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Catalysis Communications



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Short Communication

Electron deficient manganese(III) corrole catalyzed oxidation of alkanes and alkylbenzenes at room temperature

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A R T I C L E I N F O

Article history: Received 10 December 2010 Received in revised form 19 April 2011 Accepted 22 April 2011 Available online 30 April 2011

Keywords: Manganese Corrole Catalysis Oxygenation Alkane

ABSTRACT

At room temperature electron deficient manganese (III) corrole complexes (1–3) were successfully employed as catalysts in the oxidation of alkanes and alkylbenzenes using *m*-chloroperbenzoic acid (*m*-CPBA) as the terminal oxidant. Adamantane has been selectively hydroxylated to adamantane 1-ol and 2-ol with higher preference for the tertiary position. Cyclohexane has also been oxidized. The present oxidizing system also oxidizes toluene, ethylbenzene and diphenylmethane. High valent oxomanganese(V) species has been proposed to be the active oxidant. The high-valent oxomanganese(V) corrole undergoes hydrogen atom transfer (HAT) reaction with 2,4,6-tri-t-butylphenol (TTBP) resulting in the formation of oxidized phenoxyl radicals. Kinetic studies have led to the determination of second-order rate constants for the hydrogen atom transfer reactions. The kinetic experiments reveal a first order reaction rate dependence on the concentration of catalyst as well as on that of the oxidant.

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1. Introduction

The oxidative functionalization of saturated hydrocarbons to more valuable products is of great interest in synthetic organic chemistry and industrial chemistry [1,2]. The inertness of alkanes towards chemical conversion demands a great deal of effort to develop efficient catalysts operating at ambient conditions [3]. Considerable attention has been focused on a variety of coordination complexes to utilize them as efficient homogeneous catalysts for oxygenation of hydrocarbons. In this direction transition metal complexes of porphyrins, phthalocyanines, chlorins, triazacylononanes and Schiff bases have been explored as homogeneous catalysts for oxygenation of alkanes and alkenes [4-6]. Metalloporphyrin catalyzed oxidation of hydrocarbons has been most extensively studied [7-9]. Corrole, another tetrapyrrolic macrocycle similar to porphyrin, is gaining importance due to the applications of its metallo-derivatives as catalysts in diverse areas like oxygenation of organic compounds, cyclopropanation and aziridination [10–12]. The metallocorrole catalyzed hydrocarbon oxidation is mainly confined to iron-corrole and manganese-corrole systems [12] and the only other instance is photocatalytic oxygenation of cumene by difluoroantimony(V)corrole [13]. Manganese corroles have evoked more interest than iron-corroles as catalysts in hydrocarbon oxidation [12,14–16]. The synthesis of manganese(III) complex with 5,10,15tris(pentafluorophenyl)corrole, [Mn(III)(tpfc)], and its successful use as catalyst in the oxidation of styrene with PhIO were first reported by Gross et al. [14]. The substitution of the β -pyrrolic hydrogens of corrole macrocycles with bromine [15] or fluorine [16] enhances the catalytic activity of the manganese(III) corroles in terms of yield and reaction time. The catalytic activity of (tpfc)Mn(V)O in alkene oxidation has been found to be enhanced by the axial coordination with imidazole [17].

Despite considerable progress in manganese(III) corrole catalyzed alkene oxidation, only one report on the catalytic oxygenation of alkanes by manganese(III) corrole has appeared so far [18].

In continuation of our earlier work [18–21] on metallocorrole catalyzed oxidation of hydrocarbons, here we wish to report the manganese(III) corrole catalyzed oxygenation of adamantane, cyclohexane, toluene, ethylbenzene and diphenylmethane at room temperature with *m*-CPBA as terminal oxidant. The kinetic studies of the present oxidizing systems with 2,4,6-tri-*t*-butylphenol (TTBP) have also been undertaken. A plausible reaction mechanism has been proposed on the basis of experimental results.

2. Experimental

2.1. Instrument and reagents

Acetonitrile and dichloromethane were distilled under argon from CaH_2 and $CaCl_2$ and stored over molecular sieves (4 Å). 2,4,6-tri-t-butyl phenol (TTBP) and *m*-CPBA were purchased from Aldrich and purified accordingly [22]. Other substrates, all the reaction products and dodecane (internal standard) were purchased from Aldrich and used as received. The exact active oxygen content of the oxidant was determined iodometrically prior to use. UV-vis spectral measurements

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^{1566-7367/\$ -} see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.catcom.2011.04.026

were taken with a JASCO V 530 spectrophotometer connected with a thermostat at $25 \pm 1^{\circ}$ C.

The product analysis was done by Perkin Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column) by injecting 1 μ L aliquot from the reaction vial taken after addition of dodecane as internal standard. The identification and quantification of the products were done from the response factors of standard product samples.

2.2. Synthesis of the catalysts

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 described by Gross et al. [23]. The respective manganese(III) corroles were prepared by refluxing the free base corrole with Mn(OAc)₂. 4H₂O in DMF [14,18]. Perbrominated manganese(III) corrole [Br₈Mn(III)(tpfc)] (**3**) was prepared and characterized following the reported procedure [15].

2.3. Catalytic oxidation

Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction $25 \,\mu$ M of catalyst and 200 mM (100 mM in case of adamantane) of substrate were dissolved in 2 mL of acetonitrile or 3:2 acetonitrile/dichloromethane in case of adamantane. The oxidation reaction was initiated by adding 2 mM of *m*-CPBA and the contents were magnetically stirred. After periodic time intervals standard solution of dodecane was added to this reaction mixture and an aliquot was injected into a capillary column of a preheated GC.

2.4. Kinetic measurements

In a typical kinetic experiment, TTBP (24 mg, final concentration 44 mM) was taken in a cuvette fitted with silicon rubber septa. The

cuvette was degassed by blowing argon over it for 15 min. Degassed acetonitrile (2 mL) was used to dissolve the TTBP in the cuvette. A standard solution of [Mn(III)(tpfc)] in acetonitrile was added so that the final concentration of the catalyst was 13 μ M. The *m*-CPBA was prepared in degassed acetonitrile (20 mg in 2 mL). An aliquot volume (44 μ L) 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.

3. Results and discussion

3.1. Catalytic activity studies

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

The reason behind the choice of adamantane as a substrate is based on the fact that the oxidation of adamantane is a useful probe to test the regioselectivity between tertiary (3°) and secondary (2°) C—H bonds [24]. Moreover, there is a wide applicability of its hydroxylated derivatives in pharmaceutical intermediates, polymers and electronic industry [25]. However, the conversion of relatively inert C—H bond of adamantane tricycles to C—OH bond is quite difficult [25]. The present oxidizing system selectively oxidizes adamantane to the corresponding adamantanols at room temperature with a strong preference for the hydroxylation at the tertiary centre. The Mn(III) corrole complexes (1–3) have emerged as almost equally efficient catalysts, affording a total yield of 38% to 42% of adamantanols within 2 hours. The results are summarized in Table 1. The reactions showed selectivity for oxidation at the tertiary position, with a $3^{\circ}/2^{\circ}$ ratio of $7 \cdot 5 - 8 \cdot 7$ (normalized on a per-hydrogen basis).

These results encouraged us to examine the catalytic oxygenation of cyclohexane with manganese(III) corrole by *m*-CPBA. Under these reaction conditions cyclohexane has been converted to cyclohexanone



Fig. 1. Manganese(III) corrole complexes employed in this study.

Table 1

Oxidation of alkanes and alkyl benzenes by Mn(III) corroles and m-CPBA.

Substrate	Time (h)	Catalyst	Product profile (%) ^a			
			Adamantane-1-ol		Adamantane-2-ol	
Adamantane	2	1	33		9	
	2	2	31		8	
	2	3	30		8	
			Cyclohexanol		Cyclohexanone	
Cyclohexane	2	1	4		2	
	2	2	10		2	
	2	3	12		3	
			Benzaldehyde		Benzyl alcohol	
Toluene	1	1	16	4		
	1	2	12		3	
	1	3	13		3	
			Phenyl acetaldehyde	1-phenyl ethanol	Acetophenone	
Ethylbenzene	2	1	9	4	2	
	2	2	12	8	6	
	2	3	15	9	5	
			Diphenylmethanol			
Diphenylmethane	2	1		20		
	2	2		26		
	2	3		29		

^a Yields are based on concentration of oxidant.

and cyclohexanol. In this case, the perbrominated Mn(III) corrole (3) has been found to be most effective catalyst affording cyclohexanol and cyclohexanone with A/K ratio of 4.0 (Table 1).

Oxidation of alkylbenzenes is important chemical transformations in chemical synthesis, which normally undergo with a low selectivity, with the formation of various by-products [26]. In general, oxidation of toluene usually affords benzaldehyde, benzyl alcohol, cresols, benzoic acid and dibenzyl and thus design of efficient process for the selective oxidation of toluene is highly desirable. With the present oxidizing system, toluene has been oxidized under ambient condition to form benzaldehyde as the major product, while benzyl alcohol is generated as the minor one. No oxidation of the aromatic ring was observed. The results summarized in Table 1 show that overall yields of 16% to 20% were achieved within 1 hour.

The present oxidizing system has also been found effective in oxidizing ethylbenzene and diphenylmethane at room temperature. Ethylbenzene has been converted into phenylacetaldehyde, 1-phenylethanol and acetophenone (Table 1). The reaction proceeded with a greater selectivity for the formation of phenylacetaldehyde and highest conversion (29%) has been achieved with the catalyst **3**. The formation of phenylacetaldehyde in the present case is surprising. This may arise from the oxidation of ethylbenzene to styrene, followed by the oxidation of styrene by the present oxidizing system.

Diphenylmethane, on the other hand, is selectively oxidized to diphenylmethanol (Table 1). Significantly, acetophenone, the over oxidized product, was not at all detected under the reaction conditions employed. Among the manganese(III) corroles, catalyst **3** has been found to be most effective in bringing about oxidation of diphenylmethane; the relative activity of the catalysts follows the order $\mathbf{3} \rightarrow \mathbf{2} \rightarrow \mathbf{1}$.

The overall yield of the oxidized products has been found to be moderate. However, the total amount of oxidant may be accounted for by considering the pronounced anti-oxidant property of the manganese(III) corroles [27,28]. It has been demonstrated that manganese(III) corroles effectively decompose reactive oxygen species and this aspect has been receiving continuous attention for its potential application in combating against several neurodegenerative disorders [28].

3.2. Mechanistic considerations

High valent oxomanganese corroles have been frequently invoked as the key oxidant in the manganese(III) corrole catalyzed oxidation reactions with iodosylbenzene as the oxidant [14–17]. It has been established that manganese(III) corroles react with PhIO and form oxomanganese(V) species. However, the lack of reactivity of this oxospecies towards oxygenation reactions led to the proposal that a high valent Mn(VI)O species, generated by disproportionation of Mn(V)O, is the active oxidant [14,17]. Oxomanganese corroles have been shown to be effective oxo-transfer agents towards olefinic substrates like cyclohexene and styrene [14–17]. Very recently, Kumar et al. reported oxygen atom transfer reactions from isolated oxomanganese(V) corroles to organic sulfides [29]. However, C—H bond activation of alkanes using high-valent oxomanganese corroles is still unknown.

Treatment of the manganese(III) corroles (1-3) with *m*-chloroperbenzoic acid (*m*- CPBA) in acetonitrile medium at room temperature results in the formation of the oxomanganese(V) species [14]. The UVvis spectral change brought about by the treatment of *m*-CPBA to [Mn(III)(tpfc)] (**2**) has been shown in Fig. 2.

Titration experiments reveal that the characteristic peaks of the catalyst **2** gradually disappear on addition of *m*-CPBA with emergence



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

Table 2
[Mn(III)(tpfc)]-catalyzed oxidation of TTBP by <i>m</i> -CPBA in acetonitrile at 25 ± 1 °C

Entry no.	TTBP (mM)	Catalyst (µM)	Oxidant (mM)	$(dA/dt)_0$ s ⁻¹ ×10 ⁴	Yield (%) ^a	Catalyst survival (%)
1	17.53	12.97	0.96	7.922	89.40	Bleached
2	20.40	12.97	0.97	10.029	93.30	Bleached
3	31.24	12.98	0.98	12.958	96.02	24
4	42.48	12.97	0.97	21.052	98.75	48
5	60.97	12.97	0.98	29.832	99.93	59
6	83.83	12.97	0.97	28.227	99.20	65
7	95.26	12.97	0.96	28.021	98.50	82
8	106.69	12.97	0.96	26.926	97.40	88
9	162.85	12.97	0.97	25.034	84.26	93
10	44.82	13.02	0.97	23.522	98.90	-
11	44.55	28.02	0.98	28.295	99.40	-
12	44.58	37.68	0.97	32.827	99.76	-
13	44.28	51.72	0.98	34.511	99.25	-
14	44.02	12.97	0.96	22.859	99.12	-
15	44.15	12.97	1.92	24.947	95.51	-
16	44.11	12.97	2.91	27.607	88.47	-
17	44.08	12.97	3.84	29.993	80.15	-

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

of new peaks at 348 nm, 410 nm and 518 nm. It has been observed that the complete conversion of the manganese(III) corrole to the oxomanganese(V) species requires two equivalents of *m*-CPBA.

3.3. Kinetics of the catalytic reactions

The formation of oxomanganese(V) corrole having been confirmed in the present oxidizing system, we decided to follow the kinetics of the reaction with 2,4,6-tri-butylphenol (TTBP) as the substrate. The rationale behind the choice of this particular substrate was its ability to form stable phenoxyl radical via formal H-atom abstraction, which could easily be identified by UV-vis spectroscopy [30,31]. It is noteworthy that $Mn^V \equiv O$ unit is a potentially important intermediate in Photosystem II and is responsible in hydrogen atom transfer (HAT) processes with a nearby tyrosyl radical [32]. Moreover, HAT reactions of TTBP with imidomanganese(V) corrole [33] and oxomanganese(V) corrolazine [34] have been reported recently and the reaction provided significant insight into a wide range of enzymatic and synthetic processes involving high-valent metal-oxo intermediates.

The rate of the catalyst oxidation with *m*-CPBA was studied using 2,4,6-tri-*t*-butylphenol (TTBP) under argon atmosphere. The formation of oxidized product 2,4,6-tri-*t*-butylphenoxy radical was monitored by measuring its absorbance at 630 nm (\equiv 385 mol⁻¹ cm⁻¹) [30,31]. The yield of the radical was found to be dependent on substrate (TTBP) concentration. It has been observed that a minimum concentration of 40 ± 5 mM of TTBP is required to trap all the reactive intermediates in these reactions in acetonitrile. At lower concentration







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

tion 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 (entry 9). It is clear from Table 2 that considerable catalyst bleaching takes place at lower concentration of TTBP (entries 1–5). The highest catalytic activity of manganese(III) corrole has been observed in the range of 30 to 100 mM substrate concentration.

The kinetic plot of absorbance at 630 nm vs. time is shown in Fig. 3 as a representative case. The absorbance vs. time plot (Fig. 3) shows that the increase in absorbance does not fit with a simple first or second order kinetic trace.

Therefore, the data obtained were analyzed by 'Initial-rate' method [35]. All runs were carried out in at least duplicates and the values of (dA/dt)0 given in the tables are the average of the runs. The values of (dA/dt)0 at varying initial concentrations of the reaction components are presented in Table 2. The plot of (dA/dt)0 vs. [m-CPBA] at constant [Mn(III)(tpfc)] and that of (dA/dt)0 vs. [Mn(III)(tpfc)] at fixed [m-CPBA] are shown in Figs. 4 and 5 respectively. It is clear that the data are best fitted by a first order dependence of (dA/dt)0 on the concentration of m-CPBA (Fig. 4) and also on the concentration of catalyst [Mn(III)(tpfc)] (Fig. 5).

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

$$dA/dt \propto [m-CPBA] [Mn(III)(tpfc)]$$
 (1)

From the slope of the (dA/dt)0 vs. [m-CPBA] at constant [Mn(III)(tpfc)], second order rate constant $1.93 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ is obtained whereas the (dA/dt)0 vs. [Mn(III)(tpfc)] plot at constant [m-CPBA] gives a value of $3.08 \times 104 \text{ dm}^3 \text{ mol}^{-1}$. Lower value of the second order rate constant in the first case may be rationalized in terms of greater degree of catalyst bleaching at higher concentration of the oxidant.



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



Scheme 1. Manganese(III) corrole catalyzed oxidation of 2,4,6-tri-t-butylphenol.

The proposed route for the HAT process has been outlined in Scheme 1. The (oxo)manganese(V) corrole generated *in situ* by the reaction of manganese(III) corrole and peracid oxidizes the phenol (TTBP), via a formal hydrogen-atom abstraction and itself converts to Mn^{IV}–OH species. The involvement of similar species has been proposed in case of the hydrogen-atom abstraction of phenols by high-valent manganese(V)-oxo corrolazine [34]. The putative Mn^{IV}–OH species is itself highly reactive [34] and abstracts a hydrogen atom from another molecule of TTBP regenerating the manganese(III) corrole (Scheme 1). An alternative mechanism that can account for the phenol oxidation in the present case involves the disproportionation of the Mn^{IV}–OH producing the Mn(III) catalyst and the (oxo)manganese(V) corrole, that oxidizes the second phenol substrate. However, considering much greater reactivity of the Mn^{IV}–OH species than (oxo)manganese(V) species [34], this mechanistic pathway appears to be less favored.

4. Conclusion

It has been demonstrated for the first time that high-valent oxomanganese(V) corroles, generated from manganese(III) corroles, are capable of oxygenating unactivated C—H bonds of alkanes and alkylbenzenes. Adamantane undergoes exclusive hydroxylation and shows a relatively high degree of selectivity for tertiary C—H bonds over secondary C—H bonds (i.e., $3^{\circ}/2^{\circ} = 7.5-8.7$, normalized on a per-hydrogen basis). Toluene, ethylbenzene and diphenylmethane have also been found to be oxidized by the present catalytic system. The oxomanganese(V) corrole, despite having low redox potential, has been found to be capable of performing hydrogen atom transfer

(HAT) reaction with 2,4,6-tri-*t*-butylphenol. Kinetic investigations with 2,4,6-tri-*t*-butylphenol reveals a first order rate dependence on the concentration of the catalyst as well as on that of the oxidant. The results further supports the conclusion of Goldberg et al. that oxomanganese(V) transients are effective in HAT processes despite having very low redox potentials [34].

Acknowledgments

The financial support (SR/S1/IC-08/2007) from DST, Government of India, is gratefully acknowledged. We thank UGC (India) for the award of fellowships to SB and AP.

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