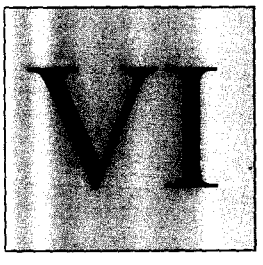
CHAPTER 

Iron-Corrole Catalyzed Hydroxylation Reactions of Alkanes: Search for Reactive Intermediates

CHAPTER VI

Iron-Corrole Catalyzed Hydroxylation Reactions of Alkanes: Search for Reactive Intermediates

Abstract

The complex *meso*-tris(pentafluorophnyl)corrolatoiron(IV)chloride [(F_{15}TPC)FeCl] emerged as efficient catalyst in hydroxylating alkanes at room temperature. Cyclohexane and adamantane have been oxidized to the corresponding alcohols using *m*-chloroperbenzoic acid (*m*-CPBA) as terminal oxidant. Cyclohexane has been converted to cyclohexanol in 45-50% yields. The reactions proceeded with 100% selectivity. Adamantane has also been hydroxylated up to 75% overall yield under identical reaction condition. Significantly high regioselectivity in adamantane oxidation has been observed. The reactive intermediates formed have been quantitatively trapped by 2,4,6-tri-*t*-butylphenol (TTBP). Kinetic analysis of the (F_{15}TPC)FeCl-catalysed oxidation of TTBP has found consistent with rapid reaction of organic substrate with an intermediate formed in the first and rate determining step. At room temperature catalytic oxidation of alkanes & alkenes by iron complex of 5,10,15-*tris*(pentafluorophenyl)corrole using 70% *t*-BuOOH as oxidant is also reported.

VI.1 Introduction

Corroles[1] are tetrapyrrolic macrocycles who owe their name to cobalt-chelating corrin of vitamin B_{12} with whom they share an identical skeleton. Corroles are extensively conjugated and more closely related to the iron-chelating porphyrins of heme enzymes and proteins. More precisely, corroles are based on the [18]annulene structural framework with just one *meso* carbon short from the porphyrin skeleton, as shown in Figure VI.1. The structure of their aliphatic counterpart, namely corrin, the tetrapyrrolic ligand of the B_{12} cofactor is presented in Figure VI.2.[2]

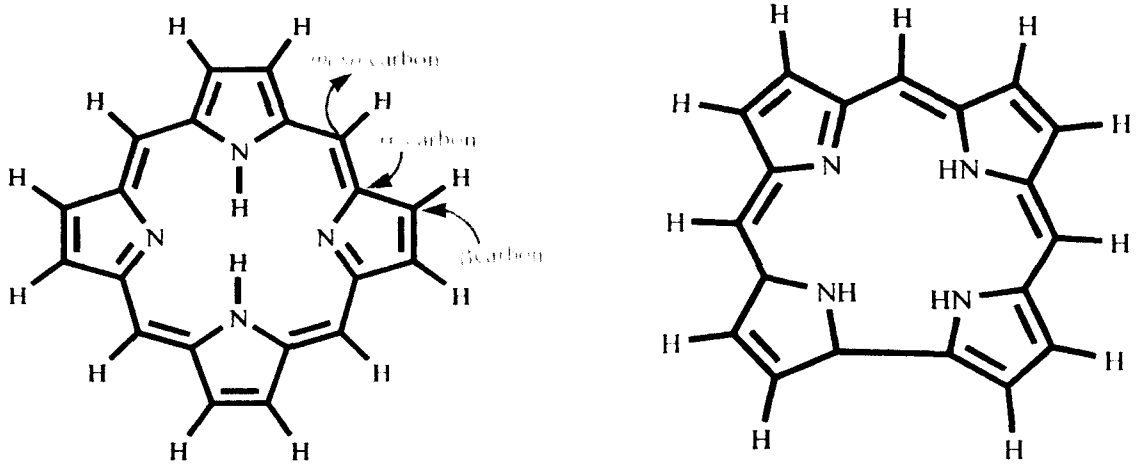


Figure VI.1 The structure of free base porphyrin (left) and free base corrole (right). The positions of C_{α}, C_{β} and C_{meso} are noted with arrows.

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. But compared with the chemistry of porphyrins, the chemistry of corroles remained comparately underdeveloped for a long period, largely due to lack of simple methods for their synthesis.[3] Corroles were first synthesized as early as in 1964 by Johnson and Kay[4] 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[6], 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.*[7] and Paolesse *et al.*[8] of one-pot corrole syntheses involving pyrrole-aldehyde condensations.

