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Manganese(III) acetate mediated catalytic oxidation of substituted dioxolene and phenols

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ABSTRACT

Manganese(III) acetate is found to be an efficient catalyst to perform oxidation of 3,5-di-*tert*-butylcatechol (DTBC) to 3,5-di-*tert*-butylbenzoquinone (DTBQ) and 2-aminophenol (OAP) to 2-aminophenoxazinone (APX). The k_{cat} values are $1.72(2) \times 10^3$ and $2.8(2) \times 10^2$ h^{-1} for the formation of DTBQ and APX, respectively. The turnover number of APX formation is highest among the synthetic mimics. ESI-MS studies of DTBC oxidation suggest formation of a Mn^{IV} intermediate. Manganese(III) acetate is also capable of oxidative C—C bond coupling in sterically hindered phenols to form biaryls in 65–94% yield.

1. Introduction

Oxidation is a fundamentally important component of organic synthesis. For economic and environmental reasons, the oxidation processes of bulk chemical industries predominantly involve the use of molecular oxygen as the primary oxidant [1–5]. But, direct oxidation of organic substrates using molecular oxygen as the oxidant under mild conditions is still difficult and also most of the time the selectivity in the oxidation reaction is not always as controlled as needed. However, nature has designed enzymes that can efficiently and selectively oxidize substrates with the help of molecular oxygen to produce desired products. Many of these enzymes, which are metal based, are targets of bioinorganic chemists to design mimics in order to gain insight into the mechanism of the reaction. To understand the mechanism, the enzymes donor sites are modelled by the syntheses of metal complexes to mimic the immediate coordination environment. Such model complexes have provided us with immense insights in to the mechanism of action of the original enzymes and also showed new alternate pathways to form the same products.

Our quest was to probe if a simple metal complex which would be rather easily available can perform the action of oxidative enzymes viz. Catechol oxidase (CO) and Phenoxazinone Synthase (PHS). Many complex molecules have been designed so far which are not always accessible for demonstrating a catalytic reaction of the above type in the laboratory and hence, a commercially available efficient catalyst would be useful. Such cheaper systems may also find use in various synthetic methods.

CO is an enzyme which has been extensively studied by modelling the active site and incorporation of various metals viz. copper [6–28], iron [29–32], cobalt [33–40], manganese [41–54], and zinc [6,55] to probe catechol oxidase activity. PHS mimics cannot be found as much as CO but yet are well studied using 2-aminophenol as substrate [46,56–59]. Apart from biomimetics, quinone formation is also important since they are component of many dyes and pigments [60–62] and quinones of lower molecular weight may have potential in host–guest liquid crystal displays and optical recording [63]. On the other hand synthesis of the phenoxazinone chromophore is an important step in biosynthesis of the antibiotic actinomycin-D by Streptomyces antibioticus using the enzyme Phenoxazinone Synthase (PHS) [64–68]. Oxidative conversion of o-aminophenol (OAP) to 2-aminophenoxazinone (2-Amino-3H-phenoxazine-3-one or APX) is a biologically relevant reaction since APX has been used as a model for the behaviour of actinomycin-D, which acts by inhibiting DNA-directed RNA synthesis and is used clinically for the treatment of certain types of cancer [69–71]. At the same time phenoxazinone containing compounds are receiving increasing attention for various industrial applications viz. as antifungal and antimicrobial agents, dyes (Scheme S1) [60] and for the development of fluorescent probes for the detection of hydroxy radicals and live cell imaging [72–74].

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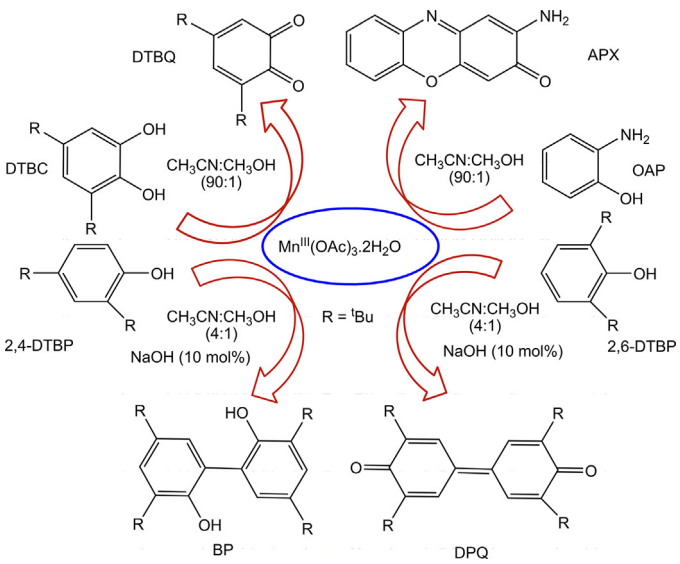


Scheme 1. Mn^{III} acetate mediated oxidation reactions of different phenols.

