. The manganese(III) porphyrin covalently bound to montmorillonite K_{10} afford remarkably good results for the hydroxylation of linear alkanes such as heptane with PhIO. The results being much better than those observed with corresponding homogeneous catalysts. The manganese(III) porphyrin covalently bound to silica was an efficient catalyst for epoxidation of alkenes with H_2O_2 [66].



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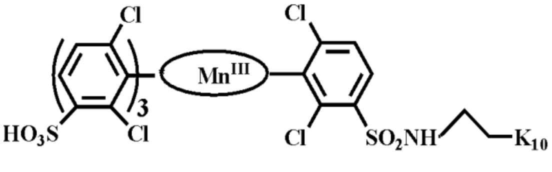

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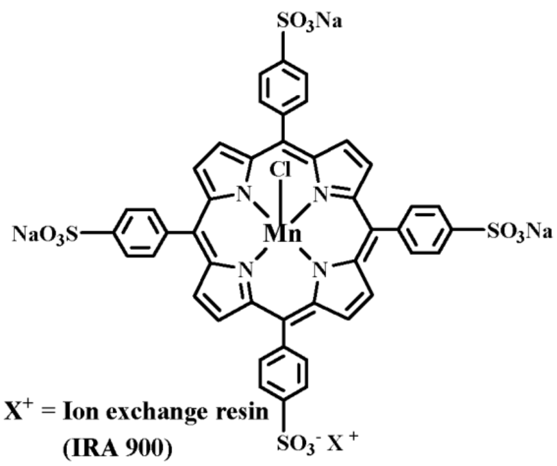
Oxidation of cyclic alcohols to ketones with *t*-butylhydroperoxide was reported by Neys and co-workers with 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato] manganese(III) chloride [TDCPP(Mn)CI] embedded in polydimethylsiloxane (PDMS) [67]. Smith and co-workers reported manganese(III) complex of 2,6-dichlorophenyl porphyrin coordinatively bonded to poly(4-vinylpyridine), imidazole modified polystyrene (PS-lm) and silica (Si-lm). These supported manganese porphyrin complexes have been used as catalysts for the oxidation of cyclohexene and cyclooctene by iodosylbenzene [68]. Tangestaninejad *et al.* reported that sulfonated manganese(III) tetraphenylporphyrin supported on poly(4-vinylpyridine), Mn(tpps)-PVP, can act as an efficient heterogeneous catalyst for alkene epoxidation and alkane hydroxylation by sodium periodate [69]. Oliveira *et al.* reported the use of oxovanadium phosphate as support of the 5,10,15,20-tetrakis(2,6-dichlorophenyl) porphyrin manganese (III) chloride catalyst for cyclohexane and cyclooctene oxidations by iodosylbenzene [70]. Xia *et al.* reported the synthesis and characterization of the cationic manganese–porphyrin [*meso*-tetrakis(1-methyl-4-pyridinio)porphyrinato]manganese(III) penta-acetate complexes encapsulated in zeolite and mesoporous molecular sieve and studied their catalytic activity in the epoxidation of styrene and cyclohexene by iodosylbenzene [71]. Sulfonated manganese(III) tetraphenylporphyrin supported on Amberlite IRA-900 ion exchange resin [Mn(TPPS)-Ad-900] (**28**) and manganese (III) *meso*-tetrakis(*p*-sulfonatophenyl)-β-octabromoporphyrin supported on Amberlite IRA-400 [Mn(Br_8TPPS)-Ad-400] (**29**) are robust and efficient catalysts for epoxidation of alkenes and hydroxylation of alkanes with sodium periodate at room temperature [72].



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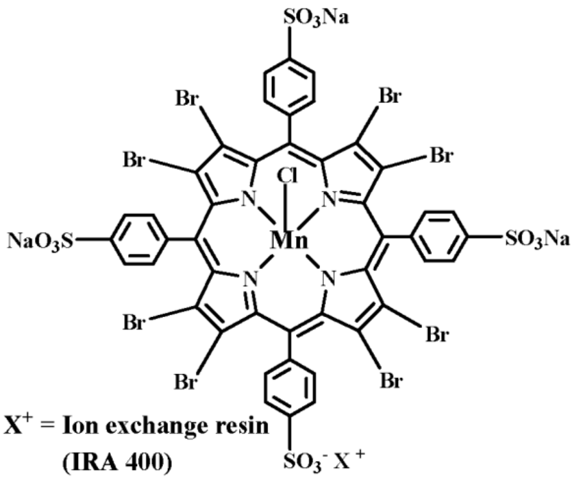

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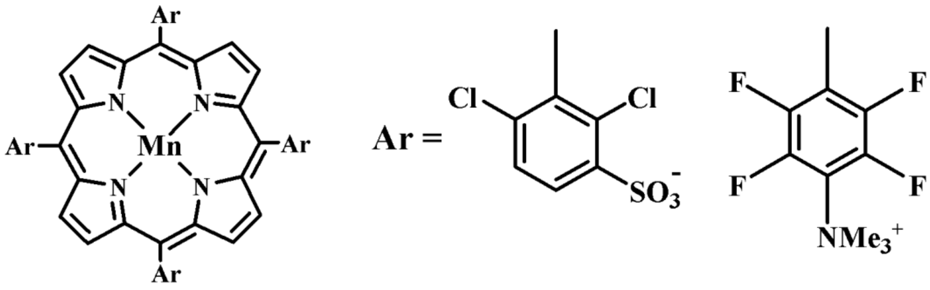
In 2006, Smith and co-workers reported that manganese(III) tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrin (**30**) and manganese(III) tetrakis[tetrafluoro-4-(trimethylammoniumyl)phenyl]porphyrin (**31**), in homogeneous solution and supported on modified silica surfaces, have been used as catalysts for the oxidation of pentane and cyclohexane with iodosylbenzene. The effects of reaction solvent, catalyst support and dioxygen on the oxidation yields and product distributions have been studied [73].



30 **31**

Recently, Moghadam *et al.* used imidazole-modified silica (SiIm) for immobilization of octabromotetraphenylporphyrinatomanganese(III) chloride [Mn(Br_8TPP)Cl] and tetraphenylporphyrinatomanganese(III) chloride [Mn(TPP)Cl]. These supported catalysts catalyze alkene epoxidation and alkane hydroxylation with $NaIO_4$ under agitation with magnetic stirring. These new heterogenized catalysts could be reused several times without significant loss of their catalytic activity [74].

I. 6 Manganese corroles as oxidation catalysts

A close analogue of porphyrin, are emerging as prospective candidates for catalyzing diverse types of reactions. Corroles are tetrapyrrolic macrocycles who owe their name to cobalt-chelating corrin of vitamin B_{12}. More precisely, corroles are based on the [18]annulene structural framework with just one *meso* carbon short from the porphyrin skeleton [75]. The structure of its aliphatic counterpart, namely corrin, the tetrapyrrolic ligand of the B_{12} cofactor is presented in Figure I. 2.

The chemistry of corroles remained comparatively underdeveloped for a long period, largely due to lack of simple methods for their synthesis. However, major breakthrough was made in 1999 by Gross *et al.*[76] and Paolesse *et al.* [77] of one-pot corrole syntheses involving pyrrole-aldehyde condensations.

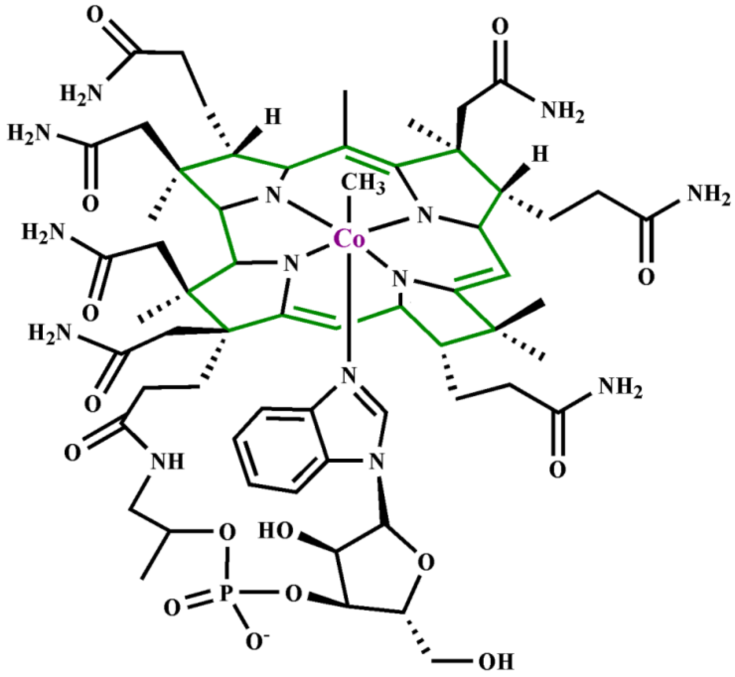
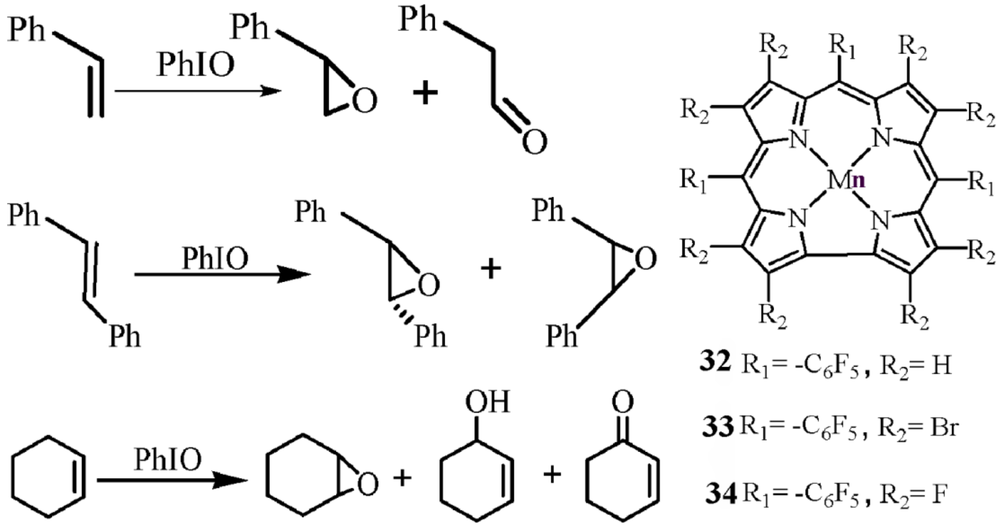


Figure I. 2 Structure of corrin, the tetrapyrrolic ligand of the B_{12} cofactor.

The first example of metallocorrole catalyzed oxidation reaction was *meso*-pentafluorophenyl substituted iron(IV) corrole catalyzed epoxidation of styrene with PhIO [78.(a)]. Styrene was converted to a mixture of stryrene oxide and phenylacetaldehyde (3:1) with an overall yield of 87%, which was significantly lower than the corresponding iron porphyrin catalysts. The results stimulated interest among the chemists to develop more effective epoxidation systems based on metallocorroles [78.(b)–(g)]. The electronegative manganese(III) corrole catalyzed epoxidation of styrene with PhIO was first reported by Gross *et al.* [78.(b)]. The addition of PhIO to the green coloured manganese(III) complex produces red coloured oxomanganese(V) corrole which is isolated in pure form. Surprisingly, the oxomanganese(V) corrole fails to transfer its oxygen atom to the olefins under stoichiometric condition. This observation raised ambiguity over the key intermediate associated with the process. Gross *et al.* proposed a high valent Mn(VI)oxo species, generated by disproportionation of oxomanganese(V) corrole, as the active oxidant [78.(b)]. The perhalogenation of manganese(III) corroles with bromine [78.(b)] or fluorine [78.(c)] shows enhanced catalytic activity with PhIO (Scheme I. 5), which is reflected from higher turnover numbers. Catalytic activity of the oxomanganese(V) corroles with axial coordination of imidazole show enhanced reactivity towards olefins [78.(i)].



32 R_1= -C_6F_5, R_2= H

33 R_1= -C_6F_5, R_2= Br

34 R_1= -C_6F_5, R_2= F

Schem I. 5 Epoxidation of olefins by electron deficient manganese(III) corrole complexes.

I. 7 Scope and purpose of the present work

The metallocorroles are receiving increasing attention in different areas of chemical science as catalysts [79]. The catalytic behavior of metallocorrole complexes towards C-H activation and oxyfunctionalization of different types of hydrocarbons appears to be promising. A beginning in this direction has already been made with iron and manganese complexes. The careful scrutiny of the reports appeared in the literature [78] on manganese corrole catalyzed oxidation of hydrocarbon reveals the following issues.

1. Manganese corrole catalyzed oxidation of hydrocarbons is limited to olefinic substrates.
2. Low selectivity of the oxidized products and complete catalyst bleaching during the course of reaction are the major limitations of manganese corrole catalyzed oxidation of alkenes.
3. Only iodosylarenes have been employed as terminal oxidants in manganese-corrole catalyzed oxidation of hydrocarbons [78].
4. The reactions were studied only in benzene or dichloromethane.

It is thus highly desirable to design efficient catalytic systems based on manganese(III) corroles for selective oxyfunctionalization of different types of organic molecules with mild oxidants at room temperature as well as the facile recovery of the catalyst.

In this thesis, attempts would be made to explore the catalytic behavior of manganese corroles towards oxidation of different types of hydrocarbon under ambient condition. To address the above mentioned issues, we wish to adopt the following steps.

1. Attempts would be made to achieve manganese corrole catalyzed activation and functionalization of C-H bond of alkanes at room temperature. Efforts would be devoted to evolve suitable reaction conditions to improve the catalytic efficiency, selectivity and Turn Over Number.
2. Benign and environment friendly terminal oxidants like H_2O_2, *t*-BuOOH *etc*. would be employed in manganese corrole catalyzed hydrocarbon oxidation.
3. The effects of different reaction media (molecular solvents) on manganese corrole catalyzed hydrocarbon oxidation would be studied.
4. Attempts would be made to develop efficient catalytic system in environmentally benign room temperature ionic liquids.
5. Commercially important oxidation of enol to ketone under very mild condition would be studied with manganese corrole as catalysts.
6. Attempts would be made to elucidate the mechanistic aspects of manganese corrole catalyzed hydrocarbon oxidation.
7. It is our endeavor to incorporate manganese(III) corroles onto solid support like surface modified silica. Manganese(III) corroles immobilized on solid support would be used as catalysts in the oxidation of different organic substrates. Efforts would be devoted to optimize the reaction conditions to attain high catalytic efficiency, product selectivity and facile catalyst recovery.

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CHAPTER II

Manganese(III) corrole catalyzed mild oxidation of hydrocarbons: Search for the reactive intermediate*

Abstract

Manganese(III) corroles have been found to be efficient in catalyzing oxidations of alkenes with mild *tert*-butylhydroperoxide (*t*-BuOOH) at room temperature. The oxygenation of cyclohexane, adamantane and toluene has also been studied under similar reaction conditions. The oxidation has been shown to proceed with participation of alkylperoxy ($ROO^{\bullet}$) radicals and organo-hydroperoxide (ROOH). A reaction mechanism is proposed based on the experimental results.

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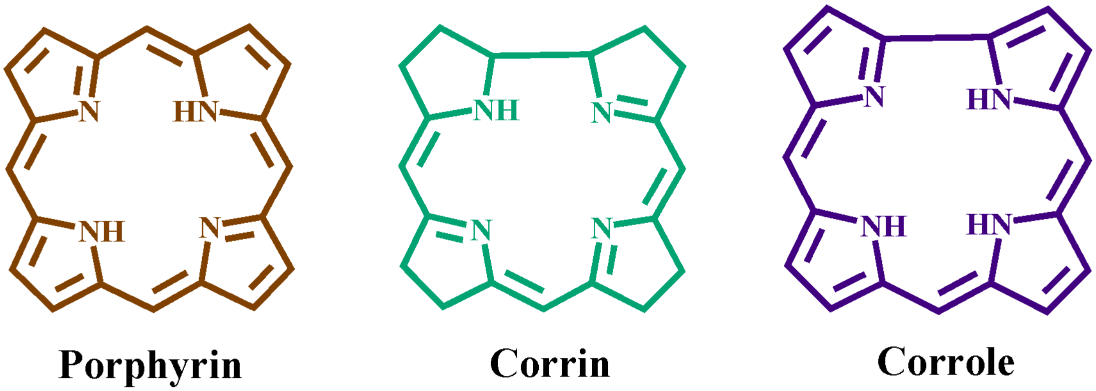
II. 1 Introduction

The oxygenation of hydrocarbons under mild conditions to more valuable products remains an area of active interest in chemical science. Extensive efforts have been devoted to develop efficient catalytic systems for selective oxygenation of hydrocarbons under mild conditions [1-8]. In this direction transition metal complexes of tetradentate diamine-dipyridine, phthalocyanines, 1,4,7-triazacyclononane, Schiff bases and porphyrins have been explored as oxidation catalysts [9-15]. The group of metalloporphyrins have attracted remarkable attention as potential catalysts to promote oxygenation of hydrocarbons under mild conditions [16-18]. Metal complexes of corroles, closely related to porphyrin ligand frame, are emerging as an important group of catalysts in recent years [19-27]. Corroles are tetrapyrrolic macrocycle with one meso carbon short from porphyrin skeleton (Scheme II. 1**)**. The missing *meso* carbon leads to a smaller central cavity compared to porphyrin and reduces symmetry from D_{4h} to C_{2v}. Free base corroles act as a trianionic ligand owing to the presence of three inner –NH protons. Being a trianionic macrocycle with a small cavity corroles have unique property of stabilizing high metal oxidation states. The most stable oxidation numbers in metallocorroles are often one positive charge higher than in the case of analogous metalloporphyrins.



Scheme II. 1 Schematic representation of porphyrin, corrin, corrole.

The chemistry of corroles remained unexplored for a long period, largely due to lack of simple methods for their synthesis [28]. Corroles were first synthesized as early as in 1964 by Johnson and Kay [29] and the first crystallography of a free base corrole was reported by Hodgkin *et al.*[5] in 1971. The first *meso* substituted corrole was reported as late as 1993, [31] almost 30 years after the first reported corrole. All these synthetic processes suffered from the limitations of very low yield, longer reaction time and non-commercially available starting materials. However, major breakthough was made in 1999 by Gross *et al.* [27,32] and Paolesse *et al.* [33] of one-pot corrole syntheses involving pyrrole-aldehyde condensations. Development into the directed synthesis of the corrole macrocycles continues to be one of the most active area of research, with contributions from the groups of Gryko [34], Bruckner [35], Collman [36] and Geier [37]. Due to their unique capacity to stabilize high metal oxidation states, various metallocorroles have been synthesized and examined successfully as catalysts for epoxidation [20,23-27,38], hydroxylation [38(a),39], cyclopropanation [38(a),40] and aziridination [41]. Apart from catalysis, various corroles and their metal complexes are shown to be excellent candidates for environmental and medicinal sensors [42]. Among these reactions activation of aliphatic C-H bonds is, perhaps, the most important goal in basic and industrial research.

Iron, manganese and chromium complexes of corroles have been prepared and utilized as catalysts for the oxidation of hydrocarbons [21, 38]. Among the *meso*-substituted corroles, 5,10,15-tris(pentafluorophenyl) derivative (abbreviated as H_3tpfc) have been most widely used [21]. Gross *et al.* first demonstrated that manganese(III) complex of 5,10,15-tris(pentafluorophenyl) corrole, [Mn(III)(tpfc)], catalyzes oxidation of styrene with PhIO [23]. Later the β-pyrrole-halogenated manganese(III) complexes, [Mn(III)(F_8tpfc)] [24] and [Mn(III)(Br_8tpfc)] [25], were used for catalyzing the oxidation of alkenes by iodosylbenzene and both the complexes emerged as better catalysts than complex [Mn(III)(tpfc)]. The catalytic activity of [Mn(III)(tpfc)] in oxidation of styrene with PhIO has been found to be enhanced by the axial coordination of imidazole [26]. All the manganese(III) corrole catalyzed oxygenation of hydrocarbons reported so far are only limited to the oxidation of alkenes [23-26] but manganese(III) corrole catalyzed alkane oxidation is yet to be explored. On the other hand, iodosylbenzene has been used as the only terminal oxidant in manganese(III) corrole catalyzed oxygenation of hydrocarbons [23-26]. No report on manganese corrole catalyzed hydrocarbon oxidation with any mild terminal oxidant is available in literature, although hydrogen peroxide has been employed in asymmetric sulfoxidation catalysed by albumin- conjugate manganese(III) corrole [43]. Recently manganese(III) corrole has emerged as an efficient decomposition catalyst for peroxynitrite to benign products *in vitro* and *in vivo* studies [44-47]. There is no known biological defence system against peroxynitrite which is involved in the damage of variety of biomolecules, specially those are of vital importance for normal cardiovascular function [48,49]. The mode of catalytic action of amphiphilic manganese(III) corrole on peroxynitrite is disproportionation to nitrite and molecular oxygen. The substrate acts as two-electron oxidant of manganese(III) corrole to (oxo)manganese(V) corrole as well as two-electron reductant of (oxo)manganese(V) species [47]. The catalytic behaviour of amphiphilic manganese(III) corrole towards hydrogen peroxide also follows the similar pattern [43]. In this context it is worthy to investigate the reactivity of manganese(III) corrole towards alkylhydroperoxide.

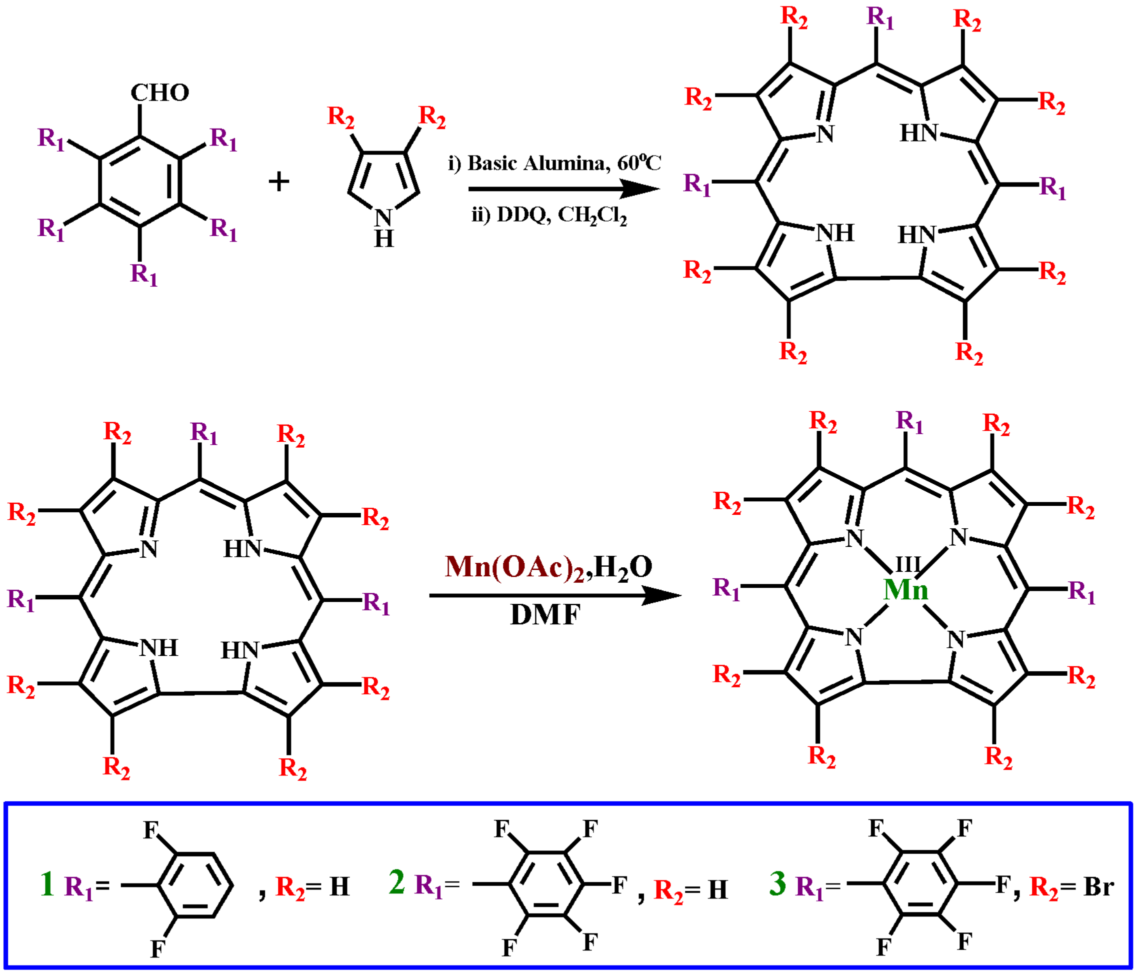
The present work provides the first ever application of mild *tert*-butyl hydroperoxide as terminal oxidant in manganese(III) corrole catalyzed oxygenation of hydrocarbons at room temperature. A plausible reaction mechanism has been proposed on the basis of experimental results.

II. 2 Results and discussion

II. 2. 1 *Synthesis of the catalysts*

The free base corroles were synthesized following the “solvent free” synthesis reported by Gross *et al.* [27,32] (Scheme II.1) since this synthetic procedure has been found to provide 5,10,15-tris(difluorophenyl)corrole (H_3tdfc) and 5,10,15-tris(pentafluorophenyl)corrole (H_3tpfc) in 8-11% yield, conversion being better than any other existing methods of corrole preparation. Thus difluorobenzaldehyde or pentafluorobenzaldehyde and purified pyrrole in 1:1 molar ratio were dissolved in methylene chloride and the mixture was added to a round-bottomed flask containing basic alumina. The slurry was stirred in an aerobic condition at 65-70^0 C. The reaction started only after the solvent evaporated. The reaction mixture was kept constant for further four hours whereupon a dark brown mass was obtained. Extraction of this brown mass with dichloromethane, followed by oxidation by DDQ provided the desired corrole contaminated with linear oligomers like dipyrromethene, pentapyromethene *etc.* and some unidentified side products. The purple coloured fluoroscent corrole was finally purified by thin layer chromatography on silica gel plate with hexane/dichloromethane as the eluant.

The free base corroles were reacted with $Mn(OAc)_2,4H_2O$ in refluxing DMF and the catalysts **1** & **2** were obtained (scheme II.1). The complex [Mn(III)(Br_8tpfc)] (**3**) were prepared following reported methods [23, 25]. The elemental analytical and spectral data of complexes **2** & **3** are in agreement with those reported in the literature [23, 25].



Scheme II. 2 The one-pot "solvent-free" corrole synthesis followed by the preparation of manganese(III) corrole complexes.

II. 2. 2 *Catalytic oxidation of alkenes*

At room temperature all the three manganese(III) corroles (**1-3**) emerged as effective catalysts in oxidizing cyclohexene with mild *tert*-butylhydroperoxide (*t*-BuOOH) under both aerobic and anaerobic conditions (Table II.1). All the reactions were carried out in neat acetonitrile (except for adamantane because of its lower solubility in acetonitrile) as it is found to be the best reaction medium for the present catalytic system (Figure II. 1).

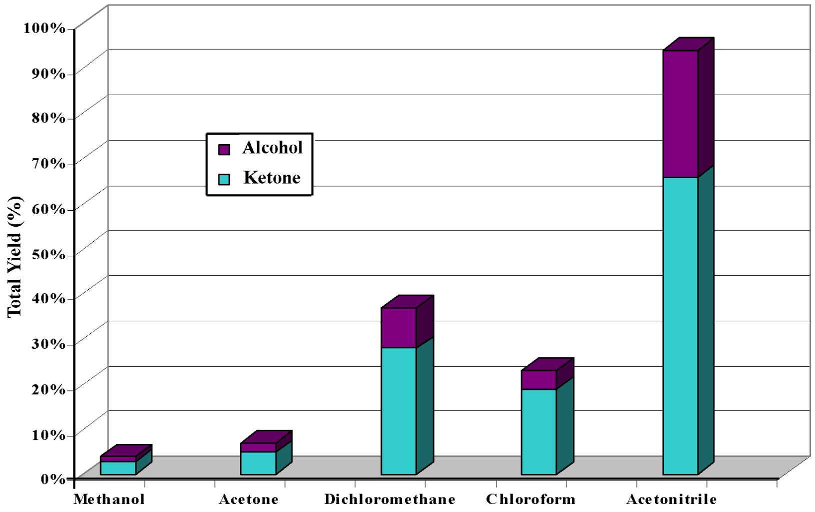


Figure II. 1 Effect of solvent media on the yield of manganese(III) corrole catalyzed oxidation of cyclohexene with *t*-BuOOH.

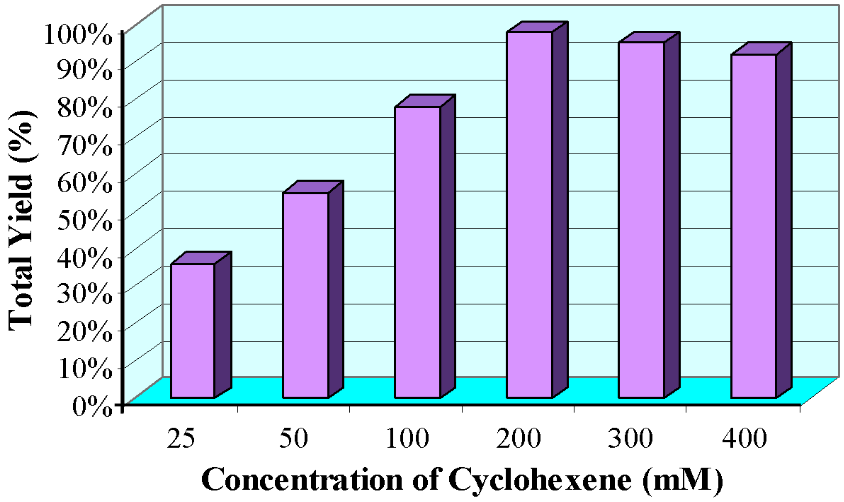


Figure II. 2 Optimization of substrate (cyclohexene) concentration for manganese(III) corrole catalyzed oxidation with *t*-BuOOH.

The reactions were carried out under oxidant limiting condition with large excess of substrate. The optimized concentrations of cyclohexene and *t*-BuOOH were found to be 200mM (Figure II. 2) and 2mM (Figure II. 3) respectively for the catalytic reactions. Complete oxidation of cyclohexene has been achieved within 6 hours in presence of dioxygen, whereas it takes 24 hours for complete conversion of the substrate in the absence of dioxygen. The faster reaction rates in presence of dioxygen clearly suggest the involvement of dioxygen in the oxygenation process by the present catalytic system.

Under both aerobic and anaerobic conditions, allylic oxidation is favoured and 2-cyclohexen-1-one is the major product along with 2-cyclohexen-1-ol as minor one. In contrast, the oxidation of cyclohexene by catalyst **2** with PhIO is limited to only 11 % [25]. The performance of catalyst **3** in the present oxidizing system is more selective than its reported performance with PhIO [25].

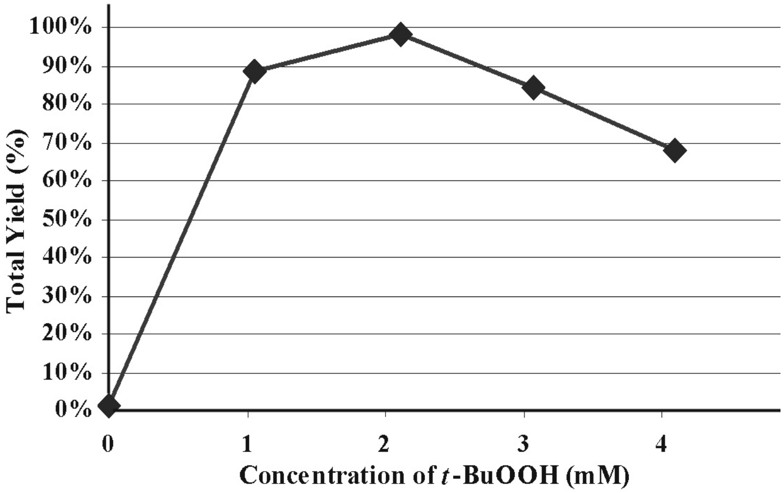


Figure II. 3 Optimization of the concentration of oxidant (*t*-BuOOH) for manganese(III) corrole catalyzed oxidation of cyclohexene.

It has been observed that if the reaction mixture is treated with excess PPh_3 before the GC analysis, the resulting product pattern drastically differs from that obtained prior to PPh_3 addition. After the reduction, 2-cyclohexen-1-ol becomes the major product whereas 2-cyclohexen-1-one appears as minor product (Table II. 1). Since alkyl hydroperoxides are known to be readily and quantitatively reduced by PPh_3 to yield the corresponding alcohols [50], the present results establish the production of cyclohexenyl hydroperoxide as an intermediate during the catalytic cycles.

The electron-deficient manganese(III) corrole catalysts (**1-3**) have been found to be effective in bringing about oxidation of styrene under identical reaction condition. In all the cases, benzaldehyde is obtained as the major product together with styrene oxide and trace amount of phenyl acetaldehyde. Under anaerobic condition, yield of styrene oxide is improved indicating the activation of dioxygen in the present catalytic system. It is noteworthy that styrene oxide is formed as the major product together with phenyl acetaldehyde in the reported oxidation of styrene by manganese(III)corrole/ PhIO systems [23-25].

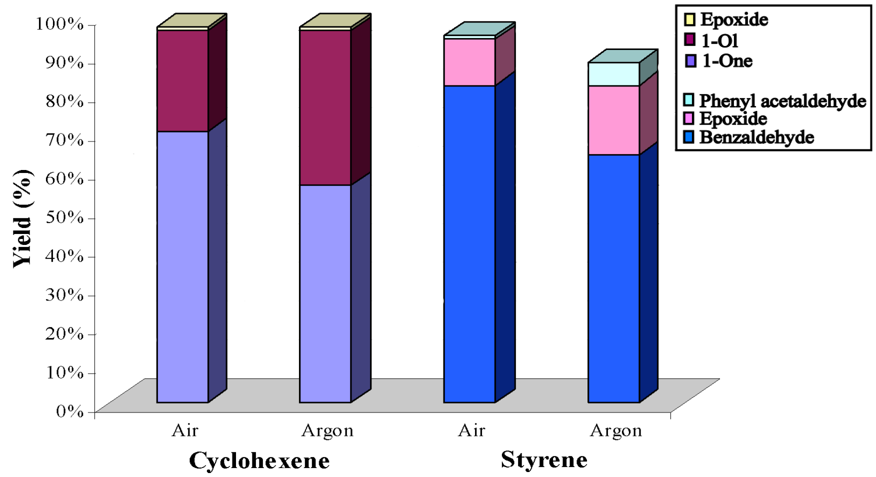


Figure II. 4 Product profile for manganese(III) corrole catalyzed oxidation of cyclohexene and styrene with *t*-BuOOH.

The present results significantly differ from the product pattern of alkene oxidation by manganese(III)corrole/PhIO system and point towards the involvement of radicals rather than the participation of the metal-oxo species.

Table II.1 Catalytic oxidation of alkenes with *t*-BuOOH

Substrate	Catalyst	Atmosphere	Product Profile (%)[a, b]		
			Cyclohexene oxide	Cyclohexenol	Cyclohexenone
Cyclohexene	**1**	Air	2 [1]	27 [73]	69 [26]
		Argon	1 [nil]	57 [66]	41 [31]
	2	Air	1 [1]	26 [70]	70 [28]
		Argon	1 [nil]	40 [62]	56 [36]
	3	Air	3 [1]	28 [72]	66 [25]
		Argon	1 [nil]	39[65]	58[32]
			Styrene oxide	Benzaldehyde	Phenyl acetaldehyde
Styrene	**1**	Air	12	82	1
		Argon	20	67	8
	2	Air	14	83	2
		Argon	30	61	7
	3	Air	12	81	2
		Argon	18	64	6

[a] yields are represented with respect to the concentration of the oxidant; [b] yields within braces after reduction with PPh_3 prior to GC analysis.

II. 2. 3 *Catalytic oxidation of alkanes*

At room temperature the catalytic activity of the manganese(III) corroles (**1**-**3**) were examined for the alkane oxidations by *tert*-butylhydroperoxide (*t*-BuOOH) in acetonitrile medium. Alkane oxidation catalyzed by manganese(III) corrole has been achieved for the first time. The results are summarized in Table II. 2. Cyclohexane has been oxidized to cyclohexanol and cyclohexanone with A/K values of 0.37-0.44. The highest overall conversion (22%) has been achieved with the perbrominated manganese(III) corrole catalyst **3**. The reduction of the reaction mixture by excess triphenylphosphine (PPh_3) prior to GC analysis shows complete reversal of the product pattern, i.e., cyclohexanol becomes the major product for all the three catalysts (Table II. 2), which establishes the formation of cyclohexyl hydroperoxide during the catalytic cycles. To gain further insight into the mechanism of alkane oxidation by the manganese(III) corroles/*t*-BuOOH system, adamantane was chosen as a substrate, which is an important mechanistic probe to diagnose the radical character of catalytic oxidation reactions [51]. Furthermore, considerable efforts have been devoted to introduce the hydroxyl group directly into poorly reactive adamantane tricycles [52] due to the importance of hydroxylated adamantane derivatives in pharmaceutical, polymers and electronic industry. The catalytic reactions were carried out in 1:1 acetonitrile/dichloromethane medium due to the limited solubility of adamantane in pure acetonitrile. The results are summarized in Table II. 2.

Table II. 2 Catalytic oxidation of alkanes with *t*-BuOOH

Substrate	Catalyst	Time (h.)	Product Profile (%)[a, b]	
			Cyclohexanol	Cyclohexanone
Cyclohexane	**1**	6	4 [9]	9 [5]
	2	6	5 [12]	13 [6]
	3	6	6 [14]	16 [8]
			Cyclooctanol	Cyclooctanone
Cyclooctane	**1**	6	8[21]	24[12]
	2	6	12[29]	28[11]
	3	6	14[32]	35[17]
			Adamantane-1-ol	Adamantane-2-ol
Adamantane	**1**	20	10	2
	2	20	12	1
	3	20	15	1

[a] yields are represented with respect to the concentration of the oxidant; [b] yields within braces after reduction with PPh_3 prior to GC analysis.

The present catalytic system oxidizes adamantane mainly into 1-adamantanol along with 2-adamantanol as minor product. Here also, the perbrominated manganese(III) corrole catalyst **3** emerges as the best among three manganese corrole catalysts.

II. 2. 4 *Catalytic oxidation of alkylbenzenes*

Oxidation of alkylbenzenes usually suffers from low selectivity and mostly it is accompanied by the formation of various products like benzaldehyde, benzyl alcohol, cresols, benzoic acid and dibenzyl. Thus design of efficient process for the selective oxidation of alkylbenzenes is highly desirable. Under ambient condition the manganese corrole complexes can efficiently catalyze the oxidation of toluene and ethylbenzene. Toluene has been oxidized to benzaldehyde as major product, while benzyl alcohol is obtained as minor one. Reduction of the reaction mixture with excess triphenylphosphine prior to the GC analysis brings about a complete reversal in the product profile. In this case, benzyl alcohol becomes the major product, supporting the involvement of benzyl peroxy radicals as one of the key intermediates [53]. The oxidation of ethylbenzene produces acetophenone along with 1-phenyl ethanol and a negligible amount of phenyl acetaldehyde. In this case also reduction with excess triphenylphosphine prior to the GC analysis brings about a complete reversal in the product profile as shown in Table II. 3.

Table II. 3 Catalytic oxidation of alkylbenzenes with *t*-BuOOH

Substrate	Time (h.)	Catalyst	Product profile (%)[a, b]		
			Benzaldehyde	Benzyl alcohol	
Toluene	18	**1**	24 [7]	3 [19]	
	18	**2**	22 [8]	2 [16]	
	18	**3**	21 [8]	2 [14]	
			Acetophenone	1-phenyl ethanol	Phenyl acetaldehyde
Ethyl benzene	15	**1**	23[10]	7[20]	3[3]
	15	**2**	36[11]	9[34]	2[2]
	15	**3**	43[15]	12[40]	2[2]

[a] yields are represented with respect to the concentration of the oxidant; [b] yields within braces after reduction with PPh_3 prior to GC analysis.

II. 2. 5 *Mechanistic consideration*

The mechanism of manganese(III) corrole catalyzed alkene oxidation by PhIO is not fully understood so far. Upon addition of PhIO to the manganese(III) corroles, stable Mn(V)-

oxo species forms [23]. However, the oxomanganese(V) species is unreactive towards alkenes and Gross *et al.* proposed that Mn(VI)-oxo species generated by disproportionation of Mn(V)-oxo complex is the active oxidant. On the other hand, Goldberg *et al.* suggested that Mn(V)O (PhIO) might be the true oxidant in the [Mn(III)(tpfc)]-catalyzed oxidation of alkenes with PhIO [50]. Collman *et al.* had performed competitive epoxidation of styrene and cyclooctene with different iodosylarenes and argued in favour of multiple oxidants (both Mn(V)O and Mn(III)-OIAr species) in [Mn(III)(tpfc)]-catalyzed oxidation reactions [55]. With this background attempt has been made to investigate the nature of oxidizing species involved in the manganese(III) corrole/t-BuOOH catalytic system. The UV–visible absorption spectral profiles of catalysts **1**–**3** in acetonitrile are shown in Figure II. 5.

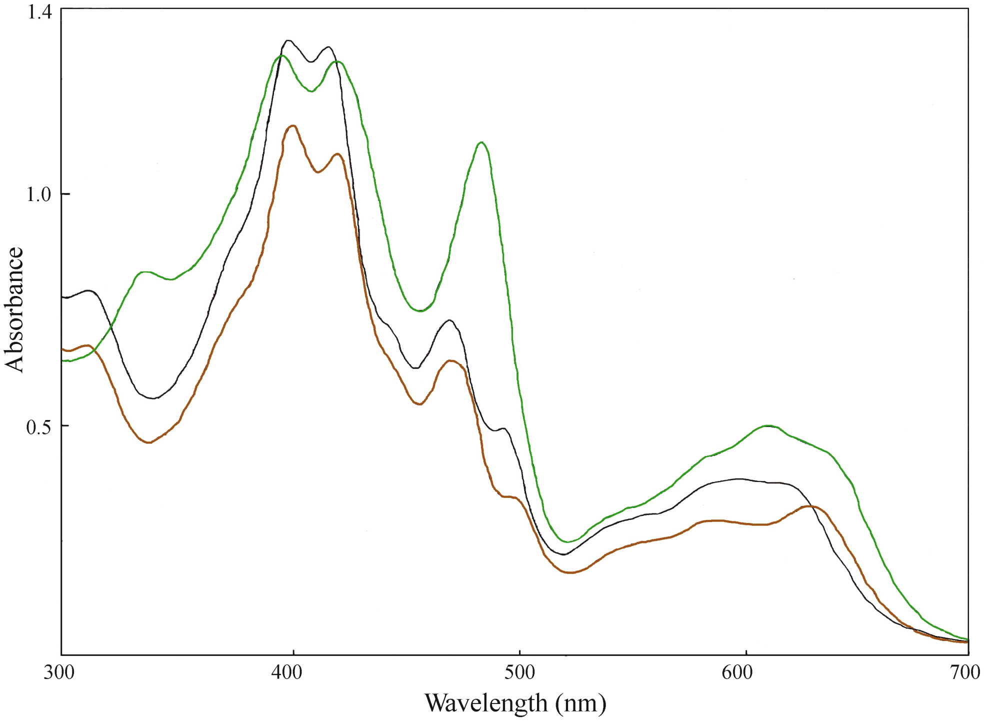


Figure II. 5. Uv–visible spectra of catalysts **1** (brown), **2** (black) and **3** (green) in acetonitrile at 25±1°C.

On addition of *t*-BuOOH to the manganese(III) corroles, the split soret band disappears and new bands are generated at 410nmand 350nm as shown in Figure II. 6. The spectral profiles do not correspond to the formation of the Mn(V)O complex. On comparison of the product pattern obtained in hydrocarbons oxidation by the present manganese(III)corrole/*t*-BuOOH system with those of manganese(III) corrole/PhIO [23] systems, it may be concluded that the present reaction route is different from those found involving the Mn(V)-oxo intermediate.

The involvement of radicals in the present oxidizing system is evident from the fact that the oxidation of cyclohexene is quenched completely in the presence of ‘radical scavenger’ 2,4,6-tri-*tert*-butyl phenol (TTBP). Also, in case of oxidation of adamantane, the tertiary carbon atoms are preferentially activated over the secondary ones pointing towards the involvement of radicals.