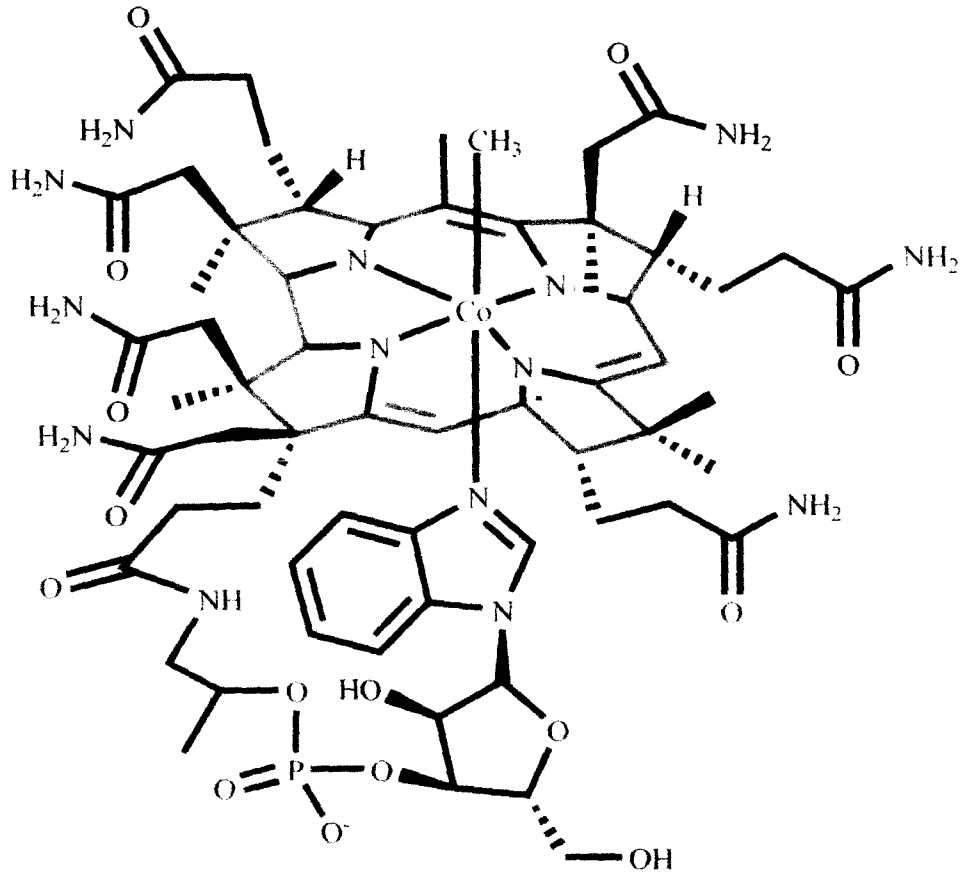
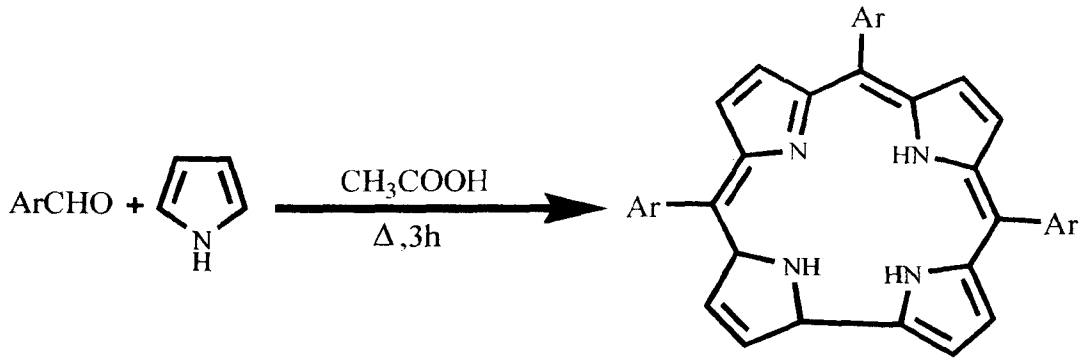
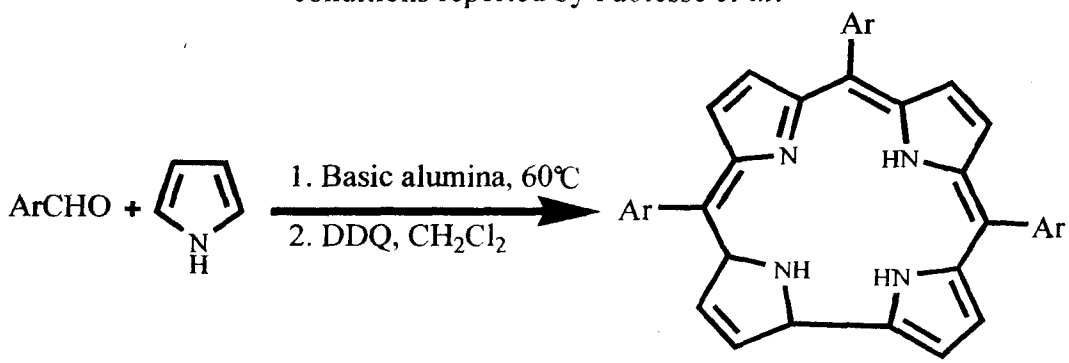


Figure VI.2 The vitamin B12 cofactor methylcobalamin. The purple colour denotes the corrin macrocycle.

The research group of Paolesse prepared a wide range of free base triaryl corroles under Alder-Longo-type protic acid catalyzed reactions using glacial acetic acid as the solvent and with a aldehyde/pyrrole molar ratio of 1:3 (Scheme VI.1).[8] In contrast, the research group of Gross reported an essentially solvent free, catalyst free condensation of pyrrole with aldehydes in aerobic condition in the presence of basic alumina as a solid support, followed by oxidation with DDQ in dichloromethane to yield the corresponding corroles (Scheme VI.2).[7] Development into the directed synthesis of the corrole macrocycles continues to be one of the most active area of research, with recent contributions from the groups of Gryko[9], Bruckner[10], Collman[11] and Geier.[12]



Scheme VI.1 One-pot corrole syntheses under Alder-Longo type protic acid catalyzed conditions reported by Paolesse *et al.*[8]



Scheme VI.2 The one-pot "solvent-free" corrole synthesis reported by Gross *et al.*[7]

Investigations into the syntheses of free-base and metal corroles have flourished in recent years and a tremendous amount of interest has been generated on the chemistry of this contracted macrocycles.[1] Due to their unique capacity to stabilize high metal oxidation states, various metallocorroles have been synthesized and examined successfully as catalysts for epoxidation[13], hydroxylation[13a,14], cyclopropanation[13a,15] and aziridination.[16] Apart from catalysis, various corroles and their metal complexes are shown to be excellent candidates for environmental and medicinal sensors.[17] Metallocorroles appear to be useful in medicinal applications, such as tumor detection and destruction.[18] Corroles are now being utilized in light-driven processes, including applications in both medical and alternative energy areas.[19] Among these reactions activation of aliphatic C-H bonds is, perhaps, the most important goal in basic and industrial research. Functionalization of such bonds by mononuclear heme and non-heme iron enzymes often invoke C-H bond cleavage by an iron(IV) intermediate that is generated by dioxygen activation.[20,21] Several enzymes accomplish such transformations in the biological world.[22-25] In particular, cytochrome P-450 model enzymes catalyze the most energetically difficult hydroxylation of unactivated C-H bonds of alkanes.[22] Thus biomimetic hydroxylation reactions with cytochrome P-450 model compounds, most

notably the metalloporphyrins have been extensively studied over the last three decades.[23-25] However, the corresponding iron corroles have not been fully exploited in this context. The first ever application of corroles showed that the iron(IV) complexes are good catalysts in the oxygenation of hydrocarbons by iodosylbenzene and also for the cyclopropanation of the olefins by carbenoids.[13a] Under the experimental conditions employed ethylbenzene has been found to be hydroxylated with an overall yield of 10.8%. No other report on iron(IV)-corrole catalyzed hydroxylation of alkane has appeared so far. Recently Newcomb *et al.* reported evidence for an (oxo)iron(V) corrole as an extremely reactive intermediate.[26] Their investigations under non-catalytic reaction conditions revealed that the rates of oxygen atom transfer from (oxo)metal corroles to alkanes are much higher than that of analogous (oxo)metal porphyrins.[27] But application of these findings towards catalytic hydroxylation reactions of unactivated alkanes has not been explored.

Herein we report the hydroxylation of cyclohexane and adamantane at room temperature catalyzed by iron-corrole, $[(F_{15}TPC)Fe^{IV}Cl]$. *m*-CPBA and *tert*-butylhydroperoxide have been used as the terminal oxidants. Kinetic analysis of the $(F_{15}TPC)FeCl$-catalysed oxidation has been done. Catalytic oxygenation of alkenes by *t*-BuOOH-$(F_{15}TPC)FeCl$ system at room temperature has also been described.

