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Editor's Choice paper

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 ($ROO^{\bullet}$) radicals and organo-hydroperoxide (ROOH). A reaction mechanism is proposed based on the experimental results.

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, [F_8Mn(III)(tpfc)] [32] and [Br_8 Mn(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 CaH_2 and $CaCl_2$ 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 $Mn(OAc)_2 \cdot 4H_2O$ 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 $C_{37}H_{17}N_4F_6Mn$: C, 64.73; H, 2.50; N, 8.16. Found: C, 64.81; H, 2.37; N, 8.25; MS (CI^+, isobutane): *m*/*z* (%): 686 (100) [M^+]; UV–vis (CH_2Cl_2): λ_{max} [nm] ($\log \varepsilon$) = 400 (4.55), 416 (4.53), 487 (4.14), 622 (4.01).

The complexes [Mn(III)(tpfc)] (**2**) and [Br_8Mn(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

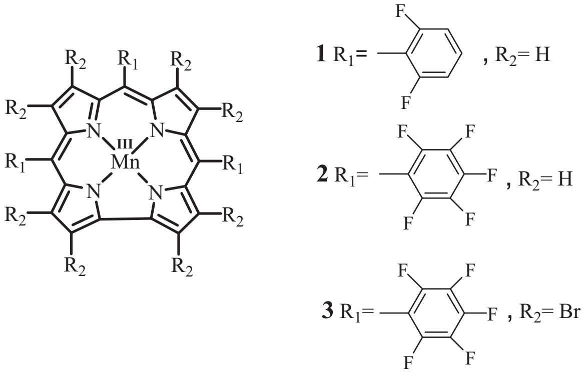
Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction 25 μM of catalyst and 200 mM (100 mM in case of adamantane) of substrate were dissolved in 2 mL of acetonitrile (argon saturated in case of anaerobic reactions) or 3:2 acetonitrile/dichloromethane 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 products were done from the response factors of standard product samples.



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

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 PPh_3 before the GC analysis, the resulting product pattern drastically differs from that obtained prior to PPh_3 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 PPh_3 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-