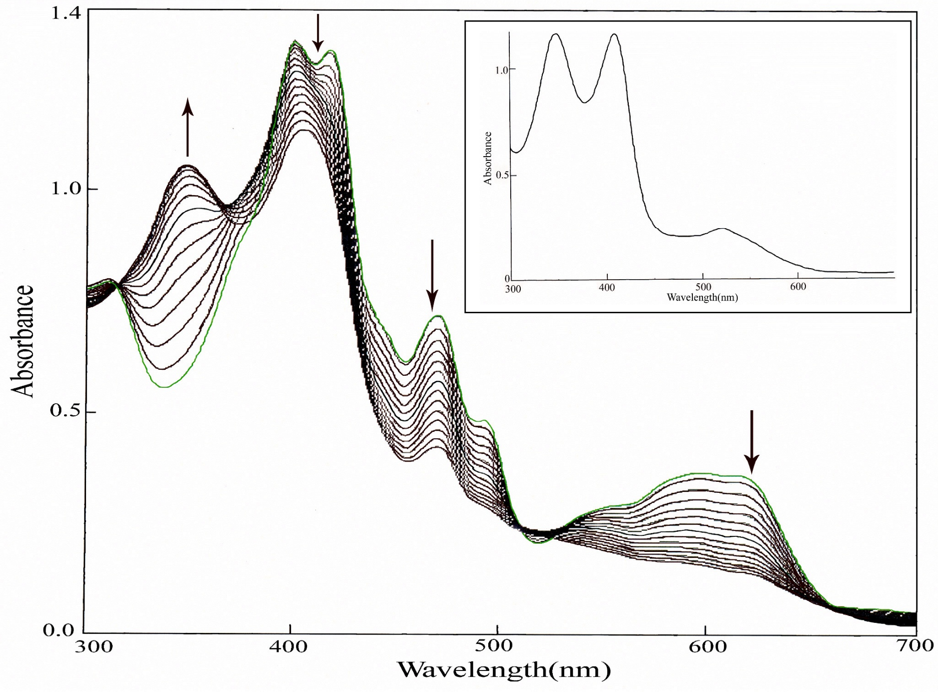


Figure II. 6. Overlay spectra of the catalyst **2** (25µM) and TBHP (2mM) in acetonitrile at 25±1°C (successive spectrum taken after 3min intervals). Inset: electronic spectrum of (oxo)Mn(V) species generated in situ by the reaction of [Mn(III)(tpfc)] and PhIO.

The plausible reaction mechanism supporting all these results obtained in the present case has been shown in Scheme II. 3. It seems reasonable that the manganese(III) corroles (**1**–**3**) with *t*-BuOOH form hydroxo-Mn(IV) species along with tert-butoxyl radical (step1). The hydroxo-Mn(IV) species can further react with *t*-BuOOH, forming Mn(IV)-corrole (OOBu-*t*), which yields the *tert*-butylperoxy radicals (step 3). The *tert*-butylperoxy radicals dismutate to *tert*-butoxyl radical and dioxygen (step 4) [56–59]. The *tert*-butoxyl radical abstracts an H-atom from the hydrocarbon with the formation of alkyl or benzyl radicals (step 5). The process proceeds to the formation of organo-peroxy radical (step 6), which either undergoes a Russel-type termination [60] to form alcohols and ketones (in case of cyclohexane and cyclohexene) (step 7) or decompose to form aldehydes (in case of styrene and toluene). Alternatively, the organo-peroxy radical can effect the homolytic cleavage of the C–H bond of the hydrocarbon forming organo-hydroperoxide (step 9) [50, 61]. This species can then undergo homolytic decomposition to the organooxyl RO• radical (step 10) followed by its H-abstraction from the hydrocarbon forming the alcohol ROH and R• (step 11).

$$\mathbf{Mn^{III}(corrole) + \mathit{t}\text{-}BuOOH \longrightarrow Mn^{IV}(corrole)(OH) + \mathit{t}\text{-}BuO^{\bullet}} \qquad \mathbf{(1)}$$

$$\mathbf{Mn^{IV}(corrole)(OH) + \mathit{t}\text{-}BuOOH \longrightarrow Mn^{IV}(corrole)(OOBu\text{-}\mathit{t}) + H_2O} \qquad \mathbf{(2)}$$

$$\mathbf{Mn^{IV}(corrole)(OOBu\text{-}\mathit{t}) \longrightarrow Mn^{III}(corrole) + \mathit{t}\text{-}BuOO^{\bullet}} \qquad \mathbf{(3)}$$

$$\mathbf{2\ \mathit{t}\text{-}BuOO^{\bullet} \longrightarrow 2\ \mathit{t}\text{-}BuO^{\bullet} + O_2} \qquad \mathbf{(4)}$$

$$\mathbf{\mathit{t}\text{-}BuO^{\bullet} + RH \longrightarrow R^{\bullet} + \mathit{t}\text{-}BuOH} \qquad \mathbf{(5)}$$

$$\mathbf{R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}} \qquad \mathbf{(6)}$$

$$\mathbf{2\ ROO^{\bullet} \longrightarrow ROH + R'{=}O + O_2} \qquad \mathbf{(7)}$$

$$\mathbf{ROO^{\bullet} + \mathit{t}\text{-}BuOO^{\bullet} \longrightarrow R'{=}O + \mathit{t}\text{-}BuOH + O_2} \qquad \mathbf{(8)}$$

$$\mathbf{ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}} \qquad \mathbf{(9)}$$

$$\mathbf{2ROOH \longrightarrow RO^{\bullet} + ROO^{\bullet} + H_2O} \qquad \mathbf{(10)}$$

$$\mathbf{RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet}} \qquad \mathbf{(11)}$$

Scheme II. 3 Simplified pathway for the oxidation of hydrocarbons by *t*-BuOOH in the presence of manganese(III) corroles.

The involvement of the organo-hydroperoxide (ROOH) in the present catalytic system is established by the significant increase in the amount of alcohol with simultaneous decrease in the amount of ketone (in case of cyclohexene, cyclohexane and toluene) when the reaction mixture is treated with excess PPh_3 prior to the GC analysis using the well known method developed by Shul'pin *et al.* [50, 62, 63].

II. 2. 6 *Kinetic studies*

The transformation of manganese(III)-corrole to manganese(IV) intermediate proceeds slowly, which is evident from Figure II. 6. The rate constants for the above transformation by *t*-BuOOH were measured in acetonitrile. The change of absorbance at 470nm was monitored with time. It is observed that the absorbance vs. time plot does not fit to a simple first or second order kinetic pattern. So the kinetic data have been analyzed using the initial rate method [64–66].

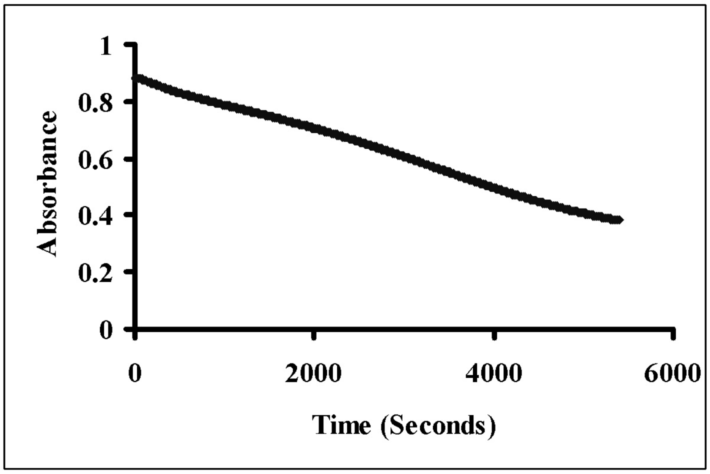


Figure II. 7. Absorbance vs. time plot recorded at 470nm in 2 ml. acetonitrile at 25±1^0 C. *t*-BuOOH = 1.92 mM; Catalyst [Mn(III)(tpfc)] = 30μM.

Values of the initial rate $(dA/dt)_0$ for the reactions are compiled in Table II. 4. The values of $(dA/dt)_0$ are plotted against [*t*-BuOOH] at constant [Mn(III)(tpfc)] as shown in Figure II. 8. Again, the plot of $(dA/dt)_0$ vs. [Mn(III)(tpfc)] at fixed [*t*-BuOOH] is displayed in Figure II. 9. It is clear from both the plots that the rate $(dA/dt)_0$ for the reaction is linear in [*t*-BuOOH] as well as in [Mn(III)(tpfc)].

Table II. 4 Values of $(dA/dt)_0$ at λ = 470nm for the oxidation of [Mn(III)(tpfc)] by *t*-BuOOH in acetonitrile at 25±1°C.

Entry	[*t*-BuOOH]$_0$/10^{-3} mol dm^{-3}	[Mn^{III}(tpfc)]$_0$/10^{-6} mol dm^{-3}	$(dA/dt_0)/10^{-5}s^{-1}$ [omitting first 60 sec.]	$(dA/dt_0)/10^{-5}s^{-1}$
1	1.04	35	7.379	6.407
2	1.92	35	12.636	10.382
3	2.88	35	15.191	13.924
4	3.84	35	18.788	17.463
5	1.92	18	6.571	6.019
6	1.92	30	12.926	10.926
7	1.92	50	15.126	15.601
8	1.92	76	21.431	19.682

The first order rate constants obtained from Figure II. 8 and Figure II. 9 are 0.0392 s^{-1} and 2.279 s^{-1} respectively. The overall the reaction can be expressed as

$$-dA/dt = k_d[t\text{-}BuOOH]\,[Mn(III)(tpfc)]$$

where k_d is the second order rate constant. The value of k_d from the slope of the $(dA/dt)_0$ vs. [*t*-BuOOH] at constant [Mn(III)(tpfc)] is 1.1197×10^3 dm^3 mol^{-1} s^{-1} while from the slope of the $(dA/dt)_0$ vs. [Mn(III)(tpfc)] at constant [*t*-BuOOH] a value of k_d of 1.187×10^3 dm^3 mol^{-1} s^{-1} was obtained. The values obtained for k_d from the two different plots are thus in good agreement. The rate constants of the elementary steps are relevant to the overall catalytic process.

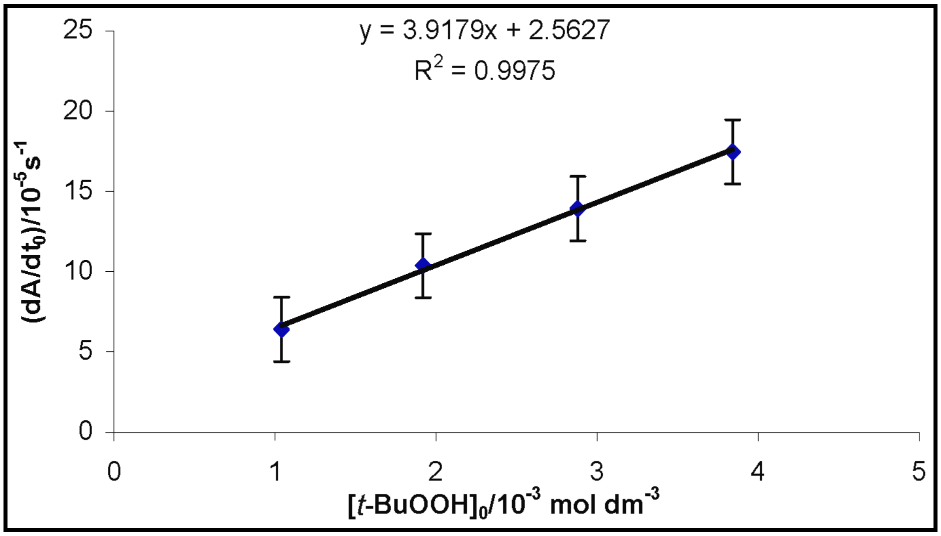


Figure II. 8. Plots of $(dA/dt)_0$ against [*t*-BuOOH] at fixed [Mn(III)(tpfc)] in acetonitrile at 25±1°C.

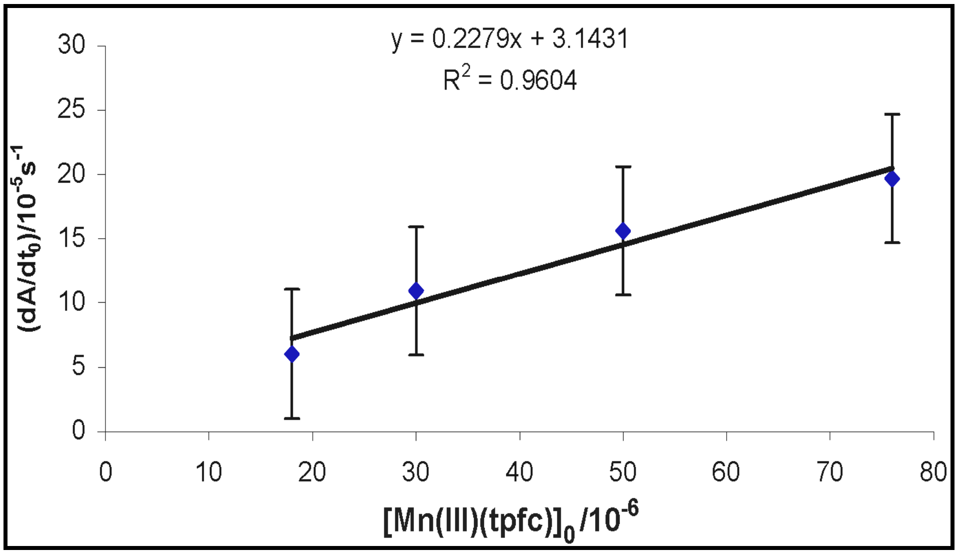


Figure II. 9. Plots of $(dA/dt)_0$ against [Mn(III)(tpfc)] at fixed [*t*-BuOOH] in acetonitrile at 25±1°C.

II. 3 Conclusion

At room temperature the oxygenation of alkenes, alkanes and alkyl benzene has been achieved by the present oxidation system comprising electron deficient manganese(III) corroles (**1**–**3**) as catalysts and mild *tert*-butylhydroperoxide as terminal oxidant. The use of *tert*-butylhydroperoxide as an oxidant in manganese(III) corrole calayzed oxidation reactions has been reported for the first time. This is also the first description of using manganese(III) corrole for catalyzing oxidation of unactivated C–H bonds of alkanes. It shows that the main role of the catalyst is the activation of alkylhydroperoxide rather than oxygen atom transfer catalysis. The achieved selectivity parameters are close to previously reported oxidizing systems [45, 50, 51(b)] that proceed with the participation of alkylperoxy (ROO•) radicals and organo-hydroperoxide (ROOH). The involvement of the organo-hydroperoxide (ROOH) has been confirmed. In contrast with the catalytic behaviour of manganese(III) corrole towards peroxynitrite and hydrogen peroxide where the catalytic cycles involve disproportionation with two-electron steps, the present catalytic system proceeds through a radical-chain mechanism in which the radicals are generated by oxidation and reduction of alkyl hydroperoxide.

II. 4 Experimental Section

II. 4. 1 ***Materials.*** Acetonitrile and dichloromethane were distilled under argon from CaH_2 and $CaCl_2$ and stored over molecular sieves (4 Å). Cyclohexene was distilled under argon to remove the inhibitor and passed through a silica gel column prior to reaction. Other substrates, all the reaction products, dodecane (internal standard) and *t*-BuOOH (as ~70% solution in water) were purchased from Aldrich and were used as received. The exact active oxygen content of the oxidant was determined iodometrically prior to use.

II. 4. 2 ***Synthesis of the catalysts.*** Difluorobenzaldehyde or pentafluorobenzaldehyde and purified pyrrole in 1:1 molar ratio were dissolved in 10 mL methylene chloride and the mixture was added to a 100 mL round-bottomed flask containing 3g basic alumina. The slurry was stirred in an aerobic condition at 65-70^0 C. The reaction started only after the solvent evaporated. The reaction mixture was kept constant for further four hours whereupon a dark brown mass was obtained. Extraction of this brown mass with dichloromethane, followed by oxidation by DDQ provided the desired corrole (H_3tdfc or

H_3tpfc) contaminated with linear oligomers like dipyrromethene, pentapyromethene *etc.* and some unidentified side products. The purple coloured fluoroscent corrole was finally purified by thin layer chromatography on silica gel plate with hexane/dichloromethane (4:1, v/v) as the eluant.

Synthesis of [Mn(III)(tdfc)] (1). The new complex [Mn(III)(tdfc)] (**1**) was prepared from $Mn(OAc)_2$. $4H_2O$ and the corresponding ligand (H_3tdfc) in refluxing DMF (10ml.) and the green product was purified by preparative TLC on a silica gel plate using 1:1 dichloromethane/hexane as the eluant. [Mn(III)(tdfc)]: Yield: 85%. Anal. Calcd. for $C_{37}H_{17}N_4F_6Mn$: C, 64.73; H, 2.50; N, 8.16. Found: C, 64.81; H, 2.37; N, 8.25; MS (CI^+, isobutane): m/z (%):686 (100) [M^+]; UV/Vis (CH_2Cl_2): λ_{max} [nm] (logε)= 400 (4.55), 416 (4.53), 487 (4.14), 622 (4.01).

Synthesis of [Mn(III)(tpfc)] (2). Complex [Mn(III)(tpfc)] (**2**) was prepared following reported procedure [23]. Yield: 88%. MS (CI^+, isobutane): m/z (%): 848 (100) [M^+]; UV/Vis (CH_2Cl_2): λ_{max} [nm] (logε)= 399 (4.58), 415 (4.61), 488 (4.12), 620 (4.06).

Synthesis of [Mn(III)(Br$_8$tpfc)] (3). Complex [Mn(III)(Br$_8$tpfc)] (**3**) was prepared following reported procedure [25]. Yield: 80%. MS^-: e/z (%): 1479 (100) [M^-]; UV/Vis (CH_2Cl_2): λ_{max} [nm] (logε)= 402 (4.72), 420 (4.70), 490 (4.34), 617 (4.22).

II. 4. 3 *Instruments.* UV-visible spectral measurements were taken with a JASCO V 530 spectrophotometer connected with a thermostat at 25 ± 1^0 C. The product analysis was done by PerkinElmer Clarus-500 GC (Elite-I, Polysiloxane, 15-m column) equipped with FID by injecting 1μL aliquot from the reaction vial taken after addition of dodecane as internal standard.

II. 4. 4 *Catalytic experiments.* Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction 25 μM of catalyst and 200 mM (100mM in case of adamantane) of substrate were dissolved in 2 mL of acetonitrile (argon saturated in case of anaerobic reactions) or 3:2 acetonitrile/dichloromethane in case of adamantane. The oxidation reaction was initiated by adding 2 mM of *t*-BuOOH and the contents were magnetically stirred. The product analysis was done by injecting 1μL aliquot from the reaction vial into a capillary column (elite 1, 15m) of a preheated GC after addition of dodecane as internal standard. The identification and quantification of the products were done from the response factors of standard product samples. Standard GC conditions for analysis were as shown in the following tables (II. 5 and II. 6).

Table II. 5 Standard GC conditions for the analysis of reactions (except cyclohexane)

Injector (split) temperature	250^{o}C		
Flame Ionization Detector temperature	250^{o}C		
Inlet flow-total (N_2)	42 mL/min		
Sampling rate	12.50000 pts/S		
Column temperature	**Rate (^{o}C/min)**	**T (^{o}C)**	**Hold time (min)**
	-	65^{o}	3
	5^{o}/min	195^{o}	5
Column pressure	**Rate (psi/min)**	**Pressure (psi)**	**Hold time (min)**
	-	5	34

Table II. 6 Standard GC conditions for the analysis of reactions of cyclohexane

Injector (split) temperature	250^{o}C		
Flame Ionization Detector temperature	250^{o}C		
Inlet flow-total (N_2)	42 mL/min		
Sampling rate	12.50000 pts/S		
Column temperature	**Rate (^{o}C/min)**	**T (^{o}C)**	**Hold time (min)**
	-	100^{o}	5
	5^{o}/min	160^{o}	10
Column pressure	**Rate (psi/min)**	**Pressure (psi)**	**Hold time (min)**
	-	3	27

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CHAPTER III

Manganese(III) corrole catalyzed oxidation of alkanes and alkylbenzenes at room temperature: Hydrogen Atom Transfer reaction by high valent manganese-oxo species*

Abstract

At room temperature manganese(III) corrole complexes were successfully employed as catalysts in the oxidation of alkanes and alkylbenzenes using *m*-chloroperbenzoic acid (*m*-CPBA) as the terminal oxidant. Adamantane has been selectively hydroxylated to adamantane 1-ol and 2-ol with higher preference for the tertiary position. Cyclohexane and cyclooctane have been oxidized to corresponding alcohols as major products. Diphenylmethane was selectively hydroxylated to diphenylmethanol. The present oxidizing system also oxidizes toluene and ethylbenzene. High valent oxomanganese(V) species has been proposed to be the active oxidant. The high-valent oxomanganese(V) corrole undergoes hydrogen atom transfer (HAT) reaction with 2,4,6-tri-*t*-butylphenol (TTBP) resulting in the formation of oxidized phenoxyl radicals. Kinetic studies have led to the determination of second-order rate constants for the hydrogen atom transfer reactions. The kinetic experiments reveal a first order reaction rate dependence on the concentration of catalyst as well as on that of the oxidant.

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III. 1 Introduction

The oxidative functionalization of hydrocarbons to more valuable products is of great interest in synthetic organic chemistry and industrial chemistry [1]. Among hydrocarbons, alkanes have long been considered inert [2]. Their low reactivity toward reagents is due to their saturation (no low energy empty π orbitals and no high energy filled n orbitals). The inertness of alkanes towards chemical conversion demands a great deal of effort to develop efficient catalysts operating at ambient conditions [3]. The catalytic alkane hydroxylation reaction is also worthy to be investigated in detail to understand the catalytic mechanisms of monooxygenase metalloenzymes. So far, considerable attention has been focused on variety of coordination complexes to utilize them as efficient homogeneous catalysts for oxygenation of saturated hydrocarbons [4]. In this direction, transition metal complexes of porphyrins, phthalocyanines, chlorins, triazacyclononanes and Schiff bases have been explored as homogeneous catalysts [5, 6]. Metalloporphyrin catalyzed hydroxylation of alkanes has been most extensively studied [7-9]. Metallocorroles have also shown to be efficient enough in catalyzing hydrocarbon oxidation though the study is mainly confined to iron and manganese corrole complexes [10] and the only other instance is photocatalytic oxygenation of cumene by difluoroantimony(V)corrole [11]. Manganese corroles have evoked more interest than iron-corroles as catalysts in hydrocarbon oxidation [10, 12-14]. The synthesis of manganese(III) complex with 5,10,15-tris(pentafluorophenyl)corrole, [Mn(III)(tpfc)], and its successful use as catalyst in the oxidation of styrene with PhIO was first reported by Gross *et al.* [12]. The substitution of the β-pyrrolic hydrogens of corrole macrocycles with bromine [13] or fluorine [14] enhances the catalytic activity of the manganese(III) corroles in terms of yield and reaction time.

