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# Mild oxidation of hydrocarbons catalyzed by iron corrole with tert-butylhydroperoxide

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#### ABSTRACT

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#### 1. Introduction

The oxidative functionalization of hydrocarbons to more valuable products under mild conditions is an area of current interest [1,2]. The selective insertion of one oxygen atom from oxygen donors into various hydrocarbon molecules under mild conditions remains a challenge in chemical science. The biological system has evolved a group of enzymes called monooxygenases which catalyze monooxygenation reaction under very mild conditions [3]. Extensive effort has been devoted to develop synthetic homogeneous catalysts as functional models for monooxygenases. In this direction metalloporphyrins catalyzed oxidation of hydrocarbons has been extensively studied [4–6]. Transition metal complexes of phthalocyanines. chlorins, triazacylononanes and Schiff bases have also been used as catalysts for hydroxylation of alkanes and epoxidation of alkenes [7-10]. There is a growing interest in catalysis by other metal complexes, especially of different macrocyclic ligands. Metal complexes of corroles [11-14], one carbon atom contracted porphyrin analogue, appear as prospective candidates in this regard. Gross et al. introduced a convenient method for synthesis of corroles [15,16] and first demonstrated the catalytic behaviour of iron corrole complex  $[Fe^{IV}(tpfc)Cl]$  (tpfc = 5,10,15-tris-(pentafluorophenyl)corrolato anion) in oxidation of styrene and ethylbenzene with iodosylbenzene [17]. Subsequently manganese (III) corroles have received more attention as catalysts in hydrocarbon oxidation [18-20]. Interestingly, only iodosylbenzene has been used as terminal oxidant in metallo-

Catalytic alkane and alkene oxidation by iron complex of 5,10,15 tris-(pentafluorophenyl)corrole, using 70% *tert*-butyl hydroperoxide as oxidant at room temperature is reported for the very first time. Involvement of freely diffusing radicals in the oxidizing system is observed. A reaction mechanism is proposed based on the experimental results.

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corrole catalyzed oxidation of hydrocarbons [17–20]. Although a catalytic system with mild oxidant operating at ambient condition is highly desirable, metallocorrole catalyzed hydrocarbon oxidation by mild oxidant is not reported so far.

Here we wish to report the catalytic oxygenation of alkanes and alkenes by  $[Fe^{IV}(tpfc)CI]$  and *t*-BuOOH at room temperature. To our knowledge, this is the first time to show that a metallocorrole efficiently catalyzes oxidation of hydrocarbons at room temperature with *t*-BuOOH as terminal oxidant. A plausible reaction mechanism is proposed based on the experimental results.

### 2. Experimental

#### 2.1. Materials

Acetonitrile and dichloromethane were distilled under argon from CaH<sub>2</sub> and CaCl<sub>2</sub> respectively prior to use. 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, pentafluoroiodobenzene (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. The iron(IV) corrole catalyst, [Fe<sup>IV</sup>(tpfc)Cl] was prepared according to the reported procedure [17]. The product analysis was done by Perkin Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column) by injecting 1 µL aliquot from the reaction vial taken after addition of iodopentafluorobenzene as internal standard. The identification and quantification of the products were done from the response factors of standard product samples.

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#### 2.2. Catalytic oxidation of hydrocarbons

Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction  $25 \,\mu$ M 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 *t*-BuOOH and the contents were magnetically stirred. After periodic time intervals standard solution of iodopentafluorobenzene 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: iodopentafluo robenzene, 2 mM).

#### 3. Results and discussion

The UV–visible spectrum of a 30  $\mu$ M solution of [Fe<sup>IV</sup>(tpfc)Cl] in acetonitrile is markedly different from that in dichloromethane (Fig. 1). The electronic spectrum of the catalyst in acetonitrile is quite similar to that of [Fe<sup>(III)</sup>(tpfc)(OEt<sub>2</sub>)<sub>2</sub>], which may arise from auto-reduction of the catalyst to form [Fe<sup>(III)</sup>(tpfc)(NCCH<sub>3</sub>)<sub>2</sub>] in the presence of excess acetonitrile [21]. The spectral changes observed upon addition of *t*-BuOOH have been shown in Fig. 2. Regeneration of an iron(IV) species with absorption bands at 370 and 396 nm followed by a gradual decay of the transient species was observed. Easy accessibility to different oxidation states of iron–corrole complex in acetonitrile encouraged us to examine the catalytic potential of iron corrole/*t*-BuOOH system to oxidize alkanes and alkenes in acetonitrile.