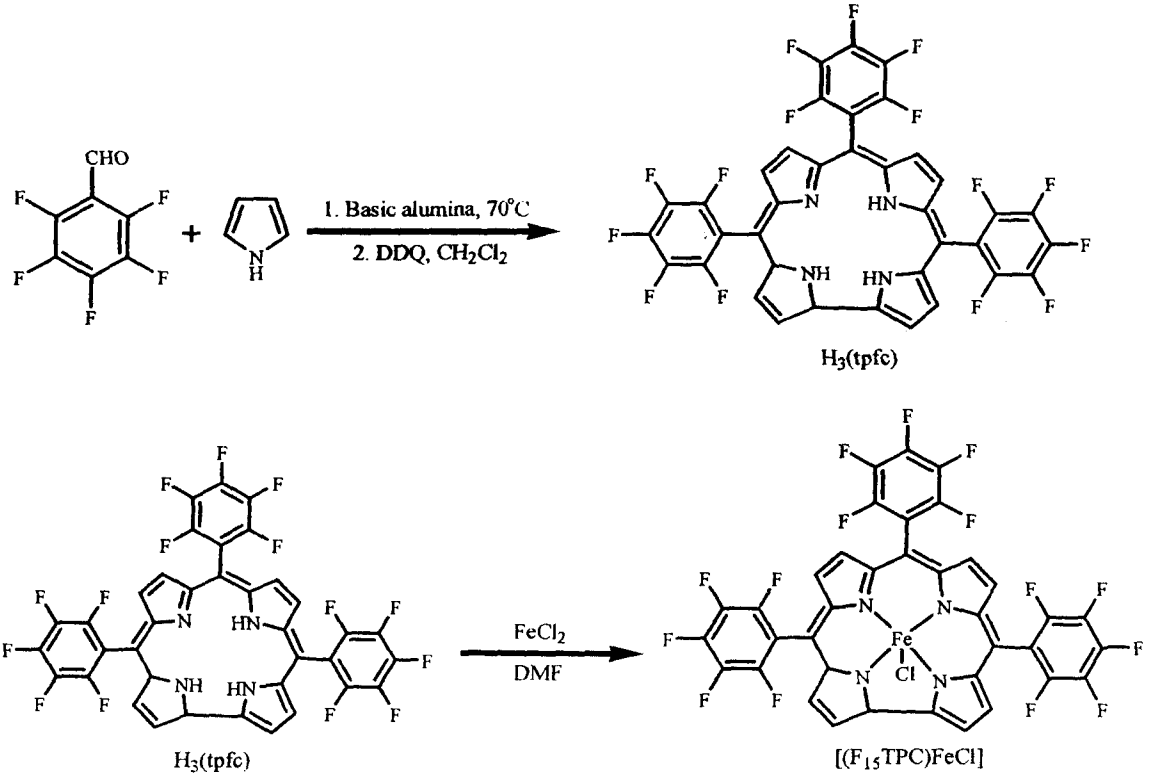
VI.2 Results and discussions

VI.2.1 *Synthesis of the catalyst*

Compound 5,10,15-tris(pentafluorophenyl)corrole, abbreviated as H_3(tpfc) (where tpfc stands for the trianionic macrocycle) with its electron withdrawing substituents appears to be the most stable free-base corrole reported to date.[12] A number of metal complexes of H_3(tpfc) were synthesized and many of them have been shown to have catalytic activities[1b-1d]. This prompted us to choose *meso*-tris(pentafluorophenyl)corrolatoiron(IV) chloride $[(F_{15}TPC)FeCl]$ as the catalyst.

The free base corrole was synthesized following the "solvent free" synthesis reported by Gross *et al.*[7] (Scheme VI.3) since this synthetic procedure has been found to provide 5,10,15-tris(pentafluorophenyl)corrole in 8-11% yield, conversion being better than any other existing methods of corrole preparation. Thus pentafluorobenzaldehyde and purified pyrrole in 1:1 molar ratio were dissolved in 10 cm^3 methylene chloride and the mixture was added to a 100 cm^3 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 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 hexanes/dichloromethane (4:1, v/v) as the eluant. The free base corrole was reacted with $FeCl_2$ in refluxing DMF and the catalyst *meso*-tris(pentafluorophnyl)-corrolatoiron(IV) chloride [(F_{15}TPC)FeCl] was obtained.[15a]



Scheme VI.3 Preparation of the catalyst *meso*-tris(pentafluorophnyl)corrolatoiron(IV) chloride [(F_{15}TPC)FeCl].[15a]

VI.2.2 *Hydroxylation of Alkanes by [(tpfc)FeCl]- mCPBA*

Catalytic activity of the *meso*-tris(pentafluorophnyl)corrolatoiron(IV)chloride, [(F_{15}TPC)FeCl] was examined in the oxygenation reaction of alkanes as summarized in Table VI.1. Adamantane and cyclohexane have been chosen as the substrate. Adamantane is an important mechanistic probe in deciding the radical character in catalytic reactions.[28,29] If C3 is defined as the total of the products oxidized at the tertiary

positions and C2 similarly for the secondary positions, the ratio of C3/C2 would be 0.33 assuming all hydrogens as equally reactive. Generally, in radical reaction the tertiary position is expected to be more reactive as may be evidenced by the facts that alkoxide radical reactions gives C3/C2 values of 6.67[30], whereas Gif-type reactions[31,32] seem to prefer oxidizing secondary positions of adamantane giving C3/C2 ratios at around 0.9. On the other hand, the oxidation of cyclohexane is an important industrial process from both economic and environmental view points. Cyclohexane's oxidized products are raw materials in the adipic synthesis, i.e., precursors of Nylon 6 and Nylon 66. Again selective transformation of unactivated C-H bonds of cyclohexane to C-OH bonds continues to be challenge to the synthetic chemists.

Table VI.1 Hydroxylation of alkanes by F_{15}TPCFe(IV)Cl and *m*-CPBA at 298 K

Entry	Substrate	Products	Yields (%)[a,b]
1	Cyclohexane	Cyclohexanol	50
		Cyclohexanone	0
2	Adamantane	Adamantan-1-ol	58
		Adamantan-2-ol	17
		Adamantan-2-one	0

[a]All the reactions were run at least triplicate, and the yields reported represent the average of these reactions.
[b]Based on the amount of *m*-CPBA added.

In the reaction of adamantane, oxidation with *m*-CPBA proceeded catalytically to give 1-adamantananol as the major product with 2-adamantananol as the minor product. The conversion of 75% (based on *m*-CPBA) has been achieved. The reaction completed within 20 minutes and not even a trace amount of ketone was detected. The reaction showed selectivity for oxidation at the tertiary position, with a 3°/2° ratio of 10.3-10.7. In case of adamantane oxidation by *t*-BuOOH catalyzed by metalloporphyrins[33], a normalized 3°/2° ratio of 10.8 was observed and authors argued that *t*-BuOO· might be the hydrogen abstracting species. The results obtained by us are quite similar to that of Minisci *et. al.*[33] and that supports the involvement of freely diffusing radicals in the present oxidizing system.

The oxidation of cyclohexane with *m*-CPBA also proceeded efficiently with a TON of 20 giving cyclohexanol as the only product. The reaction was found to be highly specific and within 30 min cyclohexanol was formed exclusively in 50-55% yields.

VI.2.3 *Mechanistic considerations*

Evidence on the nature of intermediates in iron-corroles catalysed oxygenation reactions is least available in literature.[26] This prompted us to investigate the same in the present catalytic system.

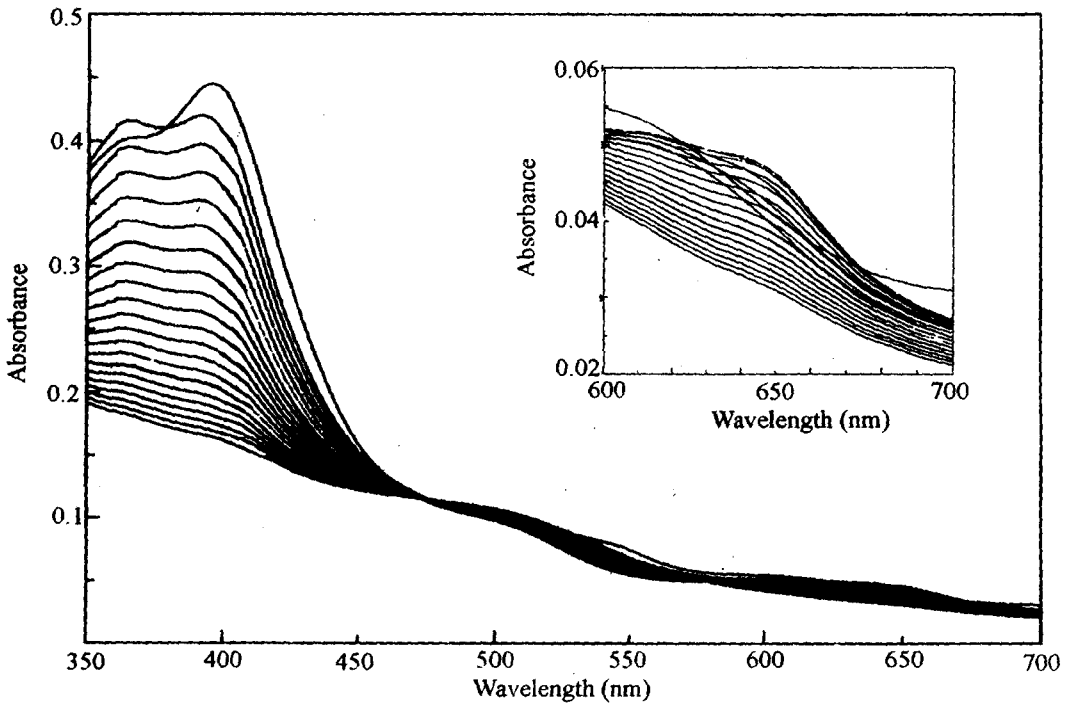


Figure VI.3 Overlay spectra catalyst 10.97 (μM) and *m*-CPBA (1.02 mM) in acetonitrile at 25±1^0 C (successive spectrum taken after 25s intervals). Inset: Growth of the weak Q-band at 645 nm and its subsequent decay.

Thus we turned our attention to the oxidation of the catalyst in the absence of organic substrate. Figure VI.3 shows the UV-vis spectral changes of the parent iron(IV)-corrole complex upon addition of large excess of *m*-CPBA in acetonitrile medium. Addition of the terminal oxidant resulted in bleaching as shown by the disappearances of the bands at 396 and 370 nm. At the same time weak Q-bands in the visible region at 645 nm was observed (Inset, Fig. VI.3). The latter formed within 25 seconds of addition of *m*-CPBA and then decayed with time. The spectral changes seemed inadequate to draw any conclusions regarding the nature of the reactive intermediates. Thus to gain an insight into the nature of oxidizing intermediates in the present case EPR spectra were recorded by rapidly mixing the catalyst and the oxidant followed by freezing the mixture at 133 K. When m-CPBA was added to the catalyst, EPR spectra showed a sharp signal at $g^{eff} \approx 2$

and another signal at $g^{eff} \approx 4$. The sharp signal at g = 2 is indicative of the formation of a free radical. The signal does not correspond to iron-coupled corrole radical. The signal at g = 4, on the other hand, could be due to some residual iron(III) corrole (known to be S=3/2, intermediate spin) from the reductive decay of the oxidized material. Detailed investigation has to be done to identify the reactive intermediates in iron(IV)corrole catalyzed reactions as the system might reveal far greater complexity that originally believed.

VI.2.4 *Kinetics and Mechanism of [(tpfc)FeCl]- mCPBA reaction*

The spectral changes upon mixing the catalyst with the oxidant and also the EPR spectral data did not provide much information regarding the identity of the reactive intermediates. Thus we shifted our attention to measure the rates of catalyst oxidation by *m*-CPBA. This was indirectly studied by monitoring the F_{15}TPCFe(III)Cl catalysed *m*-CPBA oxidation of 2,4,6-tri-*t*-butylphenol. This particular substrate was chosen because it is known to be very reactive organic reductant and its oxidized product namely 2,4,6-tri-*t*-butylphenoxy radical strongly absorb at 630 nm (ϵ=385 mol^{-1} cm^{-1}) giving us a simpler tool to monitor its generation by UV-vis spectroscopy.[34]

Our first objective was to account for the total terminal oxidant in terms of 2,4,6-tri-*t*-butylphenoxy radical (TTBP•) formation. It has been observed that a minimum concentration of 30±5 mM of TTBP is required to trap all the reactive intermediates in these reactions in acetonitrile. At lower concentration of substrate (Table VI.2, entry 1 and 2) the yield is not quantitative; again increasing the substrate concentration to 200 mM results in noticeable decrease in the overall yield. Best results were obtained in the range of 30 to 100 mM substrate concentration, which shows the highest activity of the iron(IV)corrole catalyst .

Since metallocorroles are known to get bleached almost completely[3f] at the end of catalytic reactions we decided to measure percentage survival of the catalyst following the technique described elsewhere.[35] Selected results are compiled in Table VI.2. It has been found that catalyst survival is largely dependent on the substrate concentration. A glance at Table VI.2 clearly shows that at lower [TTBP] (entry 1-5) considerable catalyst bleaching has been taken place. Again at very high [TTBP] (entry 10) iron(IV)corrole catalyst is found not to be oxidatively robust. By careful variation of concentrations of the reactants it was ultimately found that catalyst deactivation was minimal at 100mM substrate concentration (Entry 8 and 9).

Now in order to predict the reaction pathway of this reaction we measure the absorbance increase at 630 nm due to the formation of 2,4,6-tri-*t*-butylphenoxy radical. Representative kinetic plot of absorbance increase due to the formation of TTBP• radical vs. time at 630 nm is given in Figure VI.4.