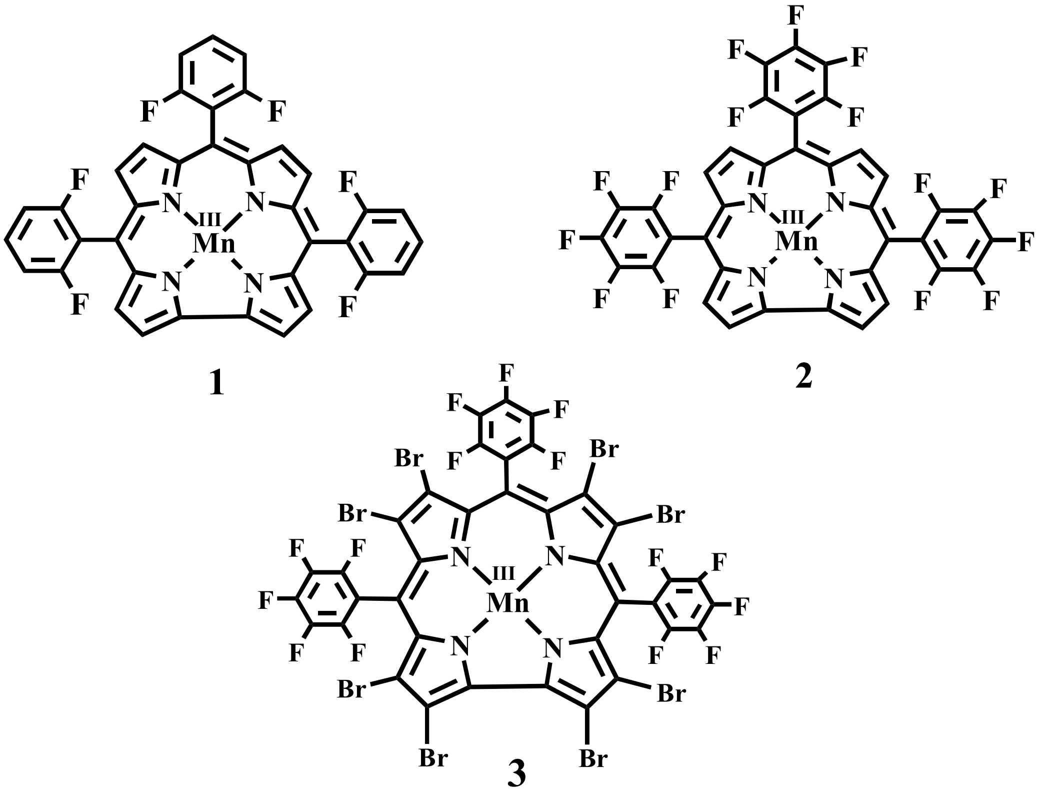
Despite considerable progress in managanese(III) corrole catalyzed alkene oxidation, no report on the catalytic oxygenation of alkanes by managanese(III) corrole has appeared so far. However, iron complex of 5,10,15-tris(pentafluorophenyl)corrole [Fe(IV)(tpfc)Cl] is known to catalyze hydroxylation of ethylbenzene with iodosylbenzene at room temperature [15]. Recent studies have also reported selective hydroxylation of alkanes by [Fe(IV)(tpfc)Cl] with *m*-chloroperbenzoic acid at room temperature [16].

Our earlier efforts to hydroxylate alkanes with mild *t*-BuOOH catalyzed by manganese corroles led to corresponding ketones as major products rather than alcohols [17]. In this context, the present study focuses on manganese(III) corrole catalyzed hydroxylation of alkanes (adamantane, cyclohexane, cyclooctane and diphenylmethane) and oxidation of alkylbenzenes (toluene and ethylbenzene) at room temperature with *m*-CPBA as terminal oxidant. The kinetic studies of the present oxidizing systems with 2,4,6-tri-*t*-butylphenol (TTBP) have also been undertaken. A plausible reaction mechanism has been proposed on the basis of experimental results.

III. 2 Results and discussion

III. 2. 1 *Catalytic oxidation of alkanes*

Initially the catalytic activities of the manganese(III) corroles (**1**-**3**) (Scheme III. 1) were examined in oxidizing adamantane by *m*-CPBA in acetonitrile medium at room temperature.



Scheme III. 1 Manganese(III) corrole complexes (**1**-**3**) employed in this study.

The reason behind the choice of adamantane as a substrate is based on the fact that the oxidation of adamantane is a useful probe to test the regioselectivity between tertiary (3°)

and secondary (2°) C-H bonds [18]. Moreover, there is a wide applicability of its hydroxylated derivatives in pharmaceutical intermediates, polymers and electronic industries [19]. However, the conversion of relatively inert C-H bond of adamantane tricycles to C-OH bond is quite difficult [19]. The present oxidizing system selectively oxidizes adamantane to the corresponding adamantanols at room temperature with a strong preference for the hydroxylation at the tertiary centre. The manganese(III) corrole complexes (**1-3**) have emerged as almost equally efficient catalysts, affording a total yield of 38 to 42% of adamantanols within two hours. The results are summarized in Table III. 1, entries 1-3. The reactions showed selectivity for oxidation at the tertiary position, with a 3°/2° ratio of 11 – 11.6 (normalized on a per-hydrogen basis).

Table III. 1 Oxidation of alkanes by manganese(III) corroles with *m*-CPBA

Entry	Substrate	Catalyst	Total yield (%)[a, b]	Product profile (%)[a]		Remarks
				1-Adamantanol	2-Adamantanol	
1	Adamantane	**1**	42	33	9	11
2		**2**	39	31	8	11.6
3		**3**	38	30	8	11.25
				Cyclohexanol	Cyclohexanone	
4	Cyclohexane	**1**	6	4	2	A/K=2
5		**2**	12	10	2	A/K=5
6		**3**	15	12	3	A/K=4
				Cyclooctanol	Cyclooctanone	
7	Cyclooctane	**1**	22	18	4	A/K=4.5
8		**2**	27	22	5	A/K=4.4
9		**3**	32	27	5	A/K=5.4
				Diphenylmethanol		
10	Diphenyl-methane	**1**	20	20		A/K=20
11		**2**	26	26		A/K=26
12		**3**	29	29		A/K=29

[a] Yields are based on concentration of oxidant, [b] reaction time = 2 hours

These results encouraged us to examine the catalytic oxygenation of cyclohexane and cyclooctane with manganese(III) corrole by *m*-CPBA. Under these reaction conditions cyclohexane has been converted to cyclohexanol as major along with cyclohexanone as minor product (Table III. 1, entries 4-6). In this case, the perbrominated manganese(III) corrole (**3**) has been found to be most effective catalyst affording cyclohexanol and cyclohexanone with a total yield of 15% and A/K ratio of 4.0 (Table III. 1, entry 6). Cyclooctane produced cyclooctanol as major product along with minor quantity of cyclooctanone (Table III. 1, entries 7-9). Diphenylmethane, on the other hand, is selectively oxidized to diphenylmethanol (Table III. 1, entries 10-12) by either of the three manganese corrole catalysts. Significantly, acetophenone, the over oxidized product, was not at all detected under the reaction conditions employed. Among the manganese(III) corroles, catalyst **3** has been found to be most effective in bringing about oxidation of diphenylmethane. The relative reactivity of the manganese corrole catalysts follows the order **3** > **2** > **1** for all the alkanes under investigation except adamantane.

III. 2. 2 *Catalytic oxidation of alkylbenzenes*

Oxidation of alkylbenzenes is important chemical transformations in chemical synthesis, which normally undergo with a low selectivity, with the formation of various by-products [20]. In general, oxidation of toluene usually affords benzaldehyde, benzyl alcohol, cresols, benzoic acid and dibenzyl and thus design of efficient process for the selective oxidation of toluene is highly desirable.

Table III. 2 Oxidation of alkyl benzenes by manganese(III) corroles with *m*-CPBA at room temperature

<table>
<tr><th rowspan="2">Entry</th><th rowspan="2">Substrate</th><th rowspan="2">Catalyst</th><th rowspan="2">Total yield (%)^{a,b}</th><th colspan="3">Product profile (%)</th></tr>
<tr><th colspan="2">Benzaldehyde</th><th>Benzyl alcohol</th></tr>
<tr><td>1</td><td rowspan="3">Toluene</td><td>1</td><td>20</td><td colspan="2">16</td><td>4</td></tr>
<tr><td>2</td><td>2</td><td>15</td><td colspan="2">12</td><td>3</td></tr>
<tr><td>3</td><td>3</td><td>16</td><td colspan="2">13</td><td>3</td></tr>
<tr><td colspan="4"></td><td>Phenyl acetaldehyde</td><td>1-phenyl ethanol</td><td>Acetophenone</td></tr>
<tr><td>4</td><td rowspan="3">Ethylbenzene</td><td>1</td><td>15</td><td>9</td><td>4</td><td>2</td></tr>
<tr><td>5</td><td>2</td><td>26</td><td>12</td><td>8</td><td>6</td></tr>
<tr><td>6</td><td>3</td><td>29</td><td>15</td><td>9</td><td>5</td></tr>
</table>

^{a} Yields are based on concentration of oxidant, ^{b} reaction time = 1 hour.

With the present oxidizing system, toluene has been oxidized under ambient condition to form benzaldehyde as the major product, while benzyl alcohol is generated as the minor one. No oxidation of the aromatic ring was observed. The results summarized in Table III. 2, entries 1-3 which show that overall yields of 16 to 20% were achieved within one hour. The present oxidizing system has also been found effective in oxidizing ethylbenzene at room temperature. Ethylbenzene has been converted into phenylacetaldehyde, 1-phenylethanol and acetophenone (Table III. 2, entries 4-6). The reaction proceeded with a greater selectivity for the formation of phenylacetaldehyde and highest conversion (29%) has been achieved with the catalyst **3** (Table III. 2, entry 6). The formation of phenylacetaldehyde in the present case is surprising. This may arise from the oxidation of ethylbenzene to styrene, followed by the oxidation of styrene by the present oxidizing system.

The overall yield of the oxidized products has been found to be moderate. However, the total amount of oxidant may be accounted for by considering the pronounced anti-oxidant property of the manganese(III) corroles [21, 22]. It has been demonstrated that manganese(III) corroles effectively decompose reactive oxygen species and this aspect has been receiving continuous attention for its potential application in combating against several neurodegenerative disorders [22].

III. 2. 3 *Mechanistic Considerations*

High valent oxomanganese corroles have been frequently invoked as the key oxidant in the manganese(III) corrole catalyzed oxidation reactions with iodosylbenzene as the oxidant [12-14]. It has been established that manganese(III) corroles react with PhIO and form oxomanganese(V) species. However, the lack of reactivity of this oxospecies towards oxygenation reactions led to the proposal that a high valent manganese(VI)-oxo species, generated by disproportionation of manganese(V)-oxo, is the active oxidant [12, 14]. Oxomanganese corroles have been shown to be effective oxo-transfer agents towards olefinic substrates like cyclohexene and styrene [12-14]. Very recently, Gross *et al.* reported oxygen atom transfer reactions from isolated oxomanganese(V) corroles to organic sulfides [23]. However, C-H bond activation of alkanes using high valent oxomanganese corroles is still unknown.

Treatment of the manganese(III) corroles (**1**-**3**) with *m*-chloroperbenzoic acid (*m*-CPBA) in acetonitrile medium at room temperature results in the formation of the oxomanganese(V) species [12]. The UV-visible spectal pattern of [Mn(III)tpfc] and its corresponding oxo species has been shown in figure III. 1 and the spectral changes brought about by the treatment of *m*-CPBA to [Mn(III)(tpfc)] (**2**) has been shown in figure III. 2.

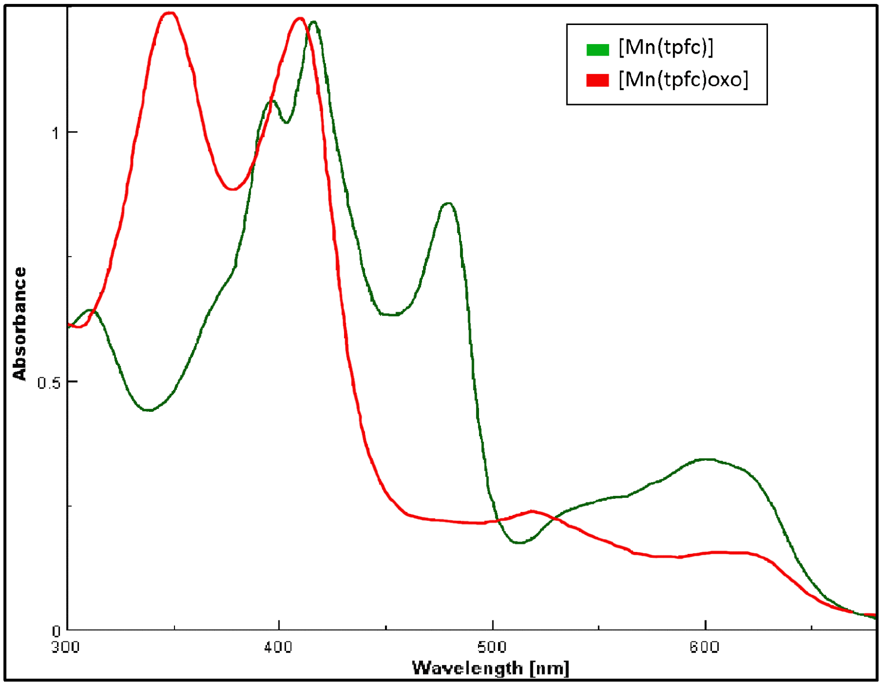


Figure III. **1** UV-visible spectal pattern of [Mn(III)tpfc] and its corresponding oxo species in acetonitrile at room temperature.

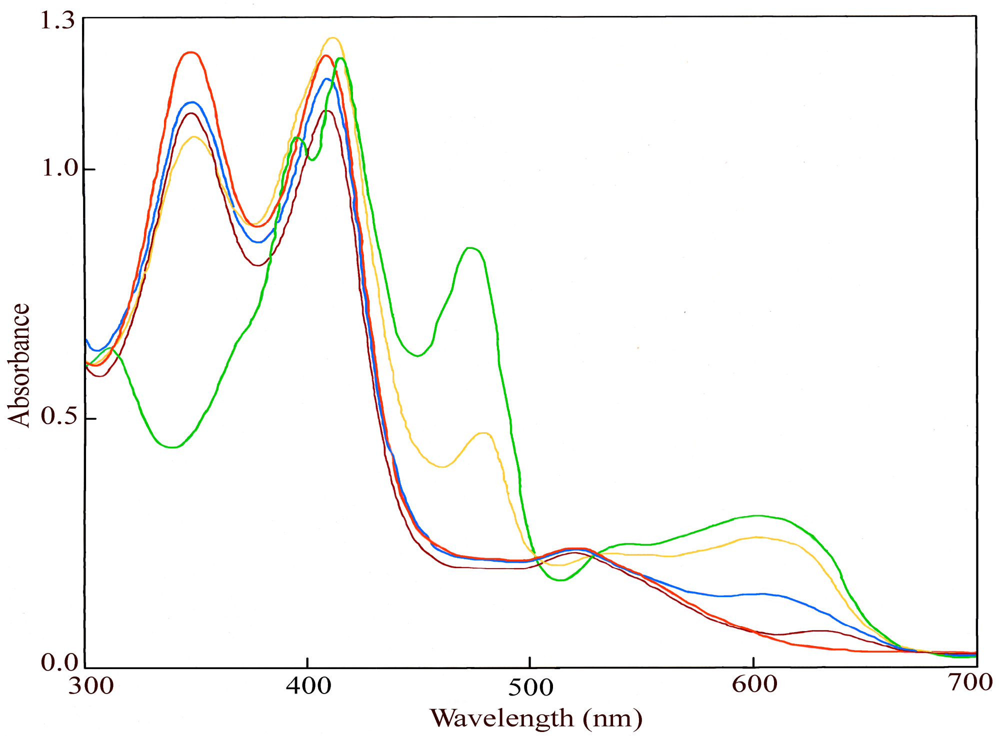


Figure III. 2 UV-visible spectroscopic changes of the catalyst **2** (green) in acetonitrile at room temperature upon addition of 1 eqv. (yellow), 2 eqv. (red), 3 eqv. (blue) and 4 eqv. (brown) *m*-CPBA solutuion.

Titration experiments reveal that the characteristic peaks of the catalyst **2** gradually disappear on addition of *m*-CPBA with emergence of new peaks at 348 nm, 410 nm and 518 nm which is characteristic of oxomanganese(V) species [13]. It has been observed that the complete conversion of the manganese(III) corrole to the oxomanganese(V) species requires two equivalent of *m*-CPBA (Figure III. 2).

III. 2. 4 *Kinetics of the catalytic reactions*

The formation of oxomanganese(V) corrole having been confirmed in the present oxidizing system, we decided to follow the kinetics of the reaction with 2,4,6-tri-*tert* butylphenol (TTBP) as the substrate. The rationale behind the choice of this particular substrate was its ability to form stable phenoxyl radical *via* formal H-atom abstraction, which could easily be identified by UV-visible spectroscopy [24, 25]. It is noteworthy that $Mn^V{\equiv}O$ unit is a potentially important intermediate in Photosystem II and is responsible in hydrogen atom transfer (HAT) processes with a nearby tyrosyl radical [26]. Moreover, HAT reactions of TTBP with imidomanganese(V) corrole [27] and oxomanganese(V) corrolazine [28] have been reported recently and the reaction provided significant insight into a wide range of enzymatic and synthetic processes involving high-valent metal-oxo intermediates.

The rate of the catalyst oxidation with *m*-CPBA was studied using 2,4,6-tri-*tert*-butylphenol (TTBP) under argon atmosphere. The formation of oxidized product 2,4,6-tri-*tert*-butylphenoxy radical was monitored by measuring it's absorbance at 630 nm (€ = 385 mol^{-1} cm^{-1}) [24, 25]. The yield of the radical was found to be dependent on substrate (TTBP) concentration. It has been observed that a minimum concentration of 40±5 mM of TTBP is required to trap all the reactive intermediates in these reactions in acetonitrile. At lower concentration of substrate (Table III. 3, entry 1 and 2) the yield is not quantitative; again decrease in the overall yield is observed on increasing the substrate concentration (Table III. 3, entry 9). It is clear from Table III. 3 that considerable catalyst bleaching takes place at lower concentration of TTBP (Table III. 3, entry 1-5). The highest catalytic activity of manganese(III) corrole has been observed in the range of 30 to 100 mM substrate concentration.

Table III. 3 [Mn(III)(tpfc)] catalyzed oxidation of TTBP by *m*-CPBA in acetonitrile at 25±1^0 C

Entry No.	TTBP (mM)	Catalyst (μM)	Oxidant (mM)	$(dA/dt)_0$ s^{-1} X 10^4	Yield (%)[a]	Catalyst survival (%)
1	17.53	12.97	0.96	7.922	89.40	Bleached
2	20.40	12.97	0.97	10.029	93.30	Bleached
3	31.24	12.98	0.98	12.958	96.02	24
4	42.48	12.97	0.97	21.052	98.75	48
5	60.97	12.97	0.98	29.832	99.93	59
6	83.83	12.97	0.97	28.227	99.20	65
7	95.26	12.97	0.96	28.021	98.50	82
8	106.69	12.97	0.96	26.926	97.40	88
9	44.82	13.02	0.97	23.522	98.90	-
10	44.55	28.02	0.98	28.295	99.40	-
11	44.58	37.68	0.97	32.827	99.76	-
12	44.28	51.72	0.98	34.511	99.25	-
13	44.02	12.97	0.96	22.859	99.12	-
14	44.15	12.97	1.92	24.947	95.51	-
15	44.11	12.97	2.91	27.607	88.47	-
16	44.08	12.97	3.84	29.993	80.15	-

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

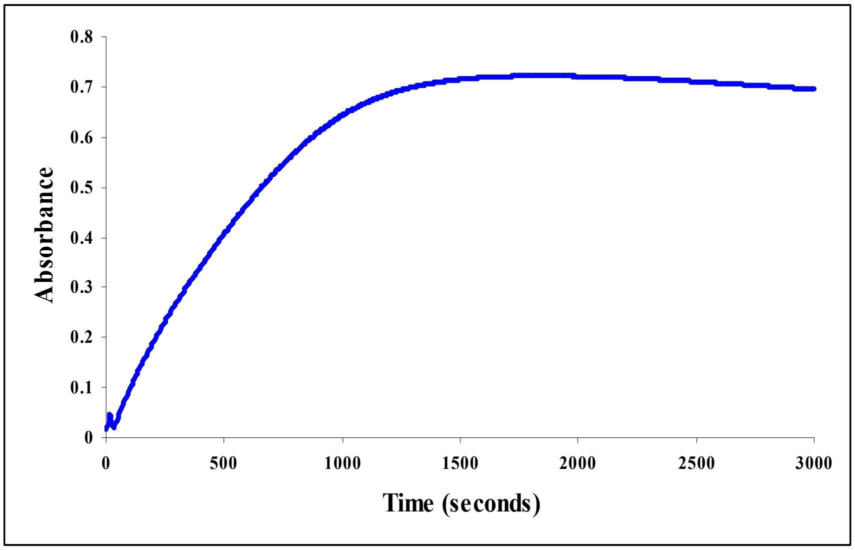


Figure III. 3 Absorbance vs. time plot of 2,4,6-tri-*t*-butylphenoxy radical formation in acetonitrile at 25±1°C. TTBP=20.40mM; catalyst=12.97μM; *m*-CPBA=0.97mM.

The kinetic plot of absorbance at 630 nm *vs*. time is shown in figure III. 3 as a representative case. The absorbance *vs*. time plot (Figure III. 3) shows that the increase in absorbance does not fit with a simple first or second order kinetic trace. Therefore, the data obtained were analyzed by 'Initial-rate' method [29]. All runs were carried out in at least duplicates and the values of $(dA/dt)_0$ given in the tables are the average of the runs. The values of $(dA/dt)_0$, at varying initial concentrations of the reaction components are presented in Table III. 3.

The plot of $(dA/dt)_0$ *vs*. [*m*-CPBA] at constant [Mn(III)(tpfc)] and that of $(dA/dt)_0$ *vs*. [Mn(III)(tpfc)] at fixed [*m*-CPBA] are shown in figure III. 4 & figure III. 5 respectively. It is clear that the data are best fitted by a first order dependence of (dA/dt)0 on the concentration of *m*-CPBA (Figure III. 4) and also on the concentration of catalyst [Mn(III)(tpfc)] (Figure III. 5).

The dependence of (dA/dt)0 on substrate concentration has been ignored due to high excess presence of the substrate and overall we propose the following relation (1).

$$dA/dt \propto [m\text{-CPBA}]\,[\mathrm{Mn(III)(tpfc)}] \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

From the slope of the $(dA/dt)_0$ *vs*. [*m*-CPBA] at constant [Mn(III)(tpfc)], second order rate constant 1.93 x 10^4 dm^3 mol^{-1} is obtained whereas the $(dA/dt)_0$ vs. [Mn(III)(tpfc)] plot at constant [*m*-CPBA] gives a value of 3.08 x 10^4 dm^3 mol^{-1}. Lower value of the second order rate constant in the first case may be rationalized in terms of greater degree of catalyst bleaching at higher concentration of the oxidant.

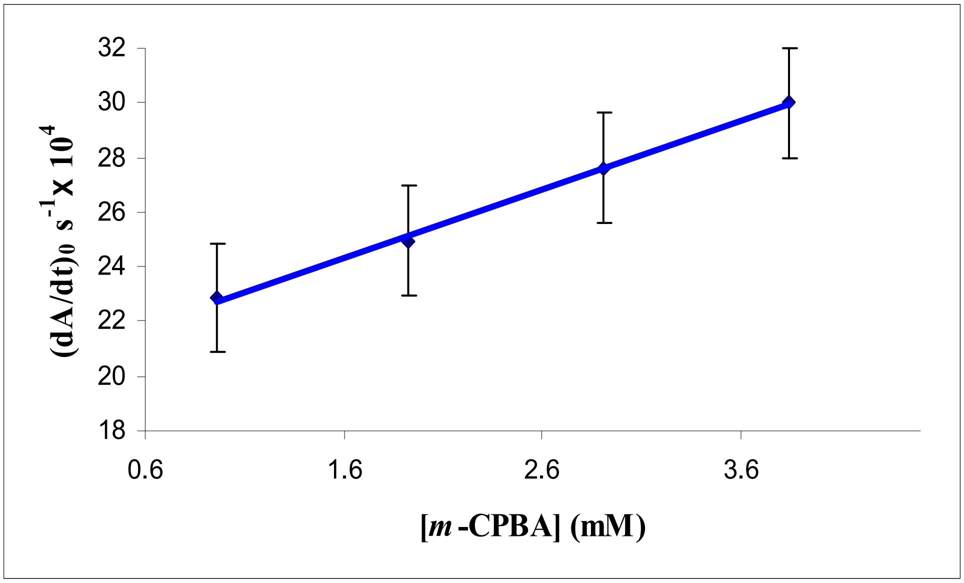


Figure III. 4 Plot of $(dA/dt)_0$ *vs*. [*m*-CPBA].

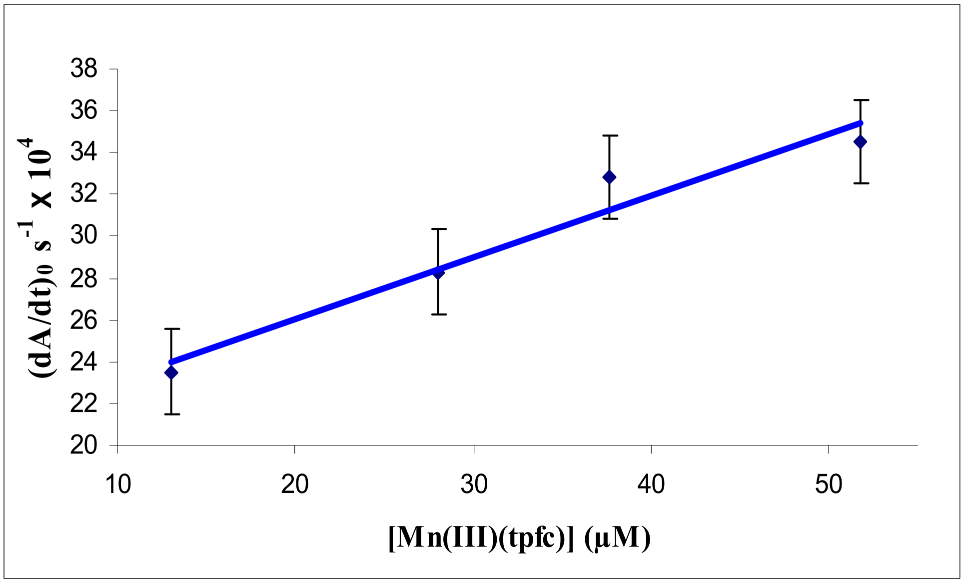
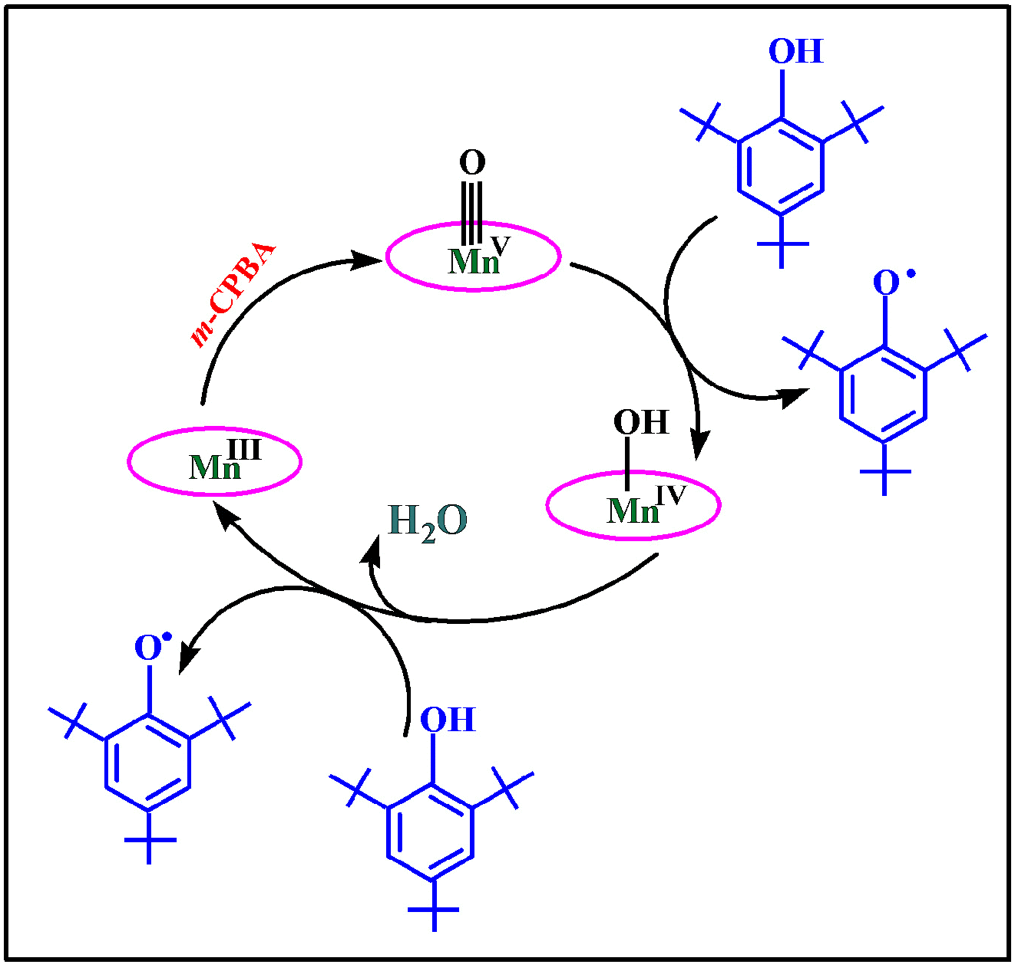


Figure III. 5 Plot of $(dA/dt)_0$ *vs.* [Mn(III)(tpfc)].

The proposed route for the hydrogen atom transfer (HAT) process has been outlined in Scheme III. 2. The (oxo)manganese(V) corrole generated *in situ* by the reaction of manganese(III) corrole and *m*-CPBA oxidizes the phenol (TTBP), *via* a formal hydrogen atom abstraction and itself gets converted to Mn^{IV}-OH species. The involvement of similar species has been proposed in case of the hydrogen atom abstraction of phenols by high valent manganese(V)-oxo corrolazine [28]. The putative Mn^{IV}-OH species is itself highly reactive and abstracts a hydrogen atom from another molecule of TTBP regenerating the manganese(III) corrole (Scheme III. 2).

An alternative mechanism that can account for the phenol oxidation in the present case involves the disproportionation of the Mn^{IV}-OH species producing the manganese(III) corrole catalyst and (oxo)manganese(V) corrole that oxidizes the second phenol substrate. However, considering much greater reactivity of the Mn^{IV}-OH species than (oxo)manganese(V) corrole [28], this mechanistic pathway appears to be less favoured.



Scheme III. 2 Proposed mechanistic route for the manganese(III) corrole catalyzed hydrogen atom abstraction (HAT) from 2,4,6-tri-*tert*-butylphenol (TTBP).

III. 3 Conclusion

It has been demonstrated for the first time that high-valent oxomanganese(V) corroles, generated from manganese(III) corroles, are capable of oxygenating unactivated C-H bonds of alkanes and alkylbenzenes. Adamantane undergoes exclusive hydroxylation and shows a relatively high degree of selectivity for tertiary C-H bonds over secondary C-H bonds (i.e., 3°/2° = 11 – 11.6, normalized on a per-hydrogen basis). Cyclohexane and cyclooctane have been converted to cyclohexanol and cyclooctanol respectively as the major products. Diphenylmethane undergoes selective hydroxylation to produce diphenylmethanol. Toluene and ethylbenzene have also been found to be oxidized by the present catalytic system. The oxomanganese(V) corrole, despite having low redox potential, has been found to be capable of performing hydrogen atom transfer (HAT) reaction with 2,4,6-tri-*tert*-butylphenol (TTBP). Kinetic investigations with TTBP reveal a first order rate dependence on the concentration of the catalyst as well as on that of the oxidant. The results further support the conclusion of Goldberg *et al.* that oxomanganese(V) transients are effective in HAT processes despite having very low redox potentials [28].

III. 4 Experimental Section

III. 4. 1 *Reagents.* Acetonitrile and dichloromethane were distilled under argon from CaH_2 and $CaCl_2$ and stored over molecular sieves (4 Å). 2,4,6-tri-*tert*-butyl phenol (TTBP) was procured from Aldrich, purified by recrystallising several times from 95% ethanol (until the ethanol solution was colourless) and finally melting point (129-132°C) was recorded to check its purity prior to use. *m*-CPBA were purchased from Aldrich and purified accordingly [30]. The exact active oxygen content of *m*-CPBA was determined iodometrically prior to use. Other substrates, all the reaction products and dodecane (internal standard) were purchased from Aldrich and used as received.

III. 4. 2 *Synthesis of the catalysts.* The syntheses of the free base corroles, 5,10,15-tris(2,6-difluorophenyl)corrole (H_3tdfc) and 5,10,15-tris(pentafluorophenyl)corrole (H_3tpfc) were carried out by using 'solvent free' condensation of pyrrole and the respective aldehydes described by Gross *et al.* [31]. The respective manganese(III) corroles were prepared by refluxing the free base corrole with $Mn(OAc)_2.4H_2O$ in DMF [12]. Perbrominated manganese(III) corrole [Mn(III)(Br_8tpfc)] (**3**) was prepared and characterized following the reported procedure [13].

III. 4. 3 *Instruments.* UV-visible spectral measurements were taken with a JASCO V 530 spectrophotometer connected with a thermostat at 25±1° C. The product analysis was done by Perkin Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column) by injecting 1μL aliquot from the reaction vial taken after addition of dodecane as internal standard. The identification and quantification of the products were done from the response factors of standard product samples.

III. 4. 4 *Catalytic experiments.* Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction 25 μM of catalyst and 200 mM (100 mM in case of adamantane) of substrate were dissolved in 2 mL of acetonitrile or 3:2 acetonitrile/dichloromethane in case of adamantane. The oxidation reaction was initiated by adding 2 mM of *m*-CPBA and the contents were magnetically stirred. After periodic time intervals standard solution of dodecane was added to this reaction mixture and an aliquot was injected into a capillary column of a preheated GC. Standard GC conditions for analysis were as shown in Chapter II, table II. 5 for all the substrates (except cyclohexane) and table II. 6 for the reactions of cyclohexane.

III. 4. 5 ***Kinetic measurements.*** In a typical kinetic experiment, TTBP (24 mg, final concentration 44 mM) was taken in a cuvette fitted with silicon rubber septa. The cuvette was degassed by blowing argon over it for 15 min. Degassed acetonitrile (2 mL) was used to dissolve the TTBP in the cuvette. A standard solution of [Mn(III)(tpfc)] in acetonitrile was added so that the final concentration of the catalyst was 13μM. The *m*-CPBA was prepared in degassed acetonitrile (20 mg in 2 mL). An aliquot volume (44 μL) of this stock solution was added to the cell to initiate the reaction. The cell was vigorously shaken and was placed immediately in a thermostatted cell holder in a spectrophotometer and the absorbance data at 630 nm were collected at 5 seconds intervals.

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CHAPTER IV

Manganese(III) corrole catalyzed selective oxidation of alcohols to carbonyl compounds under mild condition*

Abstract

Mild oxidation of alcohols has been achieved with *tert*-butylhydroperoxide (*t*-BuOOH) catalyzed by manganese(III) corrole complexes at room temperature. The effect of substitution at the corrole ligands on the catalytic activity of manganese(III) corroles has also been examined. The catalysts utilized in this study shows high activity in the oxidation of benzylic alcohols to the corresponding carbonyl compounds under ambient conditions.

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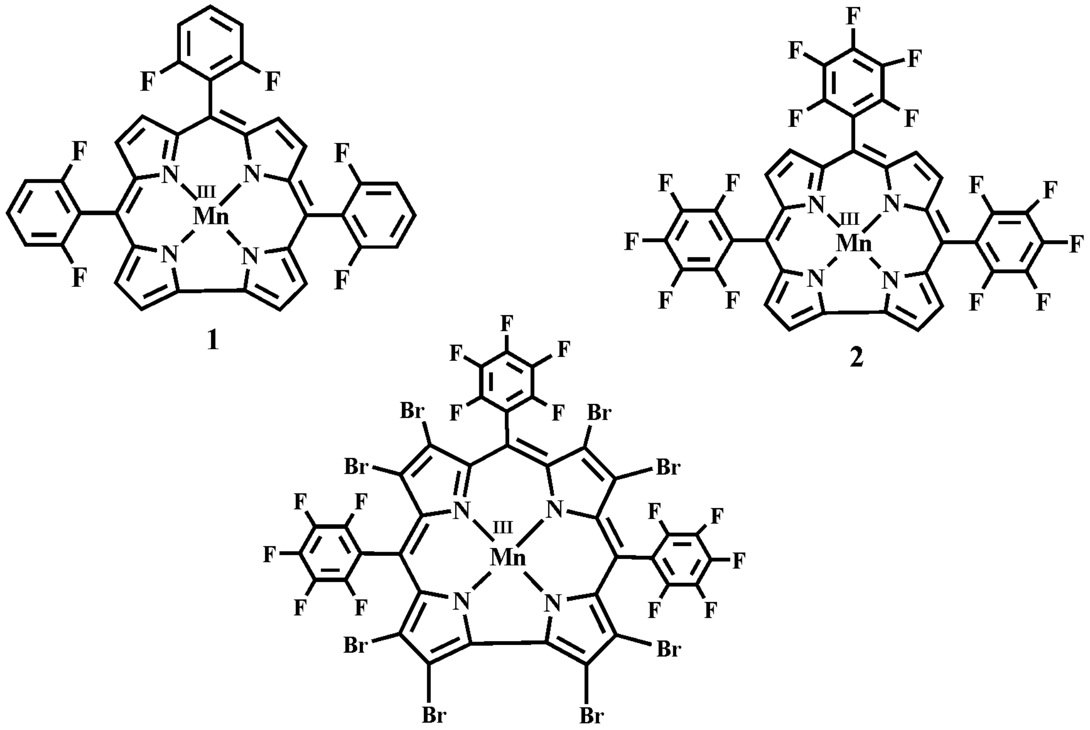
IV. 1 Introduction

Oxidation of alcohols to aldehydes or ketones is an important functional group transformation in organic synthesis [1]. The carbonyl compounds represent an important group of products and intermediates in the fine chemicals [2]. Thus, several methods have been explored to accomplish selective oxidation of alcohols to more valuable carbonyl compounds [3, 4]. The traditional methods for this purpose usually employ stoichiometric quantities of inorganic reagents such as chromate and permanganate, which often generate significant amount of inorganic salt containing effluent along with the target molecules [5]. Removal of traces of these effluents from the reaction mixture is often difficult and demands laborious work-up procedures. Among the various processes developed so far, most notable are the Oppenhauer and Swern oxidation, alcohol oxidations with the Dess-Martin reagent and the reactions utilizing high valent metal compounds such as MnO_2, ammonium perruthenates and pyridinium chlorochromate [6-10]. Although alcohol oxidation by pyridinium chlorochromate (PCC) is routinely performed in organic transformations, the requirement of at least a stoichiometric amount of PCC to complete the oxidation is a disadvantage due to the high toxicity of chromium reagents [11]. The reports of metal complex catalyzed oxidation of alcohols to carbonyl compounds specially with benign oxidants are much less than those involving stoichiometric amount of metallo-oxidants [12]. The aerobic oxidation of alcohols, catalyzed by TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) in combination with other transition metal salts or complexes, has also been utilized. TEMPO/$CuCl_2$ catalyzes the aerobic oxidation of benzyl alcohols to aromatic aldehydes, but this method is ineffective with less-reactive aliphatic and alicyclic alcohols [13], TEMPO/$[RuCl_2(PPh_3)_3]$ affords an efficient catalyst at 100°C and 10 bar pressure [14]; another system consists of TEMPO/$CuBr.Me_2S$, perfluorinated bipyridine and biphasic perfluoroctane/chlorobenzene has been utilized at 90°C [15]; TEMPO/PhenS/$Pd(OAc)_2$ at 100°C and 30 bar is an effective system for the oxidation of a variety of alcohols [16]. All these methods suffer from one or more limitations, such as the use of expensive chemicals, high temperature and pressure, strongly acidic condition and tedious work-up procedure. Sometimes large amount of toxic waste is also generated [17-19]. Thus development of catalytic method for selective oxidation of alcohol using safe, economic, and environmentally benign oxidizing agents remains a critical challenge in organic synthesis [20].

During the last decade the metallo derivatives of corroles have generated intense interest in the field of catalysis [21]. Various metallocorroles have been successfully employed as catalysts in oxygenation of organic compounds [21–23]. So far, no report of metallocorrole catalyzed oxidation of alcohols to carbonyl compounds is available in the literature.

Here, selective and efficient oxidation of alcohols under ambient condition catalyzed by electron deficient manganese(III) corrole complexes (**1-3**) (Scheme IV. 1) with an environmentally benign oxidizing agent *tert*-butyl hydroperoxide has been undertaken. The effect of substitution at the corrole ligands on the catalytic activity of manganese(III) corroles has also been examined in this study.



1

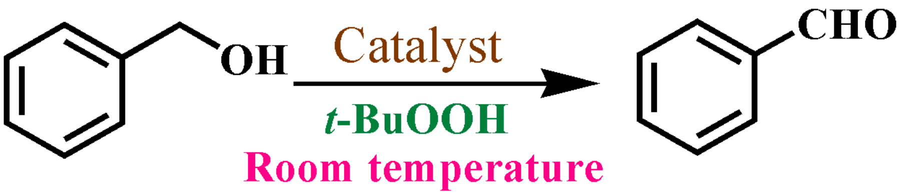
2

3

Scheme IV. 1 Manganese(III) corroles employed in the study.

IV. 2 Results and discussion

Selective oxidation of benzyl alcohol to benzaldehyde is a practically important reaction for the production of chlorine-free benzaldehyde required in the perfumery and pharmaceutical industries. Several studies have been reported on the catalytic vapor-phase oxidation of benzyl alcohol to benzaldehyde [24-31]. However, in the vapor-phase oxidation, carbon oxides are also formed, leading to very significant carbon loss. Liquid-phase oxidation of benzyl alcohol to benzaldehyde is therefore preferable. Thus the oxidation of benzyl alcohol ($PhCH_2OH$) with *tert*-butyl hydroperoxide (*t*-BuOOH) at room temperature (Scheme IV. 2) was chosen as the model reaction. In this study three electron deficient manganese(III) corrole complexes [Mn(III)(tdfc)] (**1**), [Mn(III)(tpfc)] (**2**) and [Mn(III)(Br_8tpfc)] (**3**) were utilized as catalysts (Scheme IV. 1). The influence of different factors (such as catalyst concentration, solvent nature, and substrate/oxidant concentration) on the substrate conversion as well as product selectivity of the oxidation reactions was examined to optimize the reaction conditions.



Scheme IV. 2 Schematic representation of catalytic oxidation of benzyl alcohol with *tert*-butyl hydroperoxide (*t*-BuOOH) at room temperature.

IV. 2. 1 Optimization of reaction medium

Initially the reaction was carried out with catalyst **2** in different solvents and the results are summarized in Table IV. 1. The molar ratio of benzyl alcohol/*t*-BuOOH/ **2** was 100:800:1 and the yields are reported with respect to the initial concentration of benzylalcohol.

Table IV. 1 Influence of the solvent on the oxidation of $PhCH_2OH$ using *t*-BuOOH catalyzed by **2**[a].

Solvent	PhCHO yield(%)[b]
CH_2Cl_2	11
MeOH	16
$CH_3COOC_2H_5$	22
CH_3CN	27
CH_3COCH_3	41
C_6H_6	62

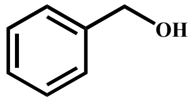
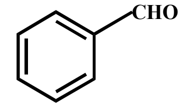
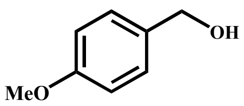
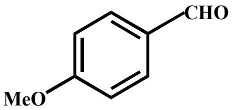
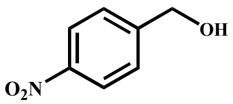
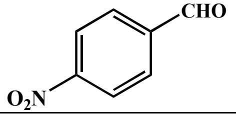
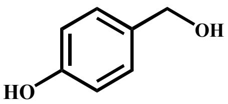
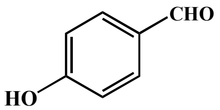
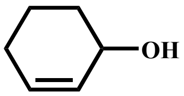
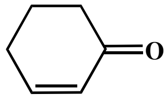
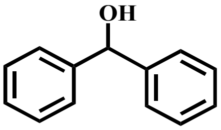
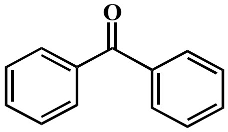
[a] The reactions were run under air at room temperature, and the molar ratio of $PhCH_2OH$/*t*-BuOOH/catalyst was 100 : 800 : 1. [b] yields are reported with respect to the initial concentration of the substrate.

Above results (Table IV. 1) reveal that non-polar medium like benzene is most effective in terms of yield and selectivity (Table IV. 2) of benzaldehyde. Hereafter, this reaction condition is described as ‘Condition A’.

IV. 2. 2 Oxygenation of alcohols under ‘Condition A’

Oxidation of different alcohols under ‘Condition A’ has been performed and the results are summarized in Table IV. 2. Substituted benzyl alcohols have been converted to corresponding aldehydes with very high selectivity. Highest yields are obtained with benzyl alcohol having electron donating substituent at *para* position i.e., p-methoxy benzylalcohol (table IV. 2, entries 4-6). Lowest yield is obtained in case of p-hydroxy benzylalcohol (table IV. 2, entries 10-12) among all the substituted benzyl alcohols studied under this reaction condition. Moreover, secondary alcohols have been selectively converted to corresponding ketones with moderate yields (table IV. 2, entries 13-18).

Table IV. 2 Oxidation of alcohols by *t*-BuOOH catalyzed by manganese(III) corroles under ‘Condition A’.