In general to probe such catalysis ligands are designed to fit the particular metal of choice and then the catalytic activities of the metal complexes are probed. A quick review of the literature shows that apart from complexes of transition metal [46,56,57,59,75–83], salts of copper [84] and cobalt [85,86] are also known for their capability to oxidize OAP to APX but the most common drawbacks reported are (i) relatively more catalyst required (stoichiometric or 1–10 mol%) and (ii) multiple product formation or polymerization of product (APX). Efforts have been made to catalyze the reaction with transition metal complexes immobilized on polymers and mesoporous silica [59] but they too face the afore-mentioned problems.

Recently we found that an o-donor based Mn^{III} complex of 9-hydroxyphenalenone showed catechol oxidase activity with highest turnover although it has no similarity to the enzyme active site [87]. It is known that biomimetic oxidation of the above type generally follow the radical based semiquinone type intermediates. $Mn^{III}(OAc)_3{\cdot}2H_2O$ has an established rich role as catalyst in various radical based organic synthesis [88–90] mainly for its oxidative free radical chemistry [88,90–100]. Since the late 1960s, $Mn(OAc)_3$-mediated radical reactions have attained significant attention as single-electron-transfer reagent due to its ability to form carbon, nitrogen, phosphorous or sulfur-centered radicals from various compounds such as β-diketones, β-keto acid, esters, phosphites, phosphine oxides, thiols, arylthioformanilides, thioglycolic acid, mercaptoketones and azides. Hence, $Mn^{III}(OAc)_3$-mediated catalysis provides alternative routes for the synthesis of important organic compounds [90–98]. It appeared to us that $Mn^{III}(OAc)_3{\cdot}2H_2O$ might be performing oxidations of phenols, dioxolenes or aminophenols since they involve carbon centered radicals.

Herein we present the catalytic studies of $Mn^{III}(OAc)_3{\cdot}2H_2O$ for the oxidation of DTBC and 2-aminophenol (OAP). The studies showed that $Mn^{III}(OAc)_3{\cdot}2H_2O$ has the highest turnover (k_{cat}) for oxidation of OAP to APX and the k_{cat} for DTBC oxidation is significantly high, of the order of $10^3\ h^{-1}$. The catalytic reactions showed first order kinetics with respect to the substrates. These results encouraged us to further probe the efficiency of the catalyst for oxidation of sterically hindered phenols and the results of the studies showed that Mn^{III} acetate is not only an efficient catalyst for oxidation of DTBC and OAP but also for oxidative coupling of sterically hindered phenols (Scheme 1).

2. Experimental

2.1. Materials and methods

All reactions were carried out using HPLC grade solvents [methanol (Merck), acetonitrile (Merck)]. Manganese(III) acetate dihydrate, 3,5-di-*tert*-butylcatechol, dimethylsulfoxide (DMSO), (±)-α-tocopherol, probucol, D/L-p-chlorophenylalanine, 2-aminophenol, potassium titanium oxide oxalate dihydrate, ethylenediaminetetraacetic acid disodium salt dihydrate were all purchased from Sigma and used without further purification. 3,5-di-*tert*-butyl benzoquinone was also purchased from Aldrich and used to calculate molar extinction coefficient (ε) in 90:1 acetonitrile, methanol mixture. L-Methionine, L-histidine [SRL (India)] and sodium hydroxide [Merck (India)] were also used as received. Methyl ester of methionine was synthesized according to a previously reported literature procedure [101]. NMR spectra were recorded on Bruker Avance III 500 MHz and also on Jeol ECS400 MHz spectrometer at room temperature (25 °C). Electronic spectra were recorded using Varian Cary 300 Bio UV–vis spectrophotometer. Electron-spray ionization mass spectra were recorded using micromass Q-Tof microTM (Waters) by +ve mode electrospray ionization. X-Band EPR spectra were recorded on a Bruker BioSpin WinEPR spectrometer.

2.2. Catalytic oxidation of DTBC

UV–vis spectra for kinetic studies were recorded by using a quartz cuvette (1.0 cm pathlength) and a Varian Cary 300 Bio UV–vis spectrophotometer equipped with a Peltier thermostating accessory. All the kinetics measurements were conducted at a constant temperature of 25 °C, monitored with a thermostat. 100 molar equiv of DTBC in acetonitrile were added to 1 μM solutions of Mn^{III}-acetate dihydrate in acetonitrile-methanol mixture under aerobic condition at room temperature (25 °C). The final ratio of acetonitrile:methanol in cuvette was 90:1 v/v. