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Selective hydroxylation of alkanes catalyzed by iron(IV)corrole

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ABSTRACT

The complex meso-tris(pentafluorophenyl)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 50% yield 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 have been quantitatively trapped by 2,4,6-tri-t-butylphenol (TTBP). Kinetic analysis of the (F$_{15}$TPC)FeCl-catalyzed oxidation of TTBP has found consistent with rapid reaction of organic substrate with an intermediate formed in the first and rate-determining step.

1. Introduction

The functionalization of saturated hydrocarbons under mild conditions is an important goal in basic and industrial chemistry [1–5]. The chemical transformation of C–H → C–OH is an energy-intensive process due to the inertness of alkanes toward chemical conversion. However the biological world has evolved several enzymes to accomplish such transformation selectively and under very mild conditions [6–9]. In particular, cytochromes P-450 catalyze the most energetically difficult hydroxylation of unactivated C–H bonds of alkanes [6]. With an aim to model the alkane hydroxylation, transition metal complexes of porphyrins, phthalocyanines and Schiff bases have been extensively studied as oxidation catalysts [10–17]. During the last decade metallo derivatives of corroles [18–21], tetrapyrrolic macrocycles with just one meso carbon short from the porphyrin skeleton have evoked keen interest in their catalytic properties. Various metallocorroles have been prepared to investigate a wide variety of applications in catalysis for epoxidation [22–28], cyclopropanation [22,29–31] and aziridination [32]. Despite progress in metallocorrole-catalyzed epoxidation [20] reports on hydroxylation of alkanes catalyzed by metallocorroles are sparse [22,28]. Iron(IV)corrole-catalyzed oxygenation of ethyl benzene to 1-phenylethanol (6.6%) and acetophenone (4.2%) is the first example of matallocorrole-catalyzed hydroxylation [22]. Difluoroantimony(V)corrole was found to act as photocatalysts

in aerobic oxidation of alkenes to the corresponding hydroperoxides which produce corresponding alcohols on treatment with triphenylphosphine. Although this system successfully oxidizes cumene to the corresponding hydroperoxide but it fails to oxygenate alkanes like adamantane and ethyl benzene [28]. In general low selectivity is a common problem in metallocorrole-catalyzed oxygenation reactions [20,23]. The selective hydroxylation of unactivated C–H bond of alkanes still remains elusive in metallocorrole chemistry.

Herein we wish to report the hydroxylation of cyclohexane and adamantane at room temperature catalyzed by iron corrole [(F$_{15}$TPC)Fe^{IV}Cl] with m-CPBA as terminal oxidant. To our knowledge, this is first report of selective hydroxylation of alkanes at room temperature by iron corrole complex. Kinetic analysis of the (F$_{15}$TPC)FeCl-catalyzed oxidation has also been reported.

2. Experimental

2.1. General

Acetonitrile and dichloromethane were distilled [33] prior to use. 2,4,6-tri-t-butylphenol (TTBP) and m-chloroperbenzoic acid (m-CPBA) were purchased from Aldrich and purified accordingly [34] and the active oxygen concentration of m-CPBA was determined iodometrically. (F$_{15}$TPC)FeCl was prepared according to the reported procedure [29]. UV–vis spectral measurements were taken with a JASCO V 530 spectrophotometer connected with a thermostat at $25 \pm 1\,^\circ$C. EPR spectral measurements were done on a JEOL JES-FA200 spectrometer fitted with a quartz Dewar for mea-

Table 1
Hydroxylation of alkanes by F_{15}TPCFe(IV)Cl and *m*-CPBA at $25 \pm 1\,^{\circ}$C.

Entry No.	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.

surement at 133 K. The product analysis was done by Pekin-Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-m column) by injecting 1 μL aliquot from the reaction vial taken after addition of pentafluoroiodobenzene as internal standard.

2.2. Catalytic oxidation of alkanes

Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction 25 μM of catalyst and 100–200 mM of substrate were dissolved in 2 mL of argon saturated acetonitrile. 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 pentafluoroiodobenzene was added to this reaction mixture and an aliquot was injected into a capillary column (elite 1, 15 m) of a preheated GC. The identification and the quantization of the products were done from the response factors of standard product samples as usual (internal standard: pentafluoroiodobenzene, 2 mM).

2.3. Kinetic measurements

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. Degassed acetonitrile (2 mL) 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 11 μM. The *m*-choloperbenzoic acid was prepared in degassed dichloromethane (9 mg in 200 μL). An aliquot volume (10 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-s intervals. Absorbance vs. time plots have been analyzed in details in the following section.

