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Mild oxidation of hydrocarbons by *tert*-butyl hydroperoxide catalyzed by electron deficient manganese(III) corroles

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ABSTRACT

Mild oxidations of alkenes with *tert*-butylhydroperoxide catalyzed by electron deficient manganese(III) corroles have been achieved 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[•]) radicals and organo-hydroperoxide (ROOH). A reaction mechanism is proposed based on the experimental results.

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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 dedicated to develop synthetic homogeneous catalysts for selective oxygenation of hydrocarbons under mild conditions [1–8]. In this direction transition metal complexes of porphyrins, tetradentate diamine-dipyridine, phthalocyanines, 1,4,7-triazacyclononane and Schiff bases have been explored as oxidation catalysts [9–15]. Much effort has been focused on metalloporphyrins in the search of efficient catalyst to promote oxygenation of hydrocarbons under mild conditions [16–18]. Metal complexes of corroles, tetrapyrrolic macrocycle with one meso carbon short from porphyrin skeleton, are emerging as an important group of catalysts in recent years [19–34]. Among the metallocorroles, manganese(III) corroles have received more attention as catalysts in hydrocarbon oxidation [31–34]. Gross and co-workers first demonstrated that manganese(III) complex of 5,10,15-tris(pentafluorophenyl) corrole, [Mn(III)(tpfc)], catalyzes oxidation of styrene with PhIO [31]. Later the β -pyrrole-halogenated manganese(III) complexes, [F₈Mn(III)(tpfc)] [32] and [Br₈Mn(III)(tpfc)] [33], were used for catalyzing the oxidation of alkenes by iodosylbenzene and both the complexes emerged as better catalysts than complex [Mn(III)(tpfc)]. Recently 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 [34]. All

the manganese(III) corrole catalyzed oxygenation of hydrocarbons reported so far are only limited to the oxidation of alkenes [31–35] but catalytic alkane oxidation by manganese(III) corrole is yet to be explored. On the other hand, iodosylbenzene has been used as the only terminal oxidant in oxygenation of hydrocarbons catalyzed by manganese(III) corrole [31–34]. No report on manganese corrole catalyzed hydrocarbon oxidation with any mild terminal oxidant is available in the literature, although hydrogen peroxide has been employed in asymmetric sulfoxidation catalysed by albumin-conjugate manganese(III) corrole [35]. Recently manganese(III) corrole has emerged as an efficient decomposition catalyst for peroxynitrite to benign products *in vitro* and *in vivo* studies [36–39]. 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 [40,41]. 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 [39]. The catalytic behaviour of amphiphilic manganese(III) corrole towards hydrogen peroxide also follows the similar pattern [35]. In this context it is worthy to investigate the reactivity of manganese(III) corrole towards alkylhydroperoxide.

Herein we wish to report the catalytic reactivity of a group of electron deficient manganese(III) corroles in oxidizing alkanes and alkenes with mild *tert*-butyl hydroperoxide at room temperature. The present work provides the first ever application of *tert*-butyl hydroperoxide as terminal oxidant in manganese(III) corrole catalyzed hydrocarbon oxygenation reactions. The rate

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constant for the reaction between the Mn(III) corroles and the *tert*-butyl hydroperoxide has been measured. A plausible reaction mechanism has been proposed on the basis of experimental results.

2. Experimental

Acetonitrile and dichloromethane were distilled under argon from CaH₂ and CaCl₂ 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, 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.

2.1. Synthesis of the complexes

The syntheses of the free base corroles, 5,10,15-tris(2,6-difluorophenyl)corrole (tdfc) and 5,10,15-tris(pentafluorophenyl)corrole (tpfc) were carried out by using 'solvent free' condensation of pyrrole and the respective aldehydes introduced by Gross et al. [42]. The complex [Mn(III)(tdfc)] (**1**) was synthesised from Mn(OAc)₂·4H₂O and the corresponding ligand in refluxing DMF (10 mL) and the green product was purified by preparative TLC on a silica gel plate using 1:1 dichloromethane/hexane as the eluant.

[Mn(tdfc)] (**1**): yield: 85%. Anal. Calcd for C₃₇H₁₇N₄F₆Mn: C, 64.73; H, 2.50; N, 8.16. Found: C, 64.81; H, 2.37; N, 8.25; MS (Cl⁺, isobutane): *m/z* (%): 686 (100) [M⁺]; UV-vis (CH₂Cl₂): λ_{max} [nm] (log ε) = 400 (4.55), 416 (4.53), 487 (4.14), 622 (4.01).

The complexes [Mn(III)(tpfc)] (**2**) and [Br₈Mn(III)(tpfc)] (**3**) were prepared following reported methods [31,33]. The elemental analytical and spectral data are in agreement with those reported in the literature [31,33].

2.2. Catalytic experiments

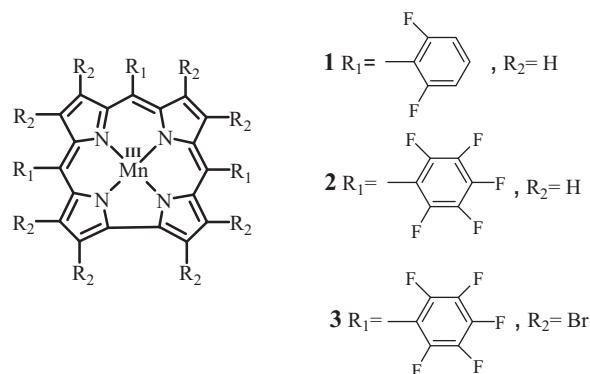
Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction 25 μM of catalyst and 200 mM (100 mM in case of adamantane) of substrate were dissolved in 2 mL of acetonitrile (argon saturated in case of anaerobic reactions) or 3:2 acetonitrile/dichloromethane in case of adamantane. The oxidation reaction was initiated by adding 2 mM of *t*-BuOOH and the contents were magnetically stirred. 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.

2.3. Kinetic measurements

In a typical kinetic experiment a cuvette fitted with silicon rubber septa was degassed by blowing argon over it for 15 min. Degassed acetonitrile (2 mL) was taken in the cuvette. Micromolar amount of [Mn(III)(tpfc)] in acetonitrile was treated with millimolar amount of *t*-BuOOH. The cell was vigorously shaken and was placed immediately in a thermostatted cell holder in a spectrophotometer and the absorbance data at 470 nm were collected at 5-s intervals. Absorbance vs. time plots have been analyzed in details in the main body of this paper.

2.4. Product analysis

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 dodecane as internal standard. The identification and quantification of the



Scheme 1. Manganese(III) corrole catalysts used in this study.

products were done from the response factors of standard product samples.

3. Results and discussion

The catalytic activities of the manganese(III) corroles (**1–3**) (Scheme 1) for hydrocarbon oxidation were examined with *tert*-butylhydroperoxide at room temperature.

3.1. Catalytic oxidation of alkenes

At room temperature all the three manganese(III) corroles (**1–3**) emerge as effective catalysts in oxidizing cyclohexene with mild *tert*-butylhydroperoxide (*t*-BuOOH) under both aerobic and anaerobic conditions (Table 1).

The complete oxidation of cyclohexene is achieved within 6 h in presence of dioxygen, whereas it takes 24 h 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% [33]. The performance of catalyst **3** in the present oxidizing system is more selective than its reported performance with PhIO [33].

It is observed that if the reaction mixture is finally treated with excess PPh₃ before the GC analysis, the resulting product pattern drastically differs from that obtained prior to PPh₃ addition. After the reduction, 2-cyclohexen-1-ol becomes the major product whereas 2-cyclohexen-1-one appears as minor product (Table 1). Since alkyl hydroperoxides are known to be readily and quantitatively reduced by PPh₃ to yield the corresponding alcohols [43], 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 [31–34]. The present results significantly differ from the product pattern of alkene oxidation by manganese(III)corrole/PhIO system and point towards the involve-

Table 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	1	Air	12	82	1
		Argon	20	67	8
		Air	14	83	2
	2	Argon	30	61	7
		Air	12	81	2
	3	Argon	18	64	6
				Styrene oxide	Benzaldehyde

^a Yields are represented with respect to the concentration of the oxidant.

^b Yields within braces after reduction with PPh₃ prior to GC analysis.

ment of radicals rather than the participation of the metal-oxo species.

3.2. 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 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 prior to GC analysis shows complete reversal of the product pattern, i.e., cyclohexanol becomes the major product for all the three catalysts (Table 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 [44–47]. Furthermore, considerable efforts have been devoted to introduce the hydroxyl group directly into poorly reactive adamantane tricycles [48] due to the impor-

tance of hydroxylated adamantane derivatives in pharmaceutical, polymers and electronic industry. The catalytic reactions were carried out in 3:2 acetonitrile/dichloromethane medium due to the limited solubility of adamantane in pure acetonitrile. The results are summarized in Table 2. The present catalytic system oxidises 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 catalysts.

3.3. Catalytic oxidation of toluene

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 toluene is highly desirable. Under ambient condition the present oxidizing system oxidises toluene 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 [49]. Among the manganese(III) corroles, catalyst **1** has been found to be most effective in bringing about oxidation of

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

Substrate	Time (h)	Catalyst	Product profile (%) ^{a,b}		
			Cyclohexanol	Cyclohexanone	
Cyclohexane	6	1	4 [9]	9 [5]	
	6	2	5 [12]	13 [6]	
	6	3	6 [14]	16 [8]	
Adamantane	20	1	10	2	
		2	12	1	
		3	15	1	
	20			Adamantane-1-ol	Adamantane-2-ol
Toluene	18	1	24 [7]	3 [19]	
		2	22 [8]	2 [16]	
		3	21 [8]	2 [14]	
			Benzaldehyde	Benzyl alcohol	

^a Yields are represented with respect to the concentration of the oxidant.

^b Yields within braces after reduction with PPh₃ prior to GC analysis.

toluene and the relative activity of the catalysts follows the order $1 > 2 > 3$.

3.4. 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 [31]. 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 [51]. 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–vis absorption spectral profiles of catalysts **1–3** in acetonitrile are shown in Fig. 1. On addition of *t*-BuOOH to the manganese(III) corroles, the split Soret band disappears and new bands are generated at 410 nm and 350 nm as shown in Fig. 2. 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 [31] 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. Also, in case of oxidation of adamantane, the tertiary carbon atoms are preferentially activated over the secondary ones pointing towards the involvement of radicals. The plausible reaction mechanism supporting all these results obtained in the present case has been shown in Scheme 2. It seems reasonable that the manganese(III) corroles (**1–3**) with *t*-BuOOH form hydroxo-Mn(IV) species along with *tert*-butoxyl radical (step 1). The

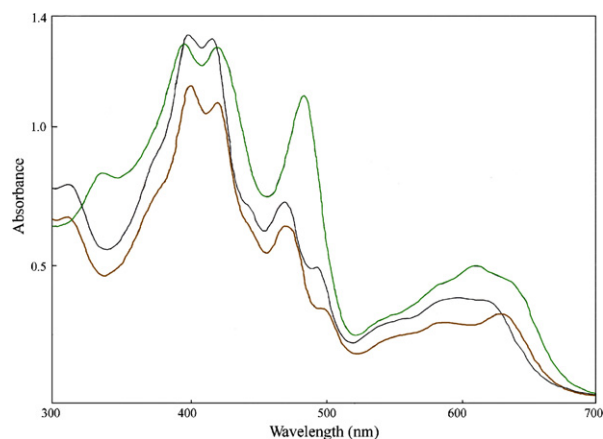
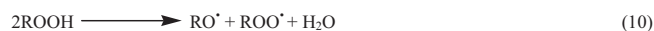
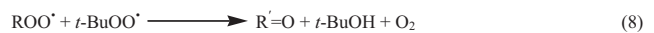
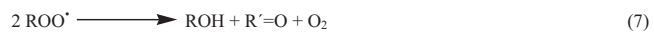
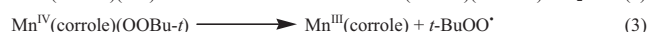
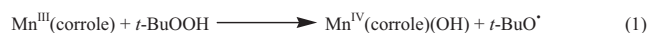


Fig. 1. Uv–vis spectra of catalysts **1** (brown), **2** (black) and **3** (green) in acetonitrile at $25 \pm 1^\circ\text{C}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



Scheme 2. Simplified pathway for the oxidation of hydrocarbons by *t*-BuOOH in the presence of manganese(III) corroles.

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) [52–55]. The *tert*-butoxyl radical

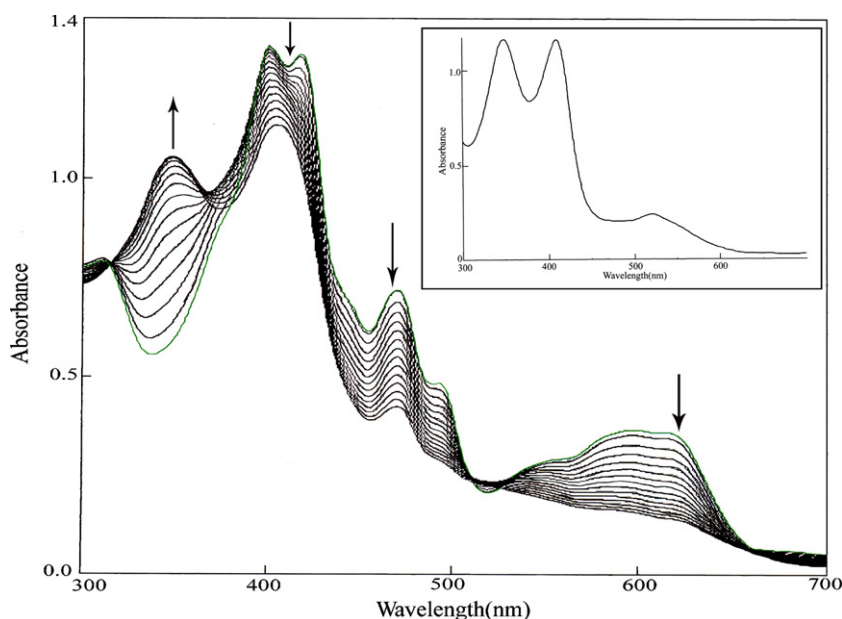


Fig. 2. Overlay spectra of the catalyst **2** (25 μM) and TBHP (2 mM) in acetonitrile at $25 \pm 1^\circ\text{C}$ (successive spectrum taken after 3 min intervals). Inset: electronic spectrum of (oxo)Mn(V) species generated *in situ* by the reaction of [Mn(III)(tpfc)] and PhIO.

Table 3

Values of $(dA/dt)_0$ at $\lambda = 470$ nm for the oxidation of $[Mn(III)(tpfc)]$ by t -BuOOH in acetonitrile at $25 \pm 1^\circ C$.

Entry	$[t\text{-BuOOH}]/10^{-3} \text{ mol dm}^{-3}$	$[Mn(III)(tpfc)]/10^{-6} \text{ mol dm}^{-3}$	$(dA/dt)_0/10^{-5} \text{ s}^{-1}$
1	1.04	35	6.407
2	1.92	35	10.382
3	2.88	35	13.924
4	3.84	35	17.463
5	1.92	18	6.019
6	1.92	30	10.926
7	1.92	50	15.601
8	1.92	76	19.682

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 [56] 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) [43,57]. This species can then undergo homolytic decomposition to the organooxyl RO^\bullet radical (step 10) followed by its H-abstraction from the hydrocarbon forming the alcohol ROH and R^\bullet (step 11). 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. [11,43,58,59].

3.5. Kinetic studies

The transformation of manganese(III)-corrole to manganese(IV) intermediate proceeds slowly, which is evident from Fig. 2. The rate constants for the above transformation by t -BuOOH were measured in acetonitrile. The change of absorbance at 470 nm 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 [60–62]. Values of the initial rate $(dA/dt)_0$ for the reactions are compiled in Table 3.

The values of $(dA/dt)_0$ are plotted against $[t\text{-BuOOH}]$ at constant $[Mn(III)(tpfc)]$ as shown in Fig. 3. Again, the plot of $(dA/dt)_0$ vs. $[Mn(III)(tpfc)]$ at fixed $[t\text{-BuOOH}]$ is displayed in Fig. 4. It is clear from both the plots that the rate $(dA/dt)_0$ for the reaction is lin-

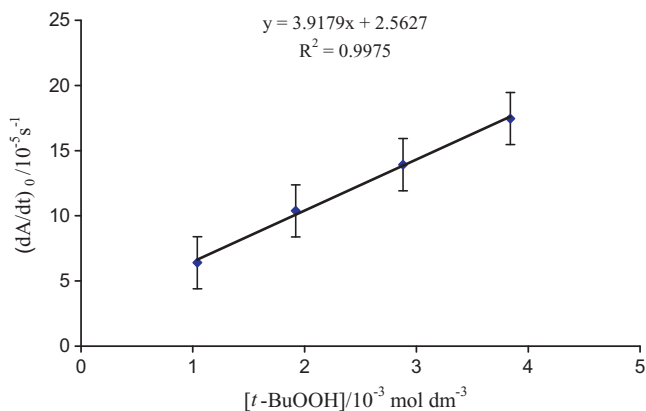


Fig. 3. Plots of $(dA/dt)_0$ against $[t\text{-BuOOH}]$ at fixed $[Mn(III)(tpfc)]$ in acetonitrile at $25 \pm 1^\circ C$.

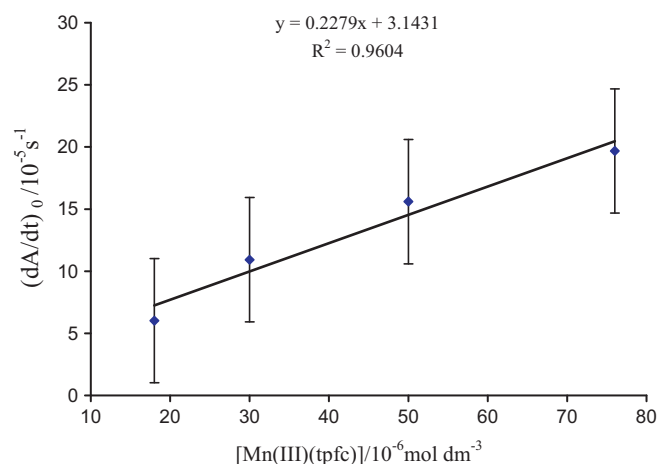


Fig. 4. Plots of $(dA/dt)_0$ against $[Mn(III)(tpfc)]$ at fixed $[t\text{-BuOOH}]$ in acetonitrile at $25 \pm 1^\circ C$.

ear in $[t\text{-BuOOH}]$ as well as in $[Mn(III)(tpfc)]$. The first order rate constants obtained from Figs. 3 and 4 are 0.0392 s^{-1} and 2.279 s^{-1} respectively. The overall the reaction can be expressed as

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

where k_d is the second order rate constant. The value of k_d from the slope of the $(dA/dt)_0$ vs. $[t\text{-BuOOH}]$ at constant $[Mn(III)(tpfc)]$ is $1.1197 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ while from the slope of the $(dA/dt)_0$ vs. $[Mn(III)(tpfc)]$ at constant $[t\text{-BuOOH}]$ a value of k_d of $1.187 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ 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.

4. 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 catalyzed 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 [37,43–45] that proceed with the participation of alkylperoxy (ROO^\bullet) radicals and organo-hydroperoxide (ROOH). During oxidation by the present oxidizing system, the involvement of the organo-hydroperoxide (ROOH) has been confirmed. In contrast with the catalytic behaviour of manganese(III) corrole towards peroxyinitrite 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.

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