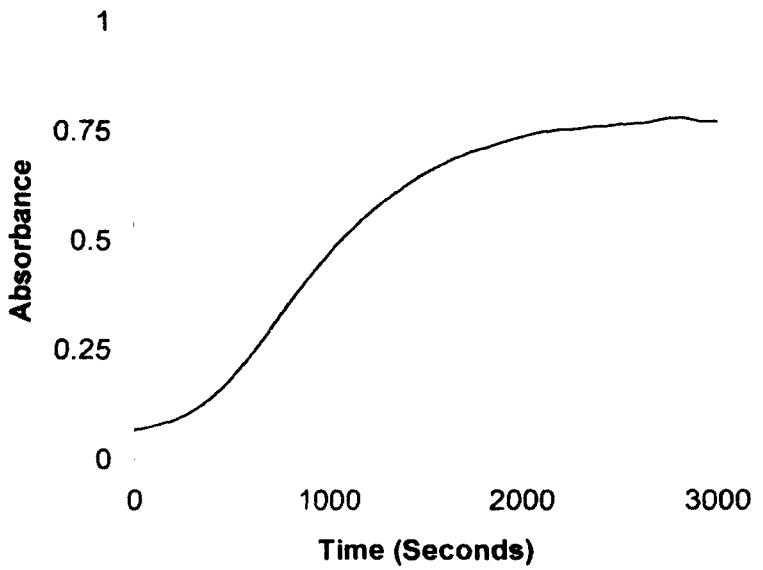


Figure VI.4 Absorbance vs. time plot of 2,4,6-tri-t-butylphenoxy radical formation in acetonitrile at 25±1^0 C.TTBP= 34 mM; *m*-CPBA= 1.06 mM; Catalyst= 11μM

A cursory glance at absorbance vs time plot shows that the increase in absorbance does not fit with a simple first or second order kinetic pattern. The complicated appearance of the absorbance vs time plot is a characteristic feature of this type of reactions. Intervening factors might include catalyst decomposition and additional oxidant decomposition (eg. *catalase*-type dismutation). To minimize such problems the method of 'Initial-rate'[36] was followed. All runs were carried out in at least duplicates and the values of dA/dt given in the tables are the average of the runs with the standard deviation quoted as the uncertainty. The data values of dA/dt_0, at varying initial concentrations of the reaction components, *m*-CPBA, F_{15}TPCFe(IV)Cl and the substrate (TTBP) are presented in Table VI.2 and plotted in Figure VI.5 (dA/dt_0 *vs.* [*m*-CPBA]) and Figure VI.6 (dA/dt_0 vs. [F_{15}TPCFe(IV)Cl]). Despite small deviations of the points in Figures VI.5 & VI.6, it is clear that the data are best fitted by a first order dependence of dA/dt_0 on the concentration of *m*-CPBA as well as on the concentration of catalyst F_{15}TPCFe(IV)Cl.

TableVI.2 F_{15}TPCFe(III)Cl-catalysed oxidation of TTBP by *m*-CPBA in acetonitrile at 25±1^{0}C TTBP•.

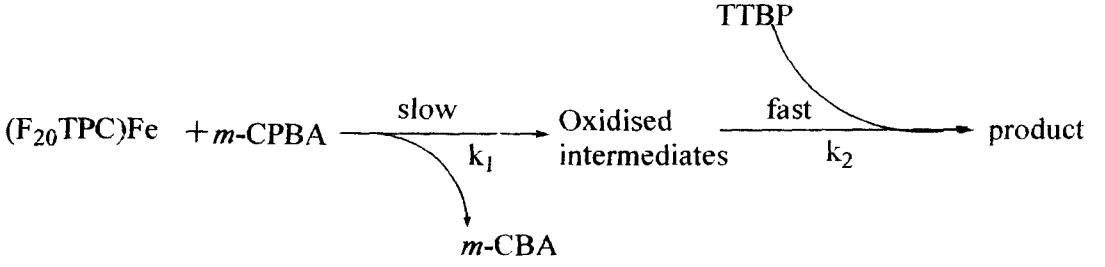
Entry No	TTBP (mM)	Catalyst (μM)	Oxidant (mM)	$(dA/dt)_0$ M s^{-1} x 10^5	Yield (%)[a]	Catalyst survival (%)
1	12.02	10.97	1.017	6.00	74.40	Bleached
2	22.14	10.97	1.017	5.935	90.01	29
3	32.25	10.97	1.06	8.464	99.08	54
4	33.58	10.97	1.06	7.303	98.75	56
5	42.75	10.97	1.04	8.73	99.92	62
6	53.62	10.97	1.04	9.333	98.79	78
7	78.63	10.97	1.2	8.601	92.30	89
8	98.47	10.97	1.2	11.96	99.13	95
9	104.39	10.97	1.09	12.04	97.30	92
10	193.7	10.97	1.028	22.55	57.80	
11	54.20	10.97	2.17	19.23	69.85	
12	53.82	10.97	3.26	30.03	34.06	
13	54.77	10.97	4.34	53.31	15.28	
14	54.00	10.97	5.60	61.03	10.55	
15	54.96	16.96	1.08	16.09	98.60	
16	54.58	22.61	1.08	20.76	97.75	
17	54.58	28.27	1.08	26.32	99.31	
18	54.39	33.92	1.08	32.77	99.10	

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

Since substrate has always been taken excess the dependence of dA/dt_0 on substrate concentration has been ignored and overall we propose that dA/dt is given by eqn. (1).

$$dA/dt \propto [m\text{-CPBA}]\,[F_{15}TPCFe(IV)Cl] \quad \ldots\ldots\ldots\ldots\ldots (1)$$

The form of equation (1) is consistent with the generally accepted mechanism of metalloporphyrin-catalysed oxidation shown in Scheme VI.3, which involves slow rate-determining conversion of the catalyst to an oxidized intermediate, which then transfers oxygen to the substrate in a fast step. This is also evident from the absorbance vs. time plot (Figure VI.4) which is clearly biphasic in nature having a hyperbolic component (slow process) followed by an exponential component (fast process).



Scheme VI.3 Metalloporphyrin catalyzed oxidation.

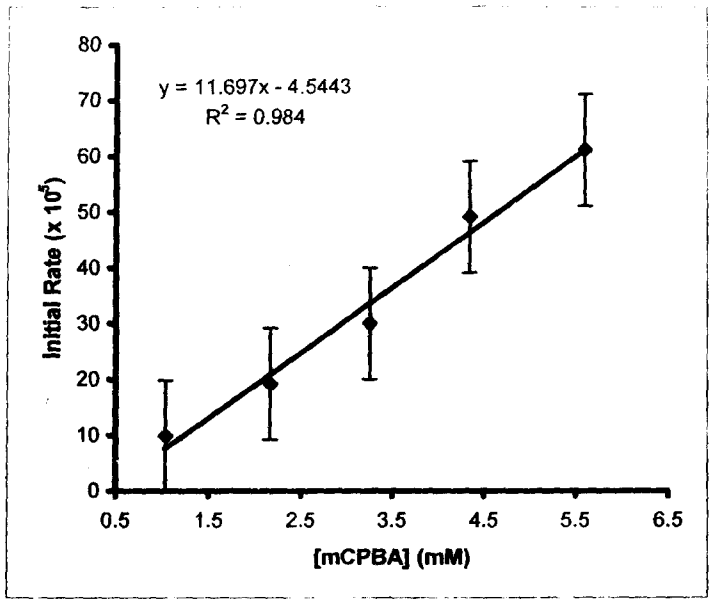


Figure VI. 5 Plot of $(dA/dt)_0$ vs. [*m*CPBA]

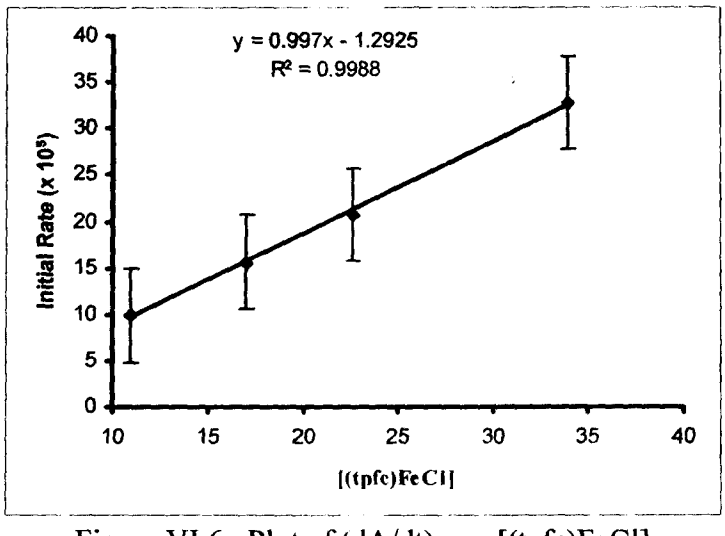


Figure VI.6 Plot of $(dA/dt)_0$ vs. [(tpfc)FeCl]

From the slope of the dA/dt_0 *vs.* [*m*-CPBA] at constant [(tpfc)FeCl], a value for k_1 of 1.21×10^4 dm^3 mol^{-1} can be calculated; while the dA/dt_0 vs. [(tpfc)FeCl] plot gives k_1 as 1.01×10^3 dm^3 mol^{-1}. Rather small value of the second order rate constant in the latter case might be rationalized in terms of greater catalyst decomposition at high catalyst concentration. It might be noted that Traylor *et al.* obtained a value of 2.5×10^5 to 2.5×10^5 dm^3 mol^{-1} using several iron(III)-porphyrin complexes as catalysts and 2,4,6-tri-*t*-butylphenol or β-carotene as substrate.[37]

VI.2.5 Hydroxylation of Alkanes by [(tpfc)FeCl]- ^{t}BuOOH

In most of the studies on metallocorrole catalyzed oxidation, iodosylbenzene or peracid was employed as terminal oxidant. No report of using *tert*-butyl hydroperoxide (TBHP) as the oxidant in metallocorrole catalyzed oxidation has appeared so far. In case of iron(III) porphyrins, Professor Traylor and his research group first demonstrated the catalytic oxidation of hydrocarbons by hydroperoxides and hydrogen peroxide. Their conclusions[38] are very useful even today. It encouraged us to explore the iron-corrole catalyzed hydroxylation reactions with 'mild' *tert*-butyl hydroperoxide (TBHP).

The UV-visible spectra of a 30 μM solution of [Fe(IV)(tpfc)Cl] in CH_3CN and that in CH_2Cl_2 are markedly different (Figure VI.7). The electronic spectrum of the catalyst in acetonitrile is quite similar to that of [Fe(III)(tpfc)$(OEt_2)_2$], which leads us to assume that the catalyst auto-reduces to form [Fe(III)(tpfc)$(NCCH_3)_2$] in presence of excess acetonitrile.[39] The spectral changes observed on addition of *t*-BuOOH have been shown in Figure VI.8. The spectra exhibits regeneration of a Fe(IV) species with bands at 370 and 396 nm. The transient species then decays gradually. The easily accessible Fe^{III}/Fe^{IV} couple appeared quite promising and encouraged us to examine the catalytic potential of iron corrole/t-BuOOH system in oxidizing alkanes.

The catalytic reactions were performed in acetonitrile at room temperature. The iron(IV) corrole or more precisely [Fe(III)(tpfc)$(NCCH_3)_2$] catalyzes the oxidation of hydrocarbons in the presence of TBHP with reasonably high TON's (Table VI.3 & VI.4). Under these conditions, cyclohexane have been found to be oxidized to cyclohexanol & cyclohexanone. Large excess of substrate were used to minimize over-oxidation of alcohols to ketones (ratio **1** : substrate : oxidant = 1 : 40 : 4000). The reactions were performed in both air and under argon. In aerobic condition the overall yield of the oxidized product was 27% with an A/K ratio of 0.66. Under argon atmosphere the total yield was 20% with an A/K ratio of 0.58.

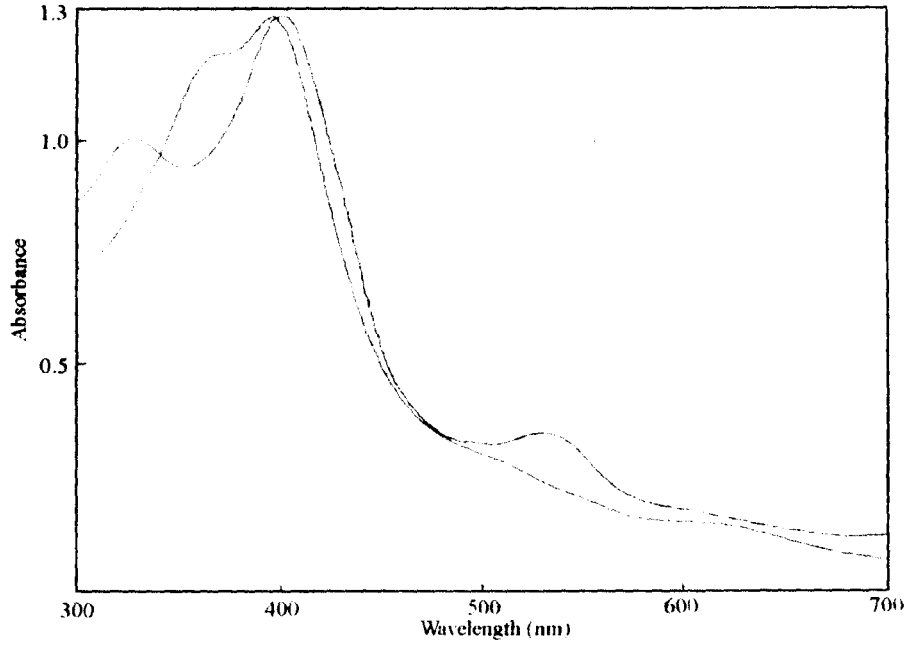


Figure VI.7 The UV-visible spectra of the catalyst in dichloromethane (pink) and in acetonitrile (blue).

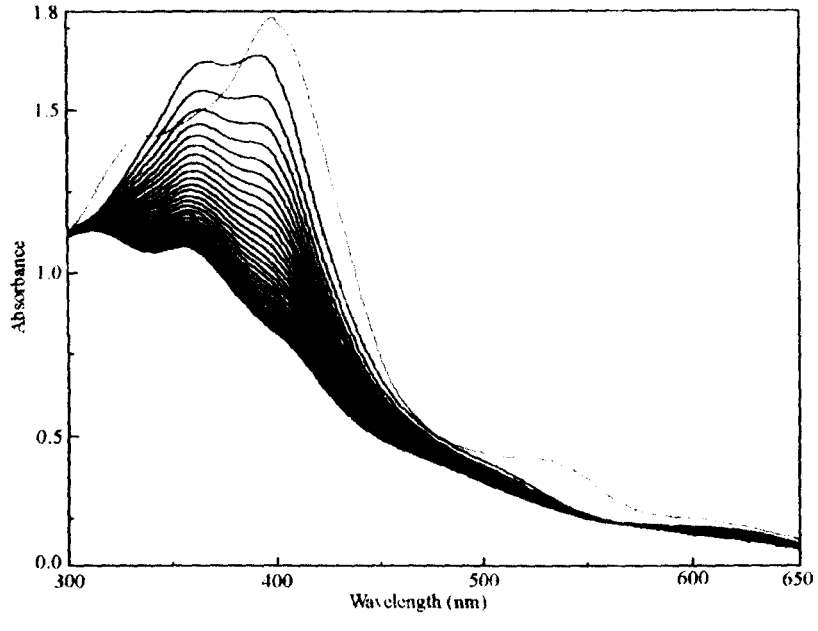


Figure VI.8 Overlay spectra of the catalyst (30 μM) and TBHP (2 mM) in acetonite at 25±1°C (successive spectrum taken after 3 minute intervals)

We then investigated the oxidation of adamantane catalyzed by [Fe(III)(tpfc)$(NCCH_3)_2$] with *t*-BuOOH. The conversion is moderate and the main reaction products are 1-adamantanol (77%), 2- adamantanol (16%) and 2-adamantanone (7%). Lower yields of the oxidation products were observed under an argon atmosphere (18% based on TBHP) (Table VI.3).

Table VI.3 (F_{15}TPC)FeCl catalyzed hydroxylation of alkanes with *t*-BuOOH. at 298 K

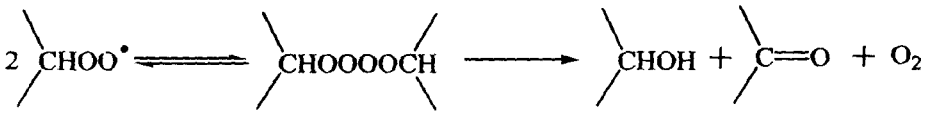
Substrate	Atm.	Yield (%)[a]	TON[b]	Selectivity (%)	Remarks
Cyclohexane	Argon	20	17	Cyclohexanol (40) Cyclohexanone (60)	A/K=0.66
	Air	27	23	Cyclohexanol (38) Cyclohexanone (62)	A/K=0.58
Adamantane	Argon	18	15	1-Adamamtanol (72) 2-Adamamtanone (11) 2-Adamamtanol (17)	C^3/C^2=7.8
	Air	53	45	1-Adamamtanol (77) 2-Adamamtanone (7.5) 2-Adamamtanol (15.5)	C^3/C^2=10.2

[a]Yields are based on concentration of oxidant.
[b]Moles of product/moles of catalyst.

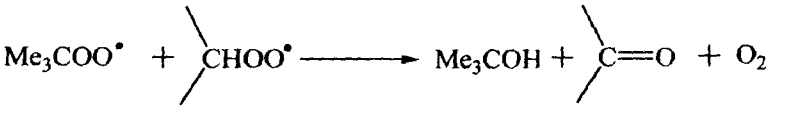
The normalized C^3/C^2 ratio (10.2) of the oxidation products is quite close to that obtained in the adamantane oxidation by metalloporphyrins/t-BuOOH system[10] (10.8), but different from the ratio (2.7) obtained by Gif reactions.[32,33]

Results summarized in Table VI.3 demonstrate that [Fe(III)(tpfc)$(NCCH_3)_2$] promotes facile oxidation of alkanes with TBHP in acetonitrile solutions at room temperature. Controlled experiments in absence of the catalyst showed little or no conversions of substrate indicating at least one key intermediate comprises the [(tpfc)Fe] moiety. Several species in the reaction mixture could be responsible for the C-H cleavage of cyclohexane (and other hydrocarbons). By analogy to the heme chemistry, one can propose homolysis of the O-O bond in the [(tpfc)Fe^{IV}-O-O^{t}Bu] intermediate producing ^{t}BuO• and hence promoting alkane oxidation *via* ^{t}BuO• mediated H atom abstraction.[40] On the contrary, one can also propose heterolytic scission of the O-O bond in the same intermediate producing the hypervalent iron oxo (Fe^V=O) perferryl species as the H atom abstractor. However, the second possibility may be excluded on the basis of very high reactivity of (Fe^V=O)corrole transients, which has been confirmed recently.[26] Again, the products of oxidation of cyclohexene by [Fe(III)(tpfc)$(NCCH_3)_2$]+anhydrous TBHP system clearly indicate the absence of perferryl intermediate in the oxidation reactions. No epoxide is detected in the products of oxidation of cyclohexene by [Fe(III)(tpfc)$(NCCH_3)_2$]+ 'dry' TBHP system. These prompted us to investigate the possibility of ^{t}BuO•-mediated alkane oxidation following homolysis of the O-O bond in the [(tpfc)Fe^{IV}-O-O^{t}Bu] intermediate. The involvement of radical in the reaction is

evident from the observation that the oxidation of cyclohexene almost quenched in presence of radical scavenger 2,4,6-tri *tert*-butyl phenol (TTBP) producing only 2-cyclohexene-1-ol (7%). Again the products of oxidation of adamantane by [Fe(III)(tpfc)($NCCH_3$)$_2$]+TBHP exhibited more reactivity at the more-substituted carbon atoms (Table VI.1) and it appeared that the $^tBuO\bullet$ radical could be directly involved in abstracting hydrogen atoms of the C-H groups. It is also feasible in terms of the so called "radical strength" of $^tBuO\bullet$ (97 kcal/mol)[41] which is sufficient to abstract an H atom from the C-H bonds of higher molecular (>C4) alkanes including cyclohexane (95 kcal/mol). On the other hand the radical strength of $^tBuOO\bullet$ (83 kcal/mol) is not strong enough to abstract an H atom from cyclohexane, it can provide the $^tBuO\bullet$ via the disproportionation reaction and eventually facilitates the formation of the cyclohexyl radical in the reaction mixture. The formation of cyclohexanol and cyclohexanone in an approximately 1:1 ratio is symptomatic of a Russel-type termination[42] of two secondary peroxyl radicals (equation 1). The formation of slight excess ketones over alcohol under aerobic condition explained via equation 2 (cross reaction).