3. Results and discussion

3.1. Hydroxylation of alkanes

Catalytic activity of the *meso*-tris(pentafluorophenyl)corrolato-iron(IV)chloride [(F15TPC)FeCl] was examined in the oxygenation reaction of alkanes as summarized in Table 1. Adamantane and cyclohexane have been chosen as the substrate.

The selective transformation of unactivated C–H bond of cyclohexane to C–OH bond continues to be challenge to the synthetic chemists. The oxidation of cyclohexane is an important industrial process from both economic and environmental viewpoints. Cyclohexane's oxidized products are raw materials in the adipic synthesis, i.e., precursors of Nylon 6 and Nylon 66. Hydroxylation of cyclohexane has been achieved by both homogeneous and heterogeneous catalytic systems [35–39]. So far attention has been paid to heme and non-heme iron complexes due to their high catalytic activity and biological relevance [40–43]. Electron deficient iron porphyrins have emerged as efficient catalysts with

tert-butyl hydroperoxide in bringing about selective hydroxylation of cyclohexane to cyclohexanol [12]. Apart from this result, selectivity for the formation of cyclohexanol is low in most of the cases [36].

The oxidation of cyclohexane with *m*-CPBA-[Fe(IV)(tpfc)Cl] proceeded efficiently giving cyclohexanol as the sole product. The reaction was found to be highly specific and cyclohexanol was formed exclusively within 30 min with 50% yield. Absence of cyclohexanone is noteworthy since most of the catalytic oxidation reactions of cyclohexane invariably contain this over oxidized product. Recently Ni^{II}(TPA) [TPA = tris(2-pyridylmethyl)amine] has been shown to hydroxylate cyclohexane by *m*-CPBA as the oxidant with an A/K of 8.5 [38]. Our results show that iron corrole-catalyzed hydroxylation of cyclohexane is much more selective and appear as prospective catalytic system for industrial applications.

Adamantane is an important mechanistic probe in deciding the radical character in catalytic reactions [44–47]. If C3 were 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 [48], whereas Gif-type reactions [49] seem to prefer oxidizing secondary positions of adamantane giving C3/C2 ratios at around 0.9.

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 (Table 1). The reaction completed within 20 min and not even a trace amount of ketone was detected. The reaction showed selectivity for oxidation at the tertiary position, with a $3^{\circ}/2^{\circ}$ ratio of 10.3–10.7. In case of adamantane oxidation by *t*-BuOOH catalyzed by metalloporphyrins, a normalized $3^{\circ}/2^{\circ}$ ratio of 10.8 was observed and it was suggested that *t*-BuOO• might be the hydrogen abstracting species [50]. Our results are quite similar to that of Minisci et al. [50] and supports the involvement of freely diffusing radicals in the present oxidizing system.

3.2. Mechanistic considerations

Evidence on the nature of intermediates in iron-corroles-catalyzed oxygenation reactions is least available in the literature [51,52]. This prompted us to investigate the same in the present catalytic system. Thus we turned our attention to the oxidation of the catalyst in the absence of organic substrate. Fig. 1 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. 1). The latter formed within 25 s of addition of *m*-CPBA and then decayed with time. The spectral changes are inadequate to draw any conclusion regarding the nature of the reactive intermediates. Thus to gain an insight into the nature of oxidizing intermediates, EPR spectra of the catalyst in the presence of the oxidant were recorded at 133 K. The EPR spectrum shows 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, may be due to some residual iron(III)corrole (known to be $S = \frac{3}{2}$, intermediate spin) from the reductive decay of the oxidized material. The spectral changes of the catalyst on addition of the oxidant and also the EPR spectral data fail to provide adequate information on the identity of the reactive intermediates.
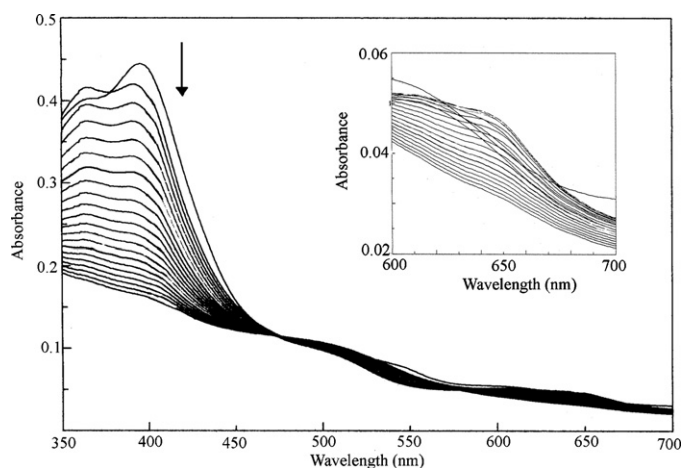
Fig. 1. Overlay spectra catalyst 10.97 μM and *m*-CPBA (1.02 mM) in acetonitrile at 25 ± 1 °C (successive spectrum taken after 25 s intervals). Inset: growth of the weak Q-band at 645 nm and its subsequent decay.

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

3.3. Kinetics of the catalytic reactions

The rate of the catalyst oxidation with *m*-CPBA was studied by monitoring the oxidation of 2,4,6-tri-*t*-butylphenol. This particular substrate was chosen because it is known to be very reactive organic reductant and it's oxidized product namely 2,4,6-tri-*t*-butylphenoxy radical absorbs at 630 nm ($\epsilon = 385$ mol^{-1} cm^{-1}) providing a simpler tool to monitor its generation by UV–vis spectroscopy [34,53].

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 2, entries 1 and 2) the yield is not quantitative; again decrease in the overall yield is observed on increasing the substrate concentration to 200 mM. Best results were obtained in the range of 30–100 mM substrate concentration, which shows the highest activity of the iron(IV)corrole catalyst.

Since metallocorroles are known to get bleached almost completely [22] at the end of catalytic reactions, the percentage survival of the catalyst was measured using the technique described elsewhere [54]. Selected results are compiled in Table 2. It has been found that ca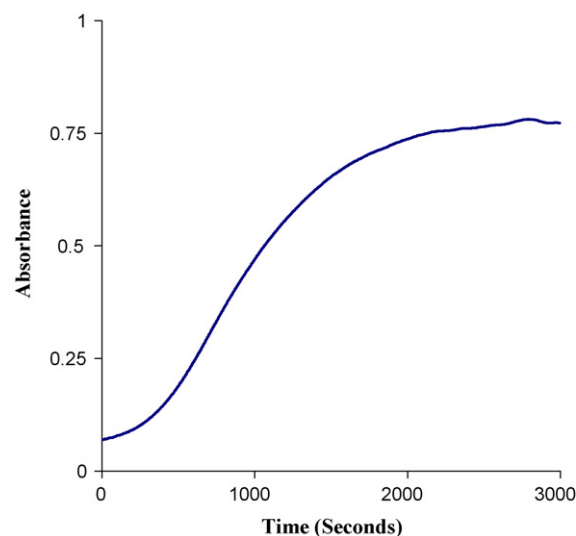talyst survival is largely dependent on the substrate concentration. A glance at Table 2 clearly shows that at lower [TTBP] (entries 1–5) considerable catalyst bleaching has been taken place. Again at very high [TTBP] (entry 10) iron(IV)corrole catalyst is found not to be oxidatively robust. By careful variation of concentrations of the reactants it was ultimately found that catalyst deactivation was minimal at 100 mM substrate concentration (entries 8 and 9).

Now in order to predict the reaction pathway of this reaction, the absorbance at 630 nm due to the formation of 2,4,6-tri-*t*-butylphenoxy radical was monitored. A representative kinetic plot of absorbance at 630 nm vs. time is shown in Fig. 2.

The absorbance vs. time plot (Fig. 2) 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 (e.g. *catalase*-type dismutation). Therefore, the method of 'Initial-rate' [55–57] was adopted. All runs were carried out in at least duplicates and the values of d*A*/d*t* given in the tables are the average of the runs with the standard deviation quoted as the uncertainty. The values of d*A*/d*t*$_0$, at varying initial concentrations of the reaction components are presented in Table 2. The plots of d*A*/d*t*$_0$ vs. [*m*-CPBA] and d*A*/d*t*$_0$ vs. [F$_{15}$TPCFe(IV)Cl] are shown in

Table 2
F$_{15}$TPCFe(IV)Cl-catalyzed oxidation of TTBP by *m*-CPBA in acetonitrile at 25 ± 1 °C.

| Entry No.	TTBP (mM)	Catalyst (μM)	Oxidant (mM)	(d*A*/d*t*)$_0$ ($\times 10^5$ M s^{-1})	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.
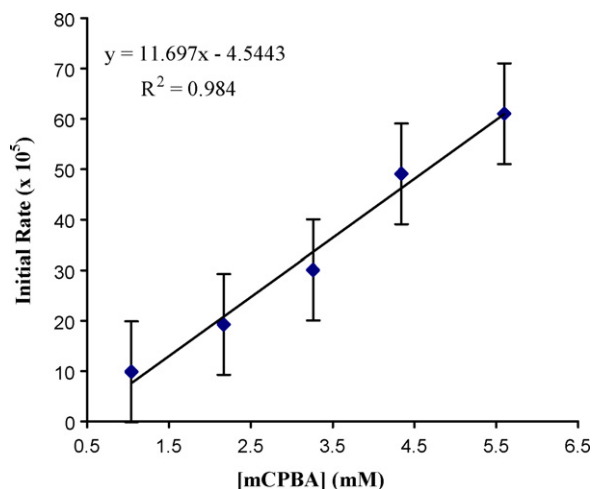
Fig. 3. Plot of $(dA/dt)_0$ vs. [m-CPBA].

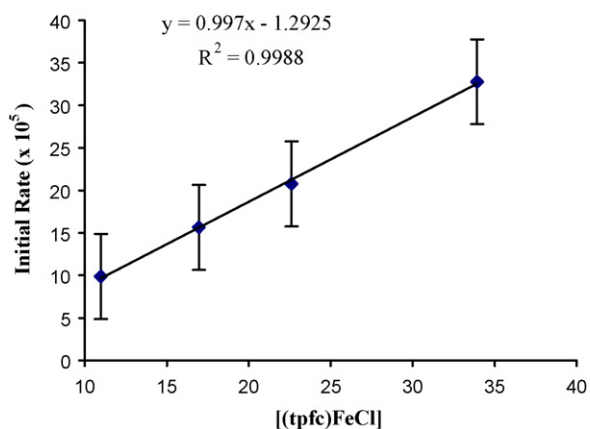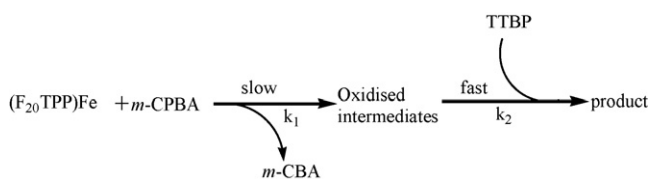**Fig. 4.** Plot of $(dA/dt)_0$ vs. [(tpfc)FeCl].

Scheme 1. Metalloporphyrin-catalyzed oxidation.

Figs. 3 and 4 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 as well as on the concentration of catalyst F_{15}TPCFe(IV)Cl.

Since substrate has always been taken in excess, the dependence of dA/dt_0 on substrate concentration has been ignored and overall we propose the following relation:

$$\frac{dA}{dt} \propto [m\text{-CPBA}][F_{15}\text{TPCFe(IV)Cl}] \tag{1}$$

The relation (1) is compatible to the generally accepted mechanism of metalloporphyrin-catalyzed oxidation shown in Scheme 1 [6], which involves slow rate-determining conversion of the catalyst to an oxidized intermediate, which then transfers oxygen to the substrate in a fast step. Here the absorbance vs. time plot (Fig. 2) is clearly biphasic in nature having a hyperbolic component (slow process) followed by an exponential component (fast process).

From the slope of the dA/dt_0 vs. [m-CPBA] at constant [F_{15}TPCFe(IV)Cl], second order rate constant k_1 (1.21×10^4 dm^3 mol^{-1})

is obtained; while the dA/dt_0 vs. [F_{15}TPCFe(IV)Cl] plot gives a value of 1.01×10^3 dm^3 mol^{-1}. In the latter case the lower value of the second order rate constant suggests greater catalyst decomposition at high catalyst concentration.

4. Conclusion

A significantly high catalytic activity of the iron(IV)corrole complex in the oxidation of alkanes at room temperature with m-CPBA has been achieved. For the first time in metallocorrole chemistry, cyclohexane has been hydroxylated with 100% selectivity producing cyclohexanol in 50% yield. This is also the first report of the hydroxylation of adamantane catalyzed by any metallocorrole. The overall conversion in the hydroxylation of adamantane is achieved up to 75% with 3°/2° ratio of 10.3–10.7. To the best of our knowledge these are the highest yield conversions of C–H bonds to C–OH bonds in metallocorrole chemistry, where the carbon is sp^3 hybridized. The kinetic investigation reveals a first order reaction rate dependence on the concentration of catalyst as well as on that of the oxidant.

Acknowledgement

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