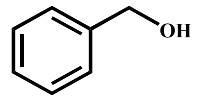
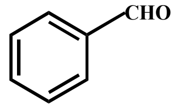
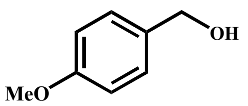
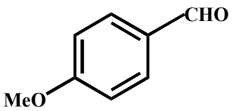
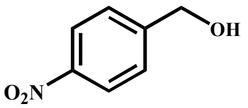
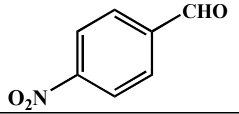
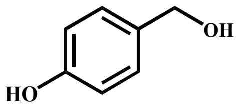
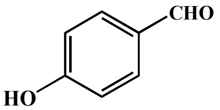
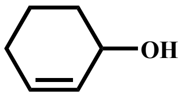
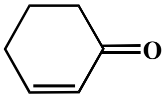
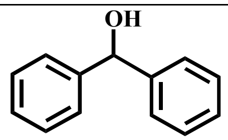
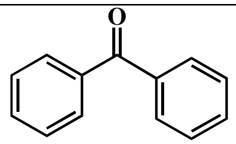
Entry	Substrate	Catalyst	Time (h)	Product	Yields (%)*	Selectivity (%)
1.		**1**	12		54	97
2.		**2**	12		62	98
3.		**3**	12		64	98
4.		**1**	12		58	97
5.		**2**	8		63	98
6.		**3**	8		66	98
7.		**1**	12		50	96
8.		**2**	12		58	96
9.		**3**	8		62	97
10.		**1**	12		36	94
11.		**2**	12		42	96
12.		**3**	12		48	96
13.		**1**	12		48	96
14.		**2**	12		52	97
15.		**3**	12		56	97
16.		**1**	12		38	94
17.		**2**	12		43	96
18.		**3**	12		46	96

*yields are reported with respect to the initial concentration of substrate.

IV. 2. 3 Oxygenation of alcohols under 'Condition B'

In our attempt to improve the yields of manganese(III) corrole catalyzed oxidation of alcohols to corresponding carbonyl compounds, it has been found that using benzyl alcohol 2.5 times more than the terminal oxidant results in almost quantitative conversion of the substrate based on the initial concentration of the oxidant. The molar ratio of substrate, *t*-BuOOH and catalyst has been optimized to 200:80:1 and this condition is termed as 'Condition B'. Oxidation of different alcohols under condition B has been performed and the results are summarized in Table IV. 3.

Table IV. 3 Oxidation of alcohols by t-BuOOH catalyzed by manganese(III) corroles under 'Condition B'.

Entry	Substrate	Catalyst	Time (h)	Product	Yields (%)*	Selectivity (%)
1.		**1**	12		76	96
2.		**2**	12		87	97
3.		**3**	12		90	97
4.		**1**	12		92	97
5.		**2**	8		100	98
6.		**3**	8		100	98
7.		**1**	12		84	97
8.		**2**	12		94	97
9.		**3**	8		99	97
10.		**1**	12		70	95
11.		**2**	12		78	96
12.		**3**	12		82	96
13.		**1**	12		80	96
14.		**2**	12		85	97
15.		**3**	12		91	97
16.		**1**	12		56	92
17.		**2**	12		61	93
18.		**3**	12		68	93

*yields are reported with respect to the initial concentration of the oxidant.

It is observed from Table IV. 3 that substituted benzyl alcohols are transformed into the corresponding benzaldehyde derivatives with very good yields and high selectivities (table IV. 2, entries 1-12). Quantitative conversion of *p*-methxy benzylalcohol has been achieved based on the initial concentration of *t*-BuOOH by either of the catalysts **2** or **3** (table IV. 2, entries 5 & 6). The secondary alcohols produce the corresponding ketones with high yields and selectivities (table IV. 2, entries 13-18). Reactions carried out under both conditions A and B take 8 to 12 hours for completion. No over oxidation by-products, carboxylic acids have been detected in the present study. The presence of an electron donating or an electron withdrawing group in the substrates has very little effect on the yield and reaction time.

IV. 2. 4 Comparison of efficiency of the catalysts

The relative efficacy of three manganese(III) corrole catalysts has also examined. The influence of electronegative substituents on the catalytic activity of the manganese(III) corroles has been examined. It is clear from Table IV. 2 and Table IV. 3 that the order of activity of the different catalysts is **3** > **2** > **1**. The performances of the manganese(III) corrole catalysts towards the oxidation of different alcohols have been shown in Figure IV. 1. The perbrominated catalyst, [Mn(III)(Br_8tpfc)] has been found to be most effective indicating that manganese(III) corroles with greater electron withdrawing substituents are better catalysts in oxidizing alcohols to corresponding carbonyl compounds.

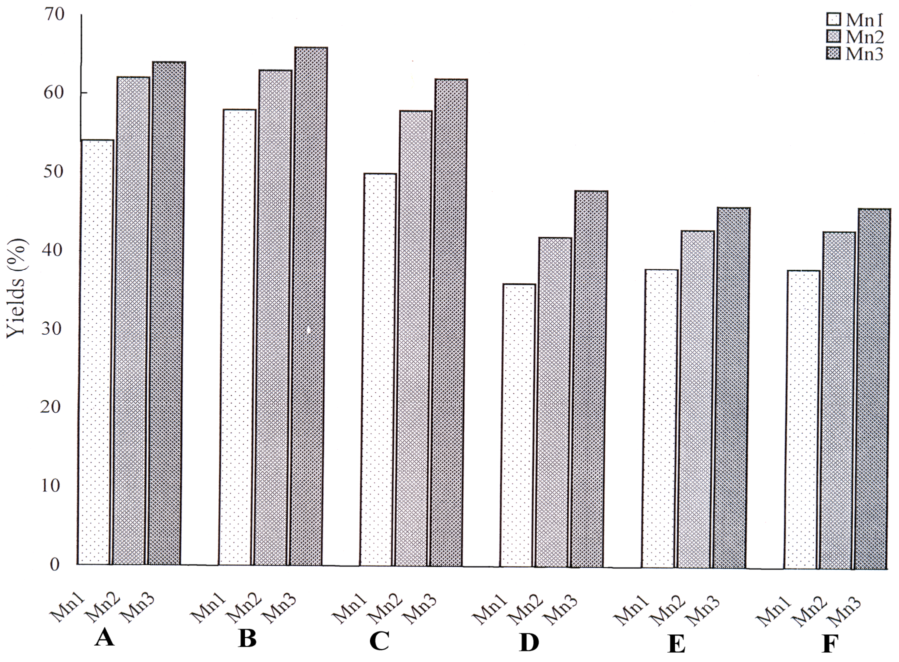


Figure IV. 1 Relative yields of ketones for different alcohols; where A, B, C, D, E & F stand for benzyl alcohol, *p*-methoxy benzyl alcohol, *p*-nitro benzyl alcohol, *p*-hydroxy benzyl alcohol, diphenyl methanol and cyclohexenol respectively.

IV. 3 Conclusion

(i) At room temperature manganese(III) corroles catalyzed selective and efficient oxidation of alcohols with *t*-BuOOH as terminal oxidant has been achieved for the first time.

(ii) The present work demonstrates that manganese(III) corrole together with environmentally benign *t*-BuOOH is an efficient, safe and low-cost system for the oxidation of benzylic alcohols.

(iii) The effect of reaction medium on the catalytic oxidation reactions has also been investigated and a non polar solvent i.e., benzene has been found to be most suitable as the reaction medium.

(iv) Electron-withdrawing groups on the *meso*-phenyl rings of the corrole ligands enhance the catalytic activity of the manganese catalysts.

The mild and room temperature oxidation of various electron rich alcohols seems promising for practical purposes.

IV. 4 Experimental Section

IV. 4. 1 ***Materials.*** All substrates, reaction products, dodecane (internal standard) and *t*-BuOOH (as ~70% solution in water) were purchased from Sigma Aldrich Inc. and were used as received. The exact active oxygen content of the oxidant was determined iodometrically prior to use.

IV. 4. 2 ***Synthesis of the catalysts.*** The syntheses of the free base corroles, 5,10,15-tris(2,6-difluorophenyl)corrole (H_3tdfc) and 5,10,15-tris(pentafluorophenyl)corrole (H_3tpfc) were carried out by using 'solvent free' condensation of pyrrole and the respective aldehydes described by Gross *et al.* [32]. The respective manganese(III) corroles [Mn(III)(tdfc)] (**1**) and [Mn(III)(tpfc)] (**2**) were prepared by refluxing the free base corrole with $Mn(OAc)_2.4H_2O$ in DMF [22.(b)]. Perbrominated manganese(III) corrole [Mn(III)(Br_8tpfc)] (**3**) was prepared and characterized following the reported procedure [22.(c)].

IV. 4. 3 ***Instrument.*** The product analysis was done by Perkin Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column). The identification and quantification of the products were done from the response factors of standard product samples.

IV. 4. 4 ***Catalytic experiments.*** Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction under 'Condition A' 25µM of catalyst and 2.5mM of substrate were dissolved in 2mL of benzene. The oxidation reaction was initiated by adding 20mM of *t*-BuOOH and the contents were magnetically stirred. Under 'Condition B' 25µM of catalyst and 5mM of substrate were dissolved in 2mL of benzene. The oxidation reaction was initiated by adding 2mM of *t*-BuOOH and the contents were magnetically stirred. After periodic time intervals standard solution of dodecane was added to this reaction mixture and an aliquot was injected into a capillary column (elite 1, 15 meter) of a preheated GC. The quantitative identification of the products was done from the response factors of standard product samples as usual (Internal standard: dodecane, 2 mM). Standard GC conditions for analysis were as shown in Chapter II, table II. 5 for all the substrates.

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CHAPTER V

Selective olefin epoxidation catalyzed by manganese(III) corrole in ionic liquid medium at room temperature*

Abstract

Manganese(III) corrole catalyzed selective epoxidation of a series of conjugated and non-conjugated olefins has been carried out in ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate medium at room temperature. Different terminal oxidants such as *t*-BuOOH, PhIO and NaOCl have been used to develop an efficient epoxidation system based on metallocorroles.

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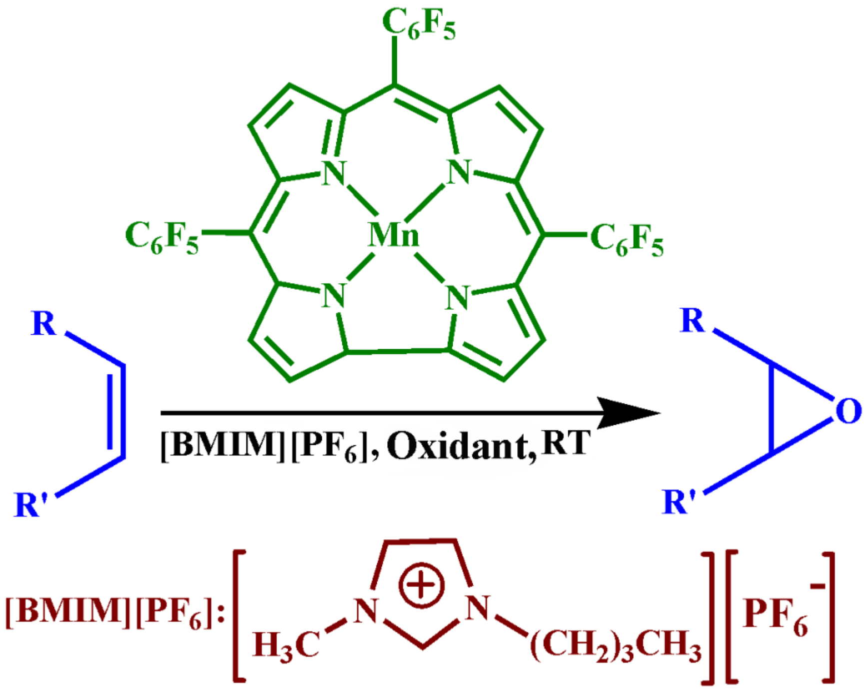
*Communicated.

V. 1 Introduction

Epoxides are highly useful intermediates for the manufacture of a range of important commercial products in fine chemical industries [1]. Selective epoxidation under mild condition is of considerable interest in chemical science [2]. Epoxidation of substituted alkenes is mostly carried out by using stoichiometric amount of peracids [3], which is not a clean method as equivalent amount of acid waste is produced [4]. Therefore, development of new catalytic system with mild oxidant is desirable. In this regard, metalloporphyrins [5.(a)-(e)] and metallosalens [5.(f)-(i)] are emerging as successful catalysts. Following the discovery of facile synthetic methodologies [6], catalytic properties of a number of metallocorroles in epoxidation reactions have been explored [7]. Iron(IV)-corrole complex [Fe(IV)(tpfc)Cl] catalyzed oxidation of styrene was the first example of metallocorrole catalyzed epoxidation reaction [8]. Later, epoxidation of alkenes with various manganese(III) corrole complexes were studied [9]. Although, solvent plays an important role in catalytic oxyfunctionalization of hydrocarbons [10], it is observed that metallocorrole catalyzed epoxidations were mostly carried out in common organic solvents i.e., either benzene or dichloromethane [8,9]. Moreover, in our earlier studies on metallocorrole ctalyzed oxidation of alkenes only allylic oxidation products were produced rather than epoxides [11,12]. In all these reactions, the major disadvantages were significant catalyst bleaching and moderate to low selectivity [8,9,11,12].

In this context, ionic liquid appears to be a promising reaction medium to develop an efficient catalytic system under ambient condition. An ionic liquid (IL) is a liquid consisting of ions only [13]. Ionic liquids usually consist of inorganic anions and nitrogen-containing organic cations, and their chemical and physical properties can be finely tuned for a range of applications by varying the cations or anions [14]. Ambient-temperature, alkylpyridinium (RPy^+) chloroaluminate based ionic liquids were first reported in the early 1950s [15]. However, the report by Wilkes and coworkers [16] of 1,3-dialkylimidazolium-based chloroaluminate ionic liquids, which possess favorable physical and electrochemical properties, provided the impetus for a dramatic increase in activity in this area [17]. Room temperature ionic liquids are recognised as environmentally benign reaction medium due to their unique properties such as non-volatility, negligible vapour pressure, high polarity, non-flammability and thermal stability [18]. Room temperature ionic liquids are also considered as potential environmentally benign solvents for various organic and biochemical transformations [19-21]. They have been employed as solvents for liquid–liquid separations, extractions and for recycling homogeneous catalysts *etc*. [19]. Catalytic reactions in ionic liquids (ILs) have been examined for at least 25 years; for example, the first report of the use of an IL as a catalyst in Friedel-Crafts acylation was reported in 1986 [20]. Research on biocatalysis in ionic liquids is driven by solubility properties, low vapor pressure, and high thermal stability of ionic liquids which lead to lower inhalatory exposure and non-flammability [21]. Stability, activity and enantioselectivity were altered through the use of ionic liquids for enzyme classes such as chloroperoxidase, dehydrogenase, hydrolases, oxidoreductases *etc.* [21, 22]. In recent years the reactions of cytochrome P-450 family of enzymes have also been studied in ionic liquids [23]. The hydrophilicity, hydrophobicity, Lewis acidity, viscocity and density of ionic liquids can be changed by the choice of oganic cation, inorganic anion and the length of the alkyl chain attached to the ionic liquids [24]. Thus the terms "designer" and "task-specific" ILs have been developed [25]. This allows not only control over the reaction but also control over solvent-solute interactions. For example, ILs with tetrefluoroborate or hexafluorophosphate ions are considered as inert solvents in most reactions [26]. Ionic liquids have also been used as novel reaction media for economically and environmentally attractive processes in aqueous mono- and biphasic systems [19, 27]. Moreover, ambient ionic liquids also provide polar, weakly coordinating environment for transition metal catalysts, which can influence stability, activity and selectivity of the catalytic system [28].

The present study specifically aims at developing selective and recyclable epoxidation system based on metallocorroles as catalysts. The epoxidation of a series of conjugated and non-conjugated olefins catalyzed by *meso*-tris(pentafluorophenyl)-corrolatomanganese(III) [Mn(III)(tpfc)] has been undertaken in ionic liquid medium using different terminal oxidants such as *t*-BuOOH, PhIO and NaOCl (Scheme V. 1). The hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6] has been chosen as reaction medium for its chemical inertness as well as stability towards dioxygen and water [26].



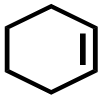
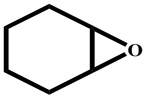
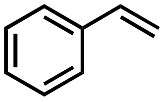
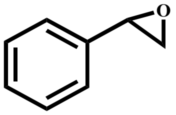
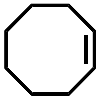
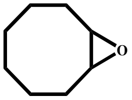
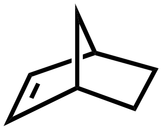
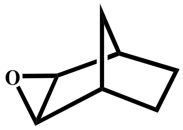
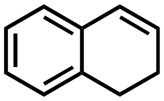
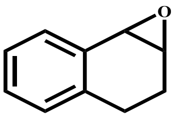
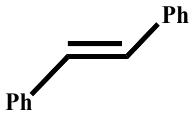
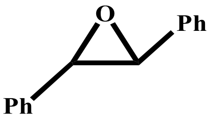
Scheme V. 1 Schematic representaion of manganese(III) corrole [Mn(III)(tpfc)] catalyzed epoxidation of olefins in ionic liquid medium at room temperature.

V. 2 Results and discussion

V. 2. 1 *Epoxidation of olefins with t*-BuOOH

The manganese corrole catalyzed epoxidation of a series of conjugated and non-conjugated alkenes in IL with benign *t*-BuOOH has been carried out at room temperature (Table V. 1). The catalytic epoxidation of cyclohexene and styrene (entry 1 & 2) by [Mn(III)(tpfc)]/*t*-BuOOH/IL produce epoxides with selectivity of 74% and 64% respectively, whereas the reported selectivity in common organic solvent for the corresponding members are 2% and 12% only [11]. It is to be noted that the highest selectivity of manganese corrole catalyzed epoxidation of alkenes in organic solvent (acetonitrile) with *t*-BuOOH reported so far is only 12% [11]. The other alkenes (cyclooctene norbornene, dihydronaphthalene and *trans*-stilbene) exhibit very high product selectivities 98-99% (Table V. 1, entries 3-6) in IL medium with *t*-BuOOH. Moreover, the recovered catalyst in IL has been reused twice although subsequent decrease in product yield has been observed.

Table V. 1 Manganese(III) corrole catalyzed epoxidation of olefins with *t*-BuOOH at room temperature

Entry	Substrate	Time (h.)	Product profile	Selectivity (%)	Yield[a] (%)	TON
1		12		74*	39	31
2		12		64*	22	18
3		8		99	7	6
4		8		98	20	16
5		12		99	11	9
6		8		99	32	26

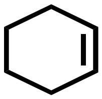
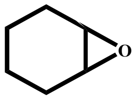
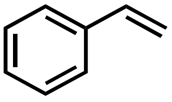
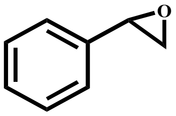
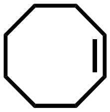
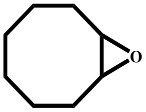
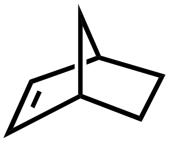
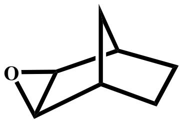
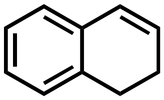
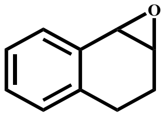
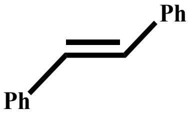
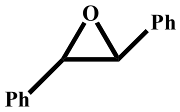
*Rest are the allylic oxidation products. [a]Yields are based on the initial concentration of the oxidant added.

The above results strongly reflect the role of medium (IL) on the product selectivity of metallocorrole catalyzed epoxidation. The improvement of selectivity observed in IL with *t*-BuOOH leads us to investigate the effect of IL as medium on metallocorrole catalyzed epoxidation reactions with other terminal oxidants.

V. 2. 2 *Epoxidation of olefins with PhIO*

Except two cases [11, 12], all other reported metallocorrole catalyzed epoxidation reactions in common organic solvents were studied with PhIO as terminal oxidant [8, 9]. Therefore, catalytic epoxidation by PhIO in IL medium has been undertaken to compare its selectivity with the corresponding results already obtained in organic solvents. The results of catalytic epoxidation in IL with PhIO as terminal oxidant are given in Table V. 2. The change of medium from organic solvents to IL exhibits unprecedented product selectivity in the range of 97-99% (Table V. 2, entries 1& 3-6) except styrene (entry 2), still the selectivity of styrene epoxidation in IL is also higher than those reported in common organic solvents [8, 9].

Table V. 2 Manganese(III) corrole catalyzed epoxidation of olefins with PhIO at room temperature

Entry	Substrate	Time (h.)	Product profile	Selectivity (%)	Yield[a] (%)	TON
1		3		99	46	37
2		3		86*	58	46
3		3		99	55	44
4		3		99	62	50
5		4		99	53	42
6		4		98	64	51

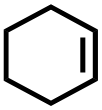
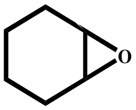
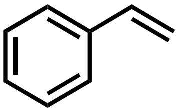
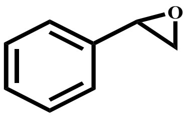
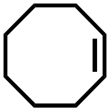
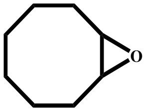
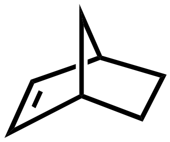
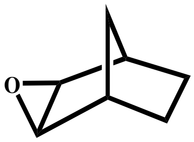
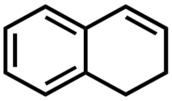
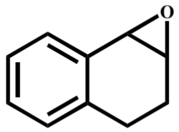
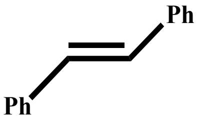
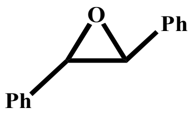
*Rest are the allylic oxidation products. [a]Yields are based on the initial concentration of the oxidant added.

Therefore, ionic liquid emerges as an efficient medium for manganese corrole catalyzed epoxidation of olefins at room temperature. The recovered catalyst from the present system is found ineffective for recycling due to catalyst bleaching. Earlier, the rate of catalyst bleaching in metallocorrole catalyzed oxidation process is known to be a function of oxidant concentration [12]. The problem of catalyst bleaching may be addressed by incorporation of heterogeneity in the IL system which would regulate the concentration of the oxidant in the vicinity of the catalyst.

V. 2. 3 *Epoxidation of olefins with NaOCl*

In this context, a biphasic system seems to be most effective to minimize the extent of catalyst bleaching. An ideal biphasic solvent system should usually comprise a lower phase that can dissolve both the catalyst and substrate and an upper phase that is environment friendly, easily removable from the product mixtures and has negligible ability to extract the lower solvent or the catalyst. Therefore, a biphasic system involving hydrophobic ionic liquid [BMIM]PF_6 and an aqueous layer of dilute sodium hypochlorite (NaOCl) as terminal oxidant has been devised. The biphasic system successfully catalyzes the epoxidation of a number of conjugated and non conjugated olefins with high selectivity (Table V. 3).

Table V. 3 Manganese(III) corrole catalyzed epoxidation of olefins with NaOCl at room temperature

Entry	Substrate	Time (h.)	Product profile	Selectivity (%)	Yield[a] (%)	TON
1		3		98	49	39
2		3		89	61	49
3		3		97	77	62
4		3		96	69	55
5		4		97	47	38
6		4		96	65	52

*Rest are the allylic oxidation products. [a]Yields are based on the initial concentration of the oxidant added.

The present system also affords highest product yield for all the substrates except dihydronaphthalene (Table V. 3, entry 5). On the other hand, the catalytic oxidation of cyclohexene in acetonitrile with NaOCl as terminal oxidant produces a mixture of 1, 2-epoxycyclohexane, 2-cyclohexene 1-one and 2-cyclohexene 1-ol in equimolar ratio, which clearly demonstrates the superiority of ionic liquid as medium for selective epoxidation process.

Moreover, the recovered catalyst from biphasic system exhibits appreciable catalytic activity up to three cycles (Figure V. 1) indicating that the extent of catalyst bleaching is minimized considerably in the ionic liquid medium. There has been a decrease in product yield for the recovered catalyst with successive use but the product selectivity is retained. The decrease in reactivity of the recovered catalyst is possibly due to physical loss and slow degradation during recovery and epoxidation processes.

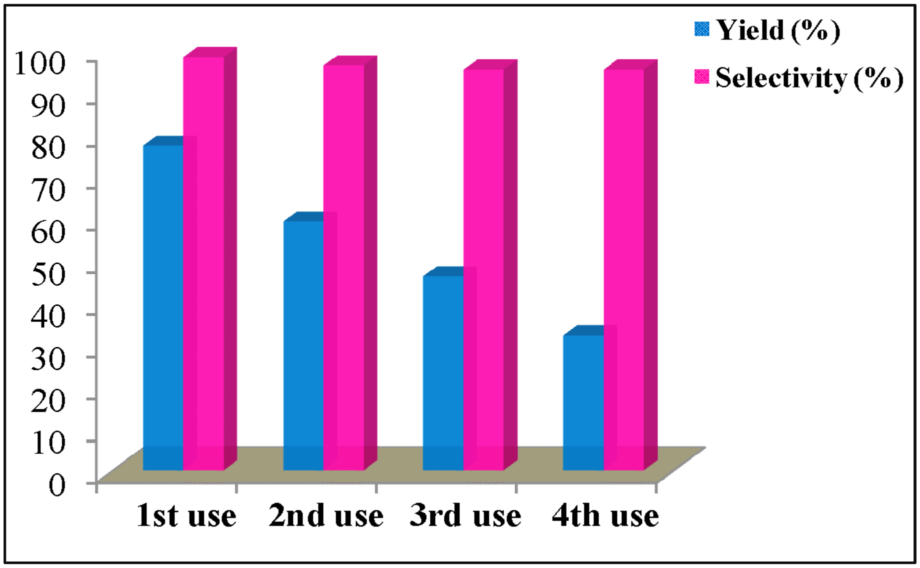


Figure V. 1 Bar diagram showing the activity of recovered manganese corrole catalyst.

V. 2. 4 *UV-visible spectroscopic studies*

The course of the manganese(III) corrole catalyzed oxidation reaction with NaOCl as the terminal oxidant has been monitored by UV-visible spectroscopy (Figure V. 2). The catalyst exhibits its characteristic soret bands at 395 nm and 415 nm in ionic liquid. With the addition of NaOCl, the reaction mixture immediately turned red indicating the generation of (oxo)manganesese(V) species with an intense soret peak at 404 nm (Figure V. 2, red line) [9]. The spectral overlay with time shows that the (oxo)manganesese(V) species slowly converts backs to manganesese(III)corrole as evident by the regeneration of the characteristic soret bands of **1** at 395 nm and 415 nm (Figure V. 2, green line) and indicating the completion of the catalytic cycle. The (oxo)manganesese(V) species has often been invoked as the key intermediate in Mn(III)corrole catalyzed oxygenation reactions [9]. It is reasonable to believe that manganesese(III) corrole is oxidized by hypochorite to manganesese(IV) corrole and subsequently to (oxo)manganesese(V) corrole.

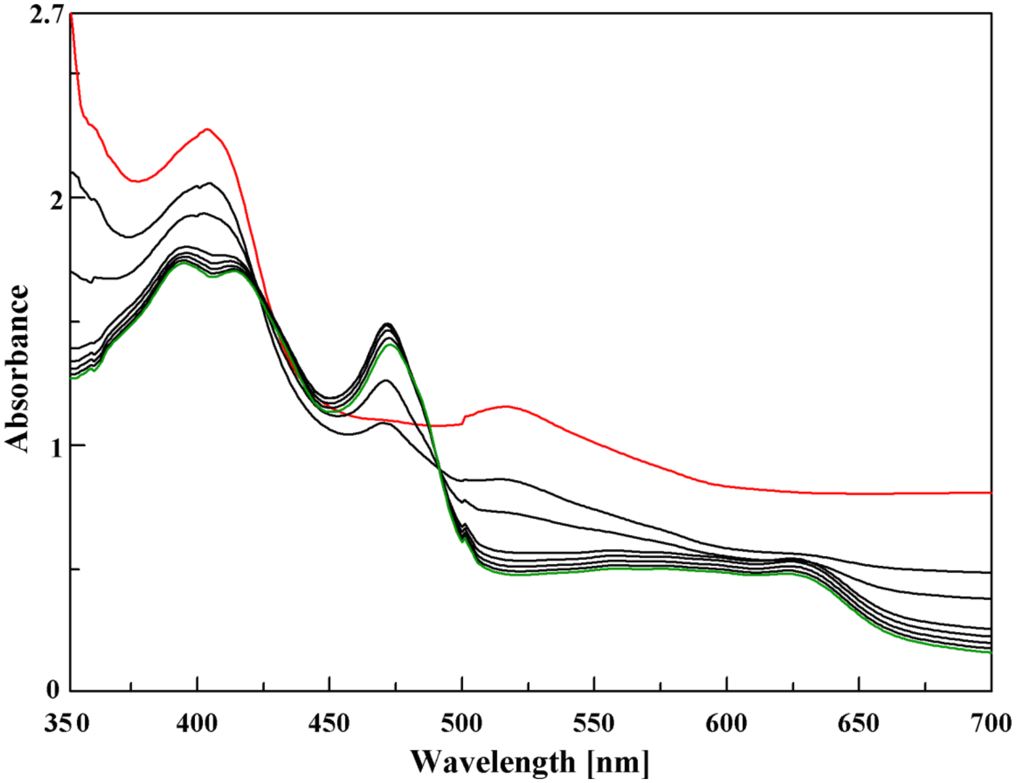


Figure V. 2 UV-visible overlay showing the generation of (oxo)manganesese(V) (red line) species on addition of NaOCl and regeneration of manganesese(III)corrole (green line) with time.

V. 3 Conclusion

For the first time, metallocorrole catalyzed epoxidation of conjugated and non-conjugated olefins has been undertaken in ionic liquid ([BMIM]PF_6) medium at room temperature using different terminal oxidants such as *t*-BuOOH, PhIO and aqueous NaOCl. Remarkable improvement of product selectivity in ionic liquid medium for each oxidant has been observed over the corresponding one in molecular solvents. The highest product yield has been achieved by a biphasic system involving ionic liquid with aqueous NaOCl as the terminal oxidant. The biphasic system provides easy recovery and recycling of the catalyst without any modification of structure. It may be proposed that the key intermediate is a catalytically active high valent metaloxo species which is stabilized by a unique ionic environment provided by the IL medium.

V. 4 Experimental section

V. 4. 1 ***Materials***. Acetonitrile was distilled under argon from CaH_2 prior to use. Cyclohexene and styrene were purified according to standard procedure [31]. The other olefins, all the reaction products and iodopentafluorobenzene (internal standard) were procured from Sigma-Aldrich Inc. and were used as received. The active oxygen content of the oxidant *t*-BuOOH (as 70% solution in water, purchased from Aldrich) was determined iodometrically prior to use. The NaOCl solution in water (4% w/v) was purchased from Merck. PhIO was prepared acoording to the standard literature method [30] and its active oxygen content was determined iodometrically prior to use.

V. 4. 2 *Synthses*

Synthesis of [BMIM]PF_6. The ionic liquid [BMIM]PF_6 was prepared following reported method [29]. 1-methylimidazole and chlorobutane were taken in equimolar amounts in a round-bottomed flask fitted with a reflux condenser and heated at 70°C with constant stirring for 48–72 h. The resulting viscous liquid was allowed to cool to room temperature and then was washed three times with 200 mL portions of ethyl acetate. After the last washing, the remaining ethyl acetate was removed by heating to 70°C under vacuum. To prepare the ionic liquid, hexafluorophosphoric acid (1.3 mol) was added (slowly to prevent the temperature from rising significantly) to a mixture of 1-butyl-3-methylimidazolium chloride (1 mol) in 500 mL of water. After stirring for 12 h, the upper acidic aqueous layer was decanted and the lower ionic liquid portion was washed with water (10 X 500 mL) until the washings were no longer acidic. The ionic liquid was then heated under vacuum at 70 °C to remove any excess water.

Synthesis of the catalyst. The free base corrole (H_3tpfc) and its manganese corrole complex [Mn(III)(tpfc)] was synthesized and characterized following the procedure reported by Gross *et al.* [6, 9. (a)].

V. 4. 3 ***Instruments.*** The identification and quantification of the products were done by Perkin Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column) from the response factors of standard product samples. The UV–vis spectral data were collected with a Agilent 8453 spectrophotometer connected with a thermostat at 25±1°C.

V. 4. 4 *Catalytic experiments.* Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction 1:3 mixture of alkene [200mM] in acetonitrile and 25μM of catalyst in ionic liquid were magnetically stirred at room temperature followed by the addition of the oxidant [2mM of *t*-BuOOH or PhIO]. The epoxidation of alkenes with NaOCl catalyzed by the mangenese corrole catalyst was carried out under biphasic conditions. A 1:3 mixture of alkene [200mM] in acetonitrile and catalyst [25μM] in ionic liquid was cooled to 0°C, followed by addition of precooled, buffered NaOCl solution (2 mmol, pH = 11.3) as an oxidant at 0°C. The two phase solution was then stirred at room temperature. In all the cases the unchanged reactants and products were removed from the reaction mixture *via* extraction with *n*-hexane after the completion of the reaction leaving behind the catalyst immobilized in ionic liquid. The reactions were monitored by GC with iodopentafluorobenzene (3.74μM) as internal standard for the product quantification. The yields are reported on the basis of initial concentration of the oxidant added. Standard GC conditions for analysis were as shown in Chapter II, table II. 5 for all the substrates except trans-stilbene and that for trans-stilbene is shown in table V. 4 below.

Table V. 4 Standard GC conditions for the analysis of reactions of *trans*-stilbene

Injector (split) temperature	250°C		
Flame Ionization Detector temperature	250°C		
Inlet flow-total (N_2)	42 mL/min		
Sampling rate	12.50000 pts/S		
Column temperature	**Rate (°C/min)**	**T (°C)**	**Hold time (min)**
		80°	**10**
	5°/min	**160°**	**10**
Column pressure	**Rate (psi/min)**	**Pressure (psi)**	**Hold time (min)**
		7	36

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CHAPTER VI

Functionalized silica supported manganese(III) corrole: Synthesis, characterization and catalytic activity

Abstract

Functionalized silica supported manganese corrole complex has been synthesized and characterized using UV-visible, AAS, IR, EPR, powder XRD, SEM and EDAX techniques. Catalytic activity of the heterogenized manganese corrole complex has been studied for the oxidation of alkenes and alkanes with mild *tert*-butylhydroperoxide (*t*-BuOOH) and environmentally benign hydrogen peroxide (H_2O_2) at room temperature. High catalytic turnovers (upto 3000) have been achieved by the heterogeneous manganese corrole catalyst with *t*-BuOOH as the terminal oxidant. Supported manganese corrole catalyzed oxidation of alkenes has also been achieved with a good catalytic turnover numbers (upto 800) with mild H_2O_2 as terminal oxidant.

VI. 1 Introduction

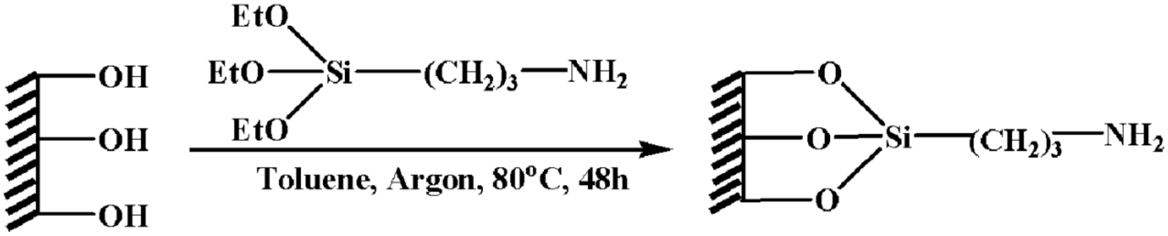
Success of the biphasic system regarding the improvement in yield and selectivity of metallocorrole catalyzed oxygenation reaction (described in Chapter V) suggests that catalytic degradation may be substantially reduced by heterogeneous catalysis. Heterogeneous catalysis refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. Most widely used solid heterogeneous catalysts are generally insoluble inorganic solids or homogeneous catalysts immobilized on an insoluble support such as silica, clay, synthetic or natural polymers *etc.* [1]. Generally, immobilization may be realized by four distinct ways: (i) by entrapment, (ii) by adsorption or ion-pair formation, (iii) by encapsulation and (iv) by formation of a covalent bond with the ligand [2]. Immobilization to a solid support *via* a covalent bond formation has become the most often employed method of heterogenization of a homogeneous catalyst [3]. Obviously the support and/or catalyst must be functionalized in such a way as to be able to effect immobilization and the support materials need to be thermally, chemically, and mechanically stable during the reaction process. Moreover, the structure of the support needs to be such that the active sites are well dispersed on its surface and that these sites are easily accessible [4]. The structure and surface characteristics of the support like rigidity and polarity often play important role by controlling the orientation of substrate and reagents during the reactions and thus potentially tune the reaction selectivity [5]. The major advantages of heterogeneous catalysis are easy separation and reuse of catalyst, which make the process simple and convenient without any additional work-up. Moreover, immobilization of catalyst arrests the loss of activity caused by catalyst aggregation or intermolecular self-oxidation [6]. In the current era of “clean technology”, the horizon of heterogeneous catalysis is fast expanding to replace the more traditional stoichiometric processes and hence help to minimize the problem of industrial waste treatment and disposal.

In this context, it would be interesting to synthesize hitherto unknown solid supported metallocorrole complexes and to study their catalytic role in oxyfunctionalization of hydrocarbons. Here, manganese(III) complex of *meso*-tris(pentafluorophenyl)corrole [Mn(III)(tpfc)] has been immobilized on amino functionalized silica support *via* the formation of covalent bond. Characterization of the solid supported complex has been done using UV-visible, IR, AAS, EPR, powder XRD, SEM, and EDAX techniques. Catalytic activity of the solid supported manganese corrole has been studied for the oxidation of alkenes and alkanes with mild *tert*-butylhydroperoxide (*t*-BuOOH) and environmentally benign hydrogen peroxide (H_2O_2) at room temperature.

VI. 2 Results and discussion

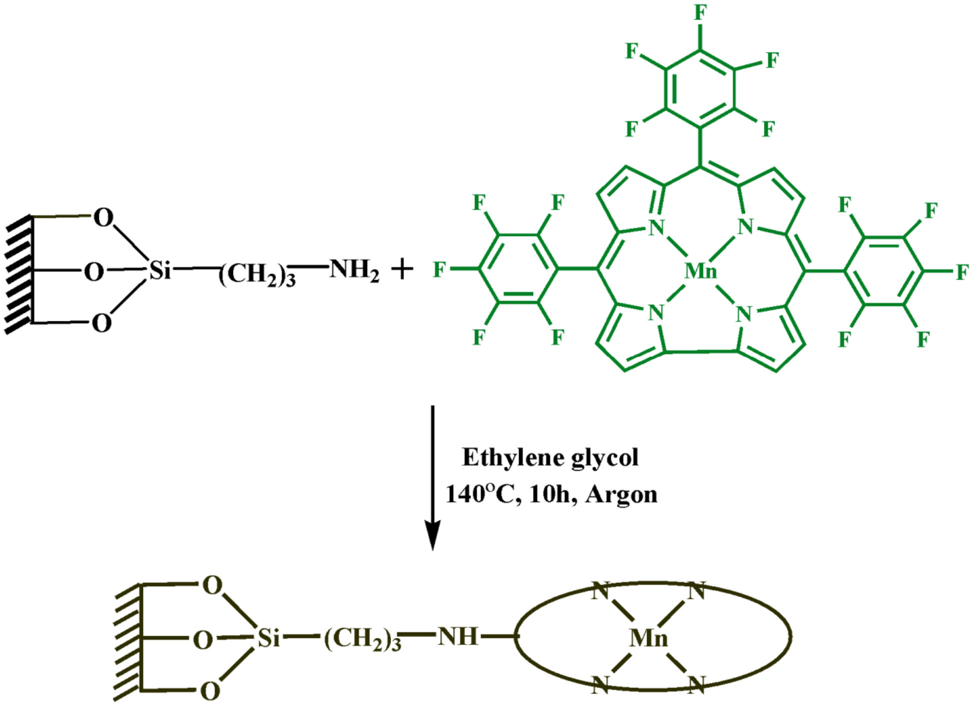
VI. 2. 1 *Synthesis of 3-aminopropyltriethoxysilane functionalized silica supported manganese corrole complex [Mn(tpfc)APTES]*

3-aminopropyltriethoxysilane functionalized silica [APTES] was synthesized using a reported procedure (Scheme VI. 1) [7]. 3-Aminopropyltriethoxysilane was added to a suspension of silica gel in anhydrous toluene. The resulting mixture was stirred under argon for 48 h at 90^{o}C. After cooling, the 3-aminopropyl-functionalized silica was filtered and washed with toluene and ethyl ether and dried at 80 °C in an oven for 24 h.



Scheme VI. 1 Schematic representation for the synthesis of 3-aminopropyltriethoxysilane functionalized silica [APTES] from silica gel.

Supported catalyst [Mn(tpfc)APTES] was prepared by reacting the [Mn(III)(tpfc)] with the aminofunctionalized silica support in a mixture of ethylene glycol and 1,4 dioxane at 150°C, with magnetic stirring under argon atmosphere. The reaction was continued for 10 h (Scheme VI. 2). The resulting solid was filtered and extracted for 24 h with CH_2Cl_2 and for other 24 h with CH_3OH using a Soxhlet procedure. The solid was then dried at 80°C for 24 h. The amount of the unreacted [Mn(III)(tpfc)], collected from reaction mixture and washings from the Soxhlet procedure, was determined by UV-Visible spectroscopy. Catalyst loading on the support was determined by atomic absorption spectroscopy (AAS).



Scheme VI. 2 Immobilization of the manganese corrole complex [Mn(III)(tpfc)] onto amino functionalized silica support.

VI. 2. 2 *Characterization of the supported catalyst*

The electronic spectra of the supported catalyst indicate the presence of manganese corrole on the functionalized silica support qualitatively.

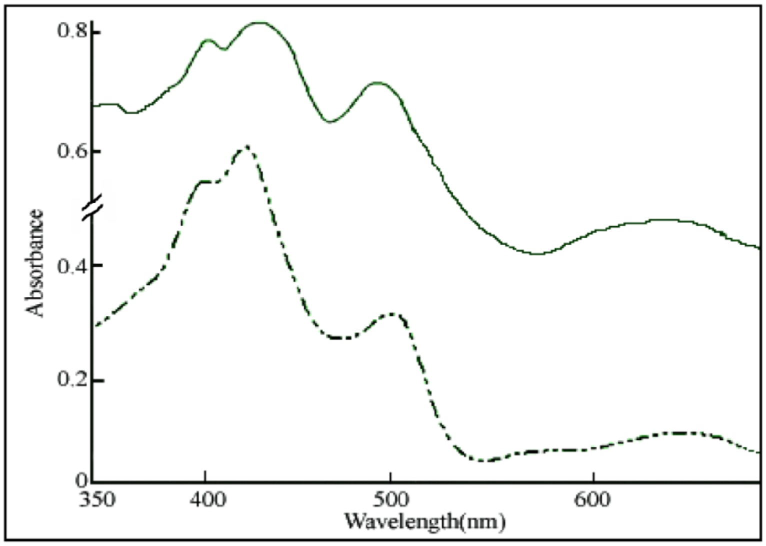


Figure VI. 1 UV-visible spectra of [Mn(III)(tpfc)] (dotted line) in CH_2Cl_2 and suspension of [Mn(tpfc)APTES] (solid line) in CH_2Cl_2 at room temperature.

The UV-visible spectra of [Mn(tpfc)APTES] has been obtained from a suspension of the solid in CH_2Cl_2 [8] at room temperature. The solid supported catalyst displays the typical split Soret band of the parent homogeneous manganese(III) corrole [Mn(III)(tpfc)] at 400nm and 416nm (Figure VI. 1), indicating that the corrole ring structure remained unchanged upon immobilization.

Catalyst loading on the support is 1.25µmol/g which is calculated by estimating the total manganese content of [Mn(tpfc)APTES] using atomic absorption spectroscopy (AAS).

In FT-IR studies of [APTES], N-H stretching vibration at 3438 cm^{-1}(m), characteristic of primary amines and a weak signal at 2935 cm^{-1}, characteristic of alkane are observed. In case of [Mn(tpfc)APTES] a weak signal at 3447 cm^{-1} due to secondary amines is observed which confirms the immobilization of the manganese corrole complex [Mn(III)(tpfc)] onto the solid support [APTES] *via* the formation of covalent bond (Scheme VI. 2). In both the cases the Si–O stretching vibrations have been observed at 794cm^{-1}, 695cm^{-1} and 458 cm^{-1} [9].

The EPR spectra of supported [Mn(tpfc)APTES] displayed signal around g = 2 which is typical of Mn(II) (S = 5/2). Mn(III) ions are EPR silent. Partial reduction of the Mn(III) ions can result from coordination of the free amino groups on the support to the central cation of corrole [7].

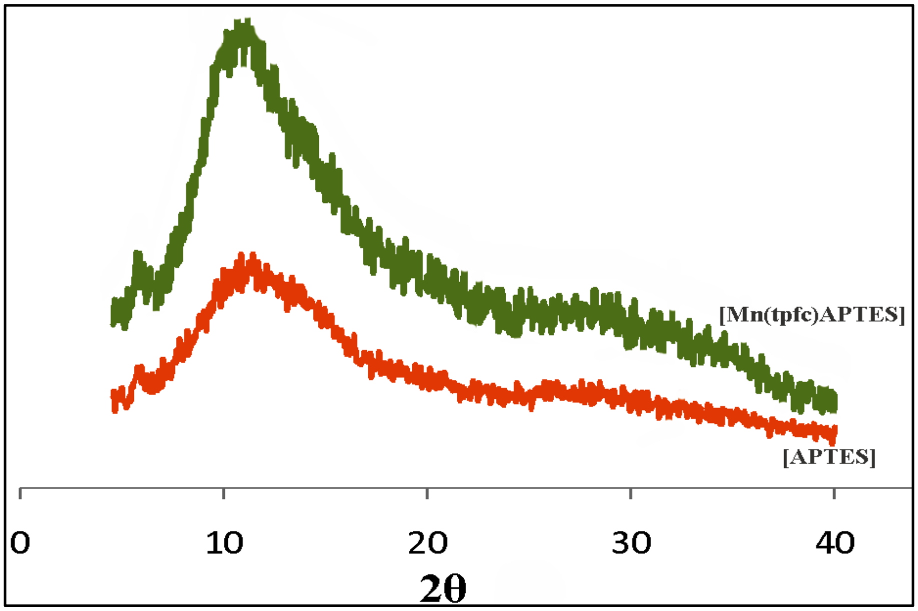
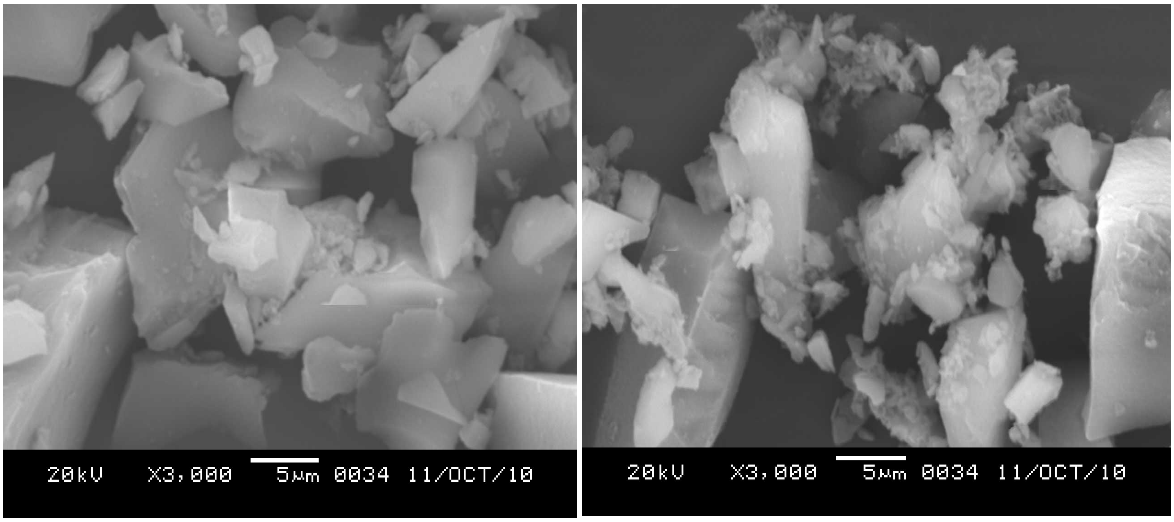


Figure VI. 2 Small angle powder XRD pattern for [Mn(tpfc)APTES] (green) and [APTES] (red).

X-ray powder diffraction is largely employed in the study of intercalated and encapsulated systems to study the changes in the interlamellar distances [7, 10]. Therefore, this technique was utilized in the present case to investigate how the metallocorroles could have immobilized on the aminofunctionalized silica, *via* their anchoring to the surface, in the interlamellar space, or in the material defects. According to the X-ray diffractograms (Figure VI. 2), there was no change in the 2θ values of the solid upon metallocorrole immobilization, which indicates that the manganese corrole complex is not intercalated between the layers rather is located in the defects of the clay and/or on its surface.

The SEM images of aminofunctionalized silica [APTES] and the supported manganese corrole complex [Mn(tpfc)APTES] are given in Figure VI. 3 (a) and (b) respectively. These images show that the morphology and the shape of silica particles remain intact upon attachment of metallocorroles [11].



(a) **(b)**

Figure VI. 3 SEM images of (a) [APTES] and (b) [Mn(tpfc)APTES].

The EDAX analysis of [APTES] and [Mn(tpfc)APTES] confirms the immobilization of [Mn(III)(tpfc)] onto aminofuntionalized silica support. The data presented in Chart VI. 1 clearly shows the wt % and at % contributions of F and Mn from [Mn(III)(tpfc)] in [Mn(tpfc)APTES] which is absent in case of [APTES].

Chart VI. 1 EDAX data for [APTES] and [Mn(tpfc)APTES]

[APTES]

Elem	Wt %	At %	K-Ratio	Z	A	F
N K	4.53	6.02	0.0109	1.0199	0.2353	1.0024
O K	61.46	71.46	0.1989	1.0124	0.3196	1.0004
Si K	34.01	22.53	0.2410	0.9743	0.7273	1.0000
Total	100.00	100.00				

[Mn(tpfc)APTES]

Elem	Wt %	At %	K-Ratio	Z	A	F
N K	4.58	6.09	0.0110	1.0204	0.2356	1.0024
O K	60.72	70.71	0.1965	1.0130	0.3194	1.0004
F K	0.72	0.71	0.0009	0.9528	0.1253	1.0008
Si K	33.82	22.44	0.2389	0.9748	0.7246	1.0000
Mn K	0.16	0.05	0.0014	0.8512	1.0040	1.0000
Total	100.00	100.00				

VI. 2. 3 *Catalytic oxidation reactions by [Mn(tpfc)APTES]*

Catalytic activity of [Mn(tpfc)APTES] was examined for cyclohexene oxidation with *t*-BuOOH at room temperature. The reactions were carried out under oxidant limiting

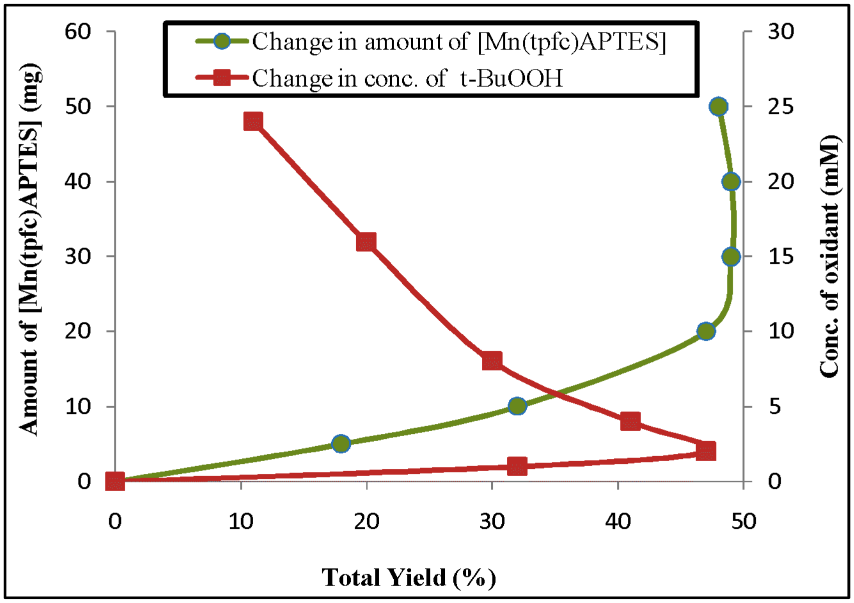


Figure VI. 4 Optimization of reaction conditions with respect to amount of the solid catalyst [Mn(tpfc)APTES] and concentration of the oxidant *t*-BuOOH in case of cyclohexene oxidation at room temperature.

condition. Oxidation of cyclohexene was carried out with varying amount of the catalyst and with different concentration of the oxidant to optimize the reaction conditions (Figure VI. 4). It was found that 20 mg of the solid catalyst along with 2 mM of *t*-BuOOH can effectively catalyze cyclohexene oxidation at room temperature.

VI. 2. 4 *Oxidation of hydrocarbons by [Mn(tpfc)APTES] with mild t*-BuOOH

At room temperature [Mn(tpfc)APTES] emerges as an effective catalyst in oxidizing alkenes, alkylbenzenes and alkanes with mild *tert*-butylhydroperoxide (*t*-BuOOH) under aerobic condition (Table VI. 1). All the heterogeneous reactions were carried out in neat acetonitrile (except for adamantane because of its lower solubility in acetonitrile) as it is found to be the best solvent for the present catalytic system. Oxidation of cyclohexene under the present catalytic system produce a 2:1 mixture of allylic oxidation products (*i. e.*, cyclohexene-1-one and cyclohexene 1-ol) along with a small amount of epoxide (Table VI. 1, entry 1). Very high catalytic turnover numbers of 2938 has been achieved which is an excellent improvement in comparison with the previously studied homogeneous systems comprised of [Mn(III)(tpfc)] along with *t*-BuOOH (TON=82) [12]. Styrene was oxidized to styrene oxide and phenylacetaldehyde with a TON=2000 which is also much higher than that (TON = 80) of the corresponding homogeneous system (Table VI. 1, entry 2) [12]. Highest product conversion and TON (= 3125) has been achieved for the oxidation of ethylbenzene (Table VI. 1, entry 3). In case of toluene considerably low product conversion as well as TON (= 813) has been encountered (Table VI. 1, entry 4). Oxidation of alkanes has also been investigated under the present catalytic system. Diphenylmethane is selectively converted to benzophenone (Table VI. 1, entry 5). Adamantane has been converted to 1-adamantanol as the major product along with minor quantities of 2-adamantanol and 2-adamantanone with a high TON of 1500 (Table VI. 1, entry 6). Cyclohexane has been oxidized to cyclohexanone and cyclohexanol with TON = 500 which is also significant (Table VI. 1, entry 7). The remarkable improvement of TON with respect to any existing homogeneous metallocorrole catalyzed hydrocarbon oxidation system [13], clearly indicates the effect of solid support. In all these reactions no catalyst leaching was observed and the solid catalyst [Mn(tpfc)APTES] could easily be removed from the reaction mixture after the completion of reaction.

Table VI. 1 Oxidation of hydrocarbons catalyzed by [Mn(tpfc)APTES] with *t*-BuOOH

Entry	Substrate	Total Yield (%) [a]	Product Profile (%)			TON
1	Cyclohexene	47	Cyclohexene oxide	Cyclohexenol	Cyclohexenone	2938
			3	14	30	
2	Styrene	32	Phenylacetaldehyde	Styrene oxide		2000
			12	20		
3	Ethylbenzene	50	1-Phenylethanol	Acetophenone	Phenylacetaldehyde	3125
			35	13	2	
4	Toluene	13	Benzylalcohol	Benzaldehyde		813
			4	9		
5	Diphenyl methane	14	Benzophenone			875
			14			
6	Adamantane	22	1-Adamantanol	2-Adamantanol	2-Adamantanone	1500
			18	2	2	
7	Cyclohexane	8	Cyclohexanol	Cyclohexanone		500
			3	5		

[a] yields are reported with respect to the initial concentration of the oxidant after 12 hours.

VI. 2. 5 *Oxidation of hydrocarbons by [Mn(tpfc)APTES] with mild* H_2O_2

Attempts have been made to explore the [Mn(tpfc)APTES] catalyzed alkene oxidation with mild and benign H_2O_2. For the first time, the oxidation of alkenes has been achieved with mild and environmentally benign H_2O_2 at room temperature by a catalytic system based on metallocorroles. Manganese corroles are known to catalyze the decomposition of H_2O_2 [14] which may be the reason for the poor reactivity of homogeneous [Mn(III)(tpfc)] towards alkenes with H_2O_2 as the terminal oxidant. [Mn(tpfc)APTES] has been found to catalyze the oxidation of alkenes (such as cyclohexene and styrene) with H_2O_2 though the product conversion is lower (Table VI. 2, entry 1 & 2) than that obtained with *t*-BuOOH as terminal oxidant. However, the heterogeneous manganese corrole system exhibits high catalytic turnover numbers (485 and 848 in case of cyclohexene and styrene respectively) as far as H_2O_2 assisted hydrocarbon oxidation in metallocorrole chemistry is concerned.

Table VI. 2 Oxidation of hydrocarbons by [Mn(tpfc)APTES] with mild H_2O_2

Entry	Substrate	Total Yield (%) [a]	Product profile (%)			TON
1	Cyclohexene	8	Cyclohexene oxide	Cyclohexenol	Cyclohexenone	485
			2	2	4	
2	Styrene	14	Phenylacetaldehyde	Styrene oxide		848
			12	2		

[a] yields are reported with respect to the initial concentration of the oxidant after 12 hours.

VI. 3 Conclusion

Functionalized silica supported manganese corrole complex has been synthesized and characterization was done using UV-visible, IR, AAS, SEM, EDXRF and powder XRD techniques. Catalytic activity of the heterogenized manganese corrole complex was studied for the oxidation of alkenes and alkanes with mild *tert*-butylhydroperoxide (*t*-BuOOH) and environmentally benign hydrogen peroxide (H_2O_2) at room temperature. High catalytic turnover numbers (upto 3000) has been achieved by the heterogeneous manganese corrole catalyst with *t*-BuOOH as the terminal oxidant. This study reports the highest turnover numbers ever achieved by metallocorrole catalyzed oxygenation of hydrocarbon. For the first time, manganese corrole catalyzed oxidation of alkenes has been achieved with a good catalytic turnover numbers (upto 800) with mild H_2O_2. The aforesaid results are encouraging and demands more rigorous investigation in the area of solid supported metallocorrole catalyzed oxidation of hydrocarbons.

VI. 4 Experimental Section

VI. 4. 1 ***Materials.*** Acetonitrile and dichloromethane were distilled under argon from CaH_2 and $CaCl_2$ and stored over molecular sieves (4 Å). Cyclohexene was distilled under argon to remove the inhibitor and passed through a silica gel column prior to reaction. All reagents were commercially available from Sigma Aldrich, Fluka or Merck and were of analytical grade purity unless otherwise stated. The oxidants were stored at 5°C. Exact active oxygen content of *t*-BuOOH (as ~70% solution in water) and H_2O_2 (as ~30% solution in water) were determined iodometrically prior to use.

VI. 4. 2 *Synthesis of 3-aminopropyltriethoxysilane functionalized silica supported manganese corrole complex [Mn(tpfc)APTES]*

Synthesis of manganese(III) corrole complex [Mn(III)(tpfc)]. The metallocorrole was prepared from the free base H_3tpfc following reported methods [15]. The elemental analytical and spectral data are in agreement with those reported in the literature.

Preparation of 3-aminopropyltriethoxysilane functionalized silica support [APTES]. 3-aminopropyltriethoxysilane functionalized silica [APTES] was synthesized following reported procedure [7]. 3-Aminopropyltriethoxysilane (14 mL 0.076 mmol) was added to a suspension of silica gel (200-400 mesh size) in anhydrous toluene (100 mL), previously treated with P_2O_5 for 24 h and distilled. The resulting mixture was stirred under argon for 48 h at 90°C. After cooling, the 3-aminopropyl-functionalized silica was filtered and washed with toluene (20 mL) and ethyl ether (20 mL), and dried in an oven for 24 h, at 80 °C.

FT-IR (in KBr): 3438 cm^{-1}(m), 2935 cm^{-1}, 794 cm^{-1}, 695cm^{-1}, 458cm^{-1}; EDAX: O 61.46 wt%, Si 34.01 wt%, N 4.53 wt%.

Immobilization of the manganese corrole complex [Mn(III)(tpfc)] onto amino functionalized silica support. Supported catalyst [Mn(tpfc)APTES] was prepared by reacting the [Mn(III)(tpfc)] 8 mg (9.4 μmol) with the aminofunctionalized silica support (0.5 g) in a mixture of ethylene glycol (60 mL) and 1,4 dioxane (10 mL) at 150°C, under argon atmosphere and magnetically stirred for 10 h. The resulting solid was filtered and extracted for 24 h with CH_2Cl_2 and for other 24 h with CH_3OH using a Soxhlet procedure. The solid was then dried at 80 °C for 24 h.

UV/Vis (CH_2Cl_2): λ_{max} [nm] = 400, 416, 490, 622; FT-IR (in KBr): 3447 cm^{-1}, 794 cm^{-1}, 695cm^{-1}, 458cm^{-1}; EDAX: O 60.72 wt%, Si 33.82 wt%, N 4.58 wt%, F 0.72 wt%, Mn 0.16 wt%.

VI. 4. 3 *Instruments*. UV-visible spectral measurements were taken with a JASCO V 530 spectrophotometer connected with a thermostat at 25±1°C. AAS was done using Perkin Elmer 3110 model Atomic Absorption spectrometer. FTIR spectra were recorded using a Shimadzu model FT-IR-8300 spectrometer in KBr pellets. EPR analysis were done in JEOL JES-FA200 with 9.155 GHz microwave frequency, 100 KHz modulation frequency, 5 mW power and 4 min of sweep time. X-Ray powder diffraction patterns were recorded with a computer-controlled Philips 1710 diffractometer (40 kV, 20 mA) equipped with a graphite monochromator. Diffractograms were collected from $2\theta = 0$ to 40. SEM analysis was done in JEOL JSM-6360 SEM using JEOL JFC-1100 "fine coat" ion sputter. EDAX analysis was performed using a Quanta FEI 200-3D scanning electron microscope (SEM) equipped with Phoenix energy dispersive analysis of X-ray (EDX). The product analysis was done by Perkin Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column). Standard GC conditions for analysis were as shown in Chapter II, Tables II. 5 and II. 6.

VI. 4. 4 *Catalytic experiments*. In a typical oxidation reaction, the supported catalyst [Mn(tpfc)APTES] (*ca*. 20 mg, corresponding to 0.25 μmol) was stirred with the substrate (200 mM) in acetonitrile (2 mL) or 3:2 acetonitrile/dichloromethane in case of adamantane and the reaction was then initiated by addition of *t*-BuOOH or H_2O_2 (2 mM) and the contents were magnetically stirred. After periodic time intervals 1μL of dodecane (internal standard) was added to this reaction mixture and an aliquot was injected into a capillary column of a preheated GC. All reactions were carried out at room temperature, under aerobic conditons. Recycling of the supported catalyst was carried out with the solid recovered by filtration after the oxidation reaction. The recovered solid catalyst was washed with methanol and dried prior to reuse.

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APPENDIX I

LIST OF PUBLICATION(S)

A. 1. Thesis related publications

1. "Electron deficient manganese(III)corrole catalyzed oxidation of alkanes and alkylbenzenes at room temperature" *Catalysis Communications,* **2011**, 12, 1193-1197. DOI: 10.1016/j.catcom.2011.04.026

2. "Manganese (III)corrole catalyzed selective oxidation of alcohols to carbonyl compounds by tert-butyl hydroperoxide under mild condition" *Catalysis Communications,* **2011**, 12, 446-449. DOI: 10.1016/j.catcom.2010.10.009

3. "Mild oxidation of hydrocarbons by tert-butyl hydroperoxide catalyzed by electron deficient manganese (III)corrole" *Journal of Molecular Catalysis A: Chemical*, **2010**, 332(1-2),1-6. DOI: 10.1016/j.molcata.2010.09.001

4. "Selective olefin epoxidation catalyzed by metallocorroles in ionic liquid medium at room temperature" communicated.

A. 2. Publications in other areas

1. "Catalytic Hydrocarbon Oxidation by Iron Complex of 5, 10, 15-tris(difluorophenyl)corrole *via* Activation of Hydroperoxides" *Catalysis Communications*, **2013**, 32, 23-27. DOI:10.1016/j.catcom.2012.11.026

2. "Fluorescence signaling systems for sensing Hg(II) ion derived from A2B-corroles" *Dalton Transactions***, 2012**, 41, 3826-3831. DOI: 10.1039/2DT12158A

3. "Mild oxidation of hydrocarbons catalyzed by iron corrole with tert-butylhydroperoxide" *Catalysis Communications*, **2010**, 11, 1008–1011. DOI:10.1016/j.catcom.2010.05.006

APPENDIX II

LIST OF WORK PRESENTED

1. Presented the work entitled '*Ligand Non-Innocent Behavior of Cu(II)-Dipyrromethene Complex in Redox-Reactions and Its Use as an Oxidation Catalyst: C-H activation at RoomTemperature*' in '15th CRSI (Chemical Research Society of India) National Symposium in Chemistry' held in Varanasi, India, 2013.

2. Presented the work entitled '*Recent developments in manganese corrole catalyzed oxygenation reactions*' in the '14th Biennial Symposium on Modern Trends in Inorganic Chemistry' held in School of Chemistry, University of Hyderabad, Hyderabad, India, 2011.

3. Presented the work entitled '*Homogeneous and supported metallocorrole catalysts in oxidation of hydrocarbons*' in the '3rd Asian Conference on Coordination Chemistry' Symposium held in Indian Habitat Centre, New Delhi, 2011.

4. Presented the work entitled '*Selective fluorescent chemical sensor for mercury ion detection in solution by a new family of corroles*' in the '13th CRSI (Chemical Research Society of India) National Symposium in Chemistry' held in Bhubneswar, India, 2011.

5. Presented the work entitled '*Fe(III) cyclam intercalated montmorillonite catalysts for selective oxidation of hydrocarbons with hydrogen peroxide at room temperature*' in the 'Frontier in Inorganic Chemistry (FIC) International Symposium' held in Indian Association for the Cultivation of Science (IACS), Kolkata, India, 2010.

6. Presented the work entitled '*Selective hydroxylation of alkanes catalyzed by iron(IV) corrole'* in the '13th Biennial Symposium on Modern Trends in Inorganic Chemistry' held in the Indian Institute of Science, Bangalore, India, 2009.

ORAL PRESENTATION

1. "National Seminar on Frontiers in Chemistry 2011 & Celebration of The International Year of Chemistry 2011" (March 14-16, 2011) held in Department of Chemistry, University of North Bengal, Darjeeling.

APPENDIX II

LIST OF WORKSHOP ATTENDED

1. Workshop on "Mass and NMR technique" on 28-29th January, 2013 by SAIF, CSIR-CDRI, Lucknow.

2. Workshop on "Intellectual property and Innovation Management in Knowledge Era" on 12th February, 2013 by NRDC, New Delhi and NBU.

LIST OF SEMINAR AND SYMPOSIUM ATTENDED

1. National Seminar on "*Frontiers in Chemistry -2013*" held in Department of Chemistry, NBU, Darjeeling, India, 2013.

2. "*Modern Trends in Chemistry and Chemistry Education*" at Department of Chemistry, University of North Bengal, Darjeeling, 2012.

3. "*Recent Trends in Chemistry*" (Science academies' Lecture Workshop) at Department of Chemistry, University of North Bengal, Darjeeling, 2011.

4. "*Trends in Surface Science and related Areas (TSSRA) V"* at Department of Chemistry, University of North Bengal, Darjeeling, on December 06, 2008.

5. "*Sixth CRSI (Kolkata Chapter) Symposium*" organized by Department of Chemistry, University of North Bengal, Darjeeling, on August 02, 2008.

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CHAPTER I

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