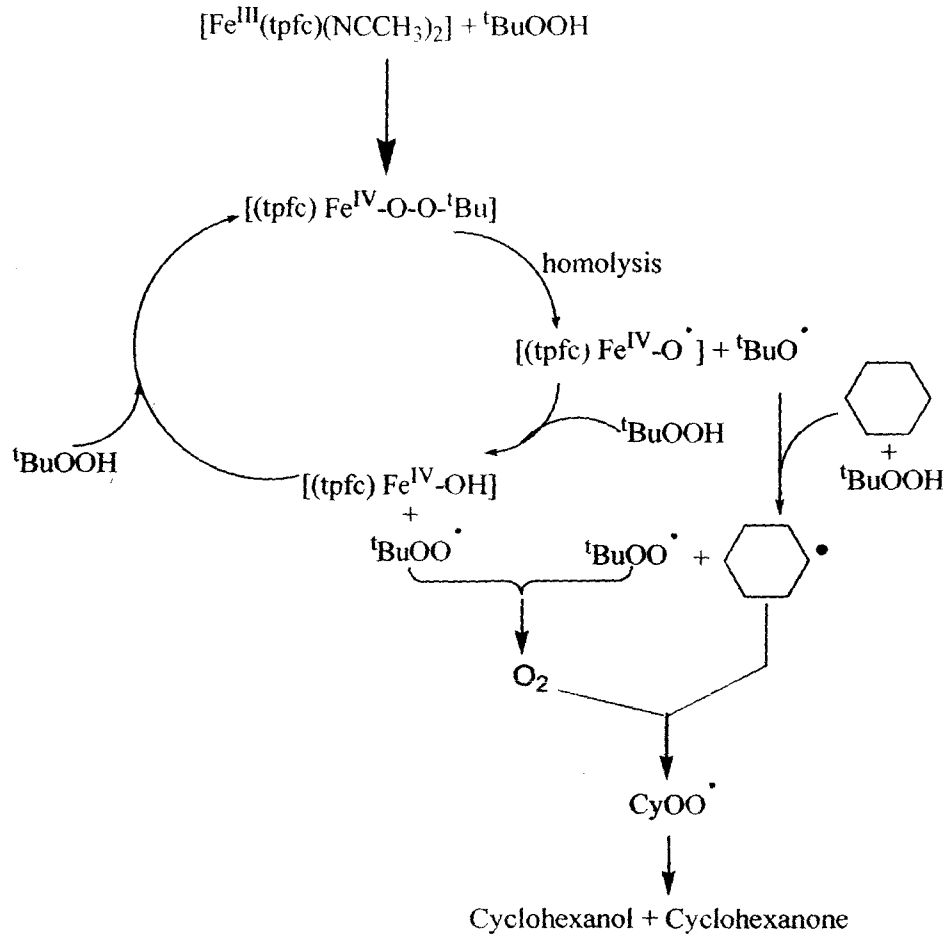


(1)



(2)

The plausible reaction mechanism supporting all these results obtained in the present case has been shown in Scheme VI.4. The catalytic cycle seems to involve the following steps: (a) formation of [(tpfc)Fe^{IV}-O-O^{t}Bu] intermediate upon addition of TBHP in acetonitrile; (b) the O-O bond homolysis forming $^tBuO\bullet$ and a lesser reactive (particularly with regards to epoxidation) [(tpfc)Fe^{IV}-OH]; (c) $^tBuO\bullet$ radical mediated reactions following H-atom abstraction from cyclohexane and TBHP; (d) formation of cyclohexanol and cycloheanone *via* the Russel-type radical termination.



Scheme VI.4 Plausible reaction mechanism

Small amount of epoxide (<10%) has been obtained in the oxidation of cyclohexene by aqueous TBHP under both aerobic & anaerobic conditions (Table VI.4). Under the proposed reaction route, the formation of epoxide is expected to be at minimum, rather allylic oxidation is a favoured destination. The ^{t}BuOO• radicals are known to yield epoxides in presence of water. Therefore, the reaction was carried out with anhydrous TBHP instead of aqueous TBHP (70%) to examine whether the presence of water has any role in epoxide formation. Only a trace amount of epoxide (<1%) is detected in the latter case which indicates that the products are derived mostly from the reactions of ^{t}BuO• radical in anhydrous media, while the formation of epoxide is favoured in presence of water. Higher selectivity for benzaldehyde can also be explained in terms of Scheme VI.4. Apparently *tert*-butyl hydroperoxide tend to undergo homolytic cleavage of the peroxide O-O bond upon coordination to the central iron resulting in formation of the poorly reactive intermediate [(tpfc)Fe^{IV}-OH], responsible for the low yields of

Table VI.4 (F_{15}TPC)FeCl catalyzed oxygenation of alkenes with t-BuOOH.

Substrate	Atm.	Time	Total yield (%)	Selectivity (%)
Cyclohexene	Argon	10hr	89%	Cyclohexene epoxide (9.5) Cyclohexene 1-ol (40) Cyclohexene 1-one (50)
	Air	5hr	96 %	Cyclohexene epoxide (7.5) Cyclohexene 1-ol (26) Cyclohexene 1-one (66.5)
Styrene	Argon	7 hr	70 %	Benzaldehyde (41) Phenyl acetaldehyde (10) Styrene oxide (49)
	Air	6hr	99%	Benzaldehyde (80) Phenyl acetaldehyde (2) Styrene oxide (17)

epoxide, and for the formation of alkoxy radicals. The latter radicals initiate a free-radical reaction that is continued by the oxygen present in the reaction medium, leading to the formation of benzaldehyde. When the reaction was carried out under an inert atmosphere, the selectivity for styrene oxide improved (Table VI.4). Thus the presence of oxygen in the reactions directly influences the benzaldehyde/epoxide ratio confirming the free-radical mechanism for the formation of benzaldehyde. But at the same time, higher yield of styrene oxide under anaerobic conditions indicates the presence of at least one more key intermediate in iron(IV) corrole catalyzed oxidation reactions. Thus, it appears that competitive pathways are operative in the oxidation of hydrocarbons catalyzed by iron(IV)corrole complex.

VI.3 Conclusion

1. A significantly high catalytic activity of the iron(IV) corrole complex in the oxidation of alkanes with *m*-CPBA has been achieved at room temperature.
2. Cyclohexane has been hydroxylated with 100% selectivity producing cyclohexanol in 45-50% yield.
3. The overall conversion in the hydroxylation of adamantane is achieved up to 75% with 3°/2° ratio of 10.3-10.7.

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

5. For the first time, *t*-BuOOH has been used as terminal oxidant in metallocorrole catalyzed oxidation of alkane & alkenes.

6. The results obtained from *t*-BuOOH-[Fe^{IV}(tpfc)Cl] oxidizing systems demonstrate the involvement of *t*-BuO· radicals as the hydrogen abstracting species. Although further studies are needed to identify unambiguously the nature of reactive intermediates involved in the *t*-BuOOH-[Fe^{IV}(tpfc)Cl] oxidizing system.

VI.4 Experimental Section

Materials. Acetonitrile and dichloromethane were distilled[43] prior to use. TTBP and *m*-CPBA were purchased from Aldrich and purified accordingly[11] and the active oxygen concentration of *m*-CPBA was determined iodometrically. (F_{15}TPC)FeCl was prepared according to the reported procedure[15a]. UV-vis spectral measurements were taken with a JASCO V 530 spectrophotometer connected with a thermostat at 25±1^0 C. EPR spectral measurements were done on a JEOL JES-FA200 spectrometer fitted with a quartz Dewar for measurement at 133 K.

Kinetic Experiments

In a typical kinetic experiment, TTBP (28 mg, final concentration 50 mM) was taken in a cuvette fitted with silicon rubber septa. The cuvette was degassed by blowing argon over it for 15 min. 2 mL degassed acetonitrile was used to dissolve the TTBP in the cuvette. A standard solution of F_{15}TPCFe(IV)Cl in acetonitrile was added so that the final concentration of the catalyst was 11μM. The *m*-choloperbenzoic acid was prepared in degassed dichloromethane (9 mg in 200μL). An aliquot volume (10μL) 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-second intervals. A vs. t plots, typified by Figure VI.4, were analyzed as detailed in the main body of this chapter.

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