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 cyclohexane in the presence of TBHP (Table 1). Under these conditions, cyclohexane has been found to be oxidized to cyclohexanol and cyclohexanone. A large excess of substrate was used to minimize over-oxidation of alcohols to ketones (catalyst: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 (Table 1).

We also investigated the oxidation of adamantane, an important mechanistic probe to diagnose the radical character of catalytic oxidation reactions [22,23]. The catalytic reactions were performed in 1:1 acetonitrile/dichloromethane medium due to the limited solubility of adamantane in acetonitrile. Here, the conversion is moderate and the major reaction products are 1-adamantanol (77%), 2-adamantanol



Fig. 1. The UV-visible spectra of the catalyst in dichloromethane (pink) and in acetonitrile (blue).



**Fig. 2.** Overlay spectra of the catalyst ( $30 \mu$ M) and TBHP (2 mM) in acetonitrile at  $25 \pm 1$  °C (successive spectrum taken after 3 min intervals).

(16%) and 2-adamantanone (7%). Under argon atmosphere lower yields of the oxidation products were observed (18% based on TBHP) (Table 1). The normalized  $C^3/C^2$  ratio (10.2) of the oxidation products is quite close to that observed in the adamantane oxidation by metalloporphyrins/t-BuOOH system (10.8) [24], but different from the ratio (2.7) obtained by Gif reactions [23].

Results summarized in Table 1 demonstrate that iron-corrole complex catalyzes facile oxidation of alkanes at room temperature with TBHP in acetonitrile medium. Controlled experiments in absence of the catalyst show little or no conversions of substrate indicating that at least one key intermediate comprises the [(tpfc)Fe] moiety. Several species in the reaction mixture may be responsible for the C-H cleavage of cyclohexane (and other hydrocarbons). In analogy to the iron-porphyrine chemistry, it can be proposed that the homolysis of O-O bond in the [(tpfc)Fe<sup>IV</sup>-O-O<sup>t</sup>Bu] intermediate produces <sup>t</sup>BuO• which in turn promotes alkane oxidation via <sup>t</sup>BuO• mediated H atom abstraction [22,23,25]. Alternatively, the hypervalent iron oxo (Fe<sup>V</sup> O) perferryl species from heterolytic scission of the O–O bond in [(tpfc) Fe<sup>IV</sup>–O–O<sup>t</sup>Bu] may be involved as the H atom abstractor [26]. However, the second possibility may be excluded on the basis of very high reactivity of (Fe<sup>V</sup>O)corrole transients, which has been confirmed recently [27]. Here, the tertiary carbon atoms of adamantane are more prone to oxidation than secondary ones (Table 1), which suggests that radicals are directly involved in abstracting hydrogen atoms of the C-H groups [22,23]. It can be explained in terms of the 'radical strength' of <sup>t</sup>BuO• (97 kcal/mol) [28] 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 <sup>t</sup>BuOO• (83 kcal/mol) is not enough

Table 1	
[Fe <sup>IV</sup> (tpfc)Cl] catalyzed hydroxylation of alkanes with <i>t</i> -BuOOH at 298 K.	

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

<sup>a</sup> Yields are based on concentration of oxidant.

<sup>b</sup> Moles of product/moles of catalyst.

to abstract an H atom from cyclohexane, it can provide the <sup>t</sup>BuO• 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 [29] of two secondary peroxyl radicals (Eq. 1). The formation of excess ketones over alcohol under aerobic condition explained via Eq. 2 (cross reaction).

$$2 \xrightarrow{\text{CHOO}} \xrightarrow{\text{CHOOOOCH}} \xrightarrow{\text{CHOH}} \xrightarrow{\text{CHOH}} + \xrightarrow{\text{CHOH}} = 0 + 0_2 \qquad (1)$$

$$Me_3COO^{\bullet} + CHOO^{\bullet} \longrightarrow Me_3COH + C=O + O_2$$
 (2)

The plausible reaction mechanism supporting all these results obtained in the present case has been shown in Scheme 1. The catalytic cycle involves the following steps: (a) formation of [(tpfc) Fe<sup>IV</sup>–O–O<sup>t</sup>Bu] intermediate upon addition of TBHP in acetonitrile; (b) the O–O bond homolysis forming <sup>t</sup>BuO• and a lesser reactive (particularly with regards to epoxidation) [(tpfc)Fe<sup>IV</sup>–OH]; (c) <sup>t</sup>BuO• radical mediated reactions following H atom abstraction from cyclohexane and TBHP; (d) formation of cyclohexanol and cyclohexanone *via* the Russel-type radical termination.

This catalytic system was applied to alkenes to gain further insight into the reaction pathways. Cyclohexene and styrene were chosen as substrates and have been found to be oxidized by iron corrole/*t*-BuOOH. The results are compiled in Table 2.

Allylic oxidation has been found to be favoured over epoxidation in the case of cyclohexene. Under aerobic condition higher amount of ketone was obtained (A/K = 0.39), whereas under argon atmosphere alcohol and ketone were formed in roughly 1:1 ratio (A/K = 0.8). Small amount of epoxide (<10%) has been obtained in the oxidation of cyclohexene by aqueous TBHP under both aerobic and anaerobic conditions (Table 2). Under the proposed reaction route, the formation of epoxide is expected to be at minimum. The <sup>t</sup>BuOO• radicals are



Cyclonexanol + Cyclonexanone

**Scheme 1.** Plausible reaction route for the oxidation of cyclohexane with  $[Fe^{IV}(tpfc)Cl]$  and *t*-BuOOH.

[Fe<sup>IV</sup>(tpfc)Cl] catalyzed oxygenation of alkenes with *t*-BuOOH at 298 K.

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

<sup>a</sup> Yields are based on concentration of oxidant.

known to yield epoxides in the presence of water [30,31]. 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 <sup>t</sup>BuO• radical in anhydrous media. It is noteworthy that perferryl intermediate, generated by heterolytic scission of the O–O bond in [(tpfc)Fe<sup>IV</sup>–O–O<sup>t</sup>Bu] is expected to be efficient in epoxidizing alkenes. Therefore, the above result indicates the absence of the hypervalent iron oxo (Fe<sup>V</sup> O) perferryl species in the present oxidizing system. Furthermore, the oxidation of cyclohexene is almost quenched in presence of radical scavenger 2,4,6-tri *tert*-butyl phenol (TTBP) producing only 2-cyclohexene-1-ol (7%) confirming the involvement of radical, generated from the homolytic scission of the O–O bond.

In [Fe<sup>IV</sup>(tpfc)Cl] catalyzed oxidation of styrene under aerobic condition, higher amount of benzaldehyde (80%) was obtained. But the same reaction under an argon atmosphere yielded styrene oxide (49%) together with 41% of benzaldehyde. In both cases a small amount of phenyl acetaldehyde was obtained.

Higher selectivity for benzaldehyde can also be explained in terms of Scheme 1. Tert-butyl hydroperoxide is known to undergo homolytic cleavage of the peroxide O–O bond on coordination to the central iron resulting in formation of alkoxy radicals and poorly reactive intermediate [(tpfc)Fe<sup>IV</sup>–OH] which is responsible for the low yields of epoxide [32]. The alkoxy radicals initiate a free-radical reaction that is propagated by the oxygen present in the reaction medium, leading to the formation of benzaldehyde [33]. When the reaction was carried out under an inert atmosphere, the selectivity for styrene oxide improved (Table 2). Thus the presence of oxygen in the reactions directly influences the benzaldehyde/epoxide ratio confirming the free-radical mechanism for the formation of benzaldehyde. The formation of styrene oxide under anaerobic conditions indicates the presence of at least one more key intermediate and suggests that competitive pathways are operative in iron corrole catalyzed oxidation of hydrocarbons with t-BuOOH [20].

#### 4. Conclusions

[Fe<sup>IV</sup>(tpfc)Cl] complex emerged as good catalyst in oxygenation of both alkanes and alkenes in acetonitrile at room temperature. To the best of our knowledge, the catalytic activity of the metallocorrole complexes with mild *t*-BuOOH has been reported here for the very first time. The results demonstrated the involvement of t-BuO• as the hydrogen abstracting species. The present work may provide important insights into the role of iron corroles/H<sub>2</sub>O<sub>2</sub> system in biomimetic sulfoxidation reactions [34] and also its role as promising cytoprotective agent against oxidative and nitrative stress [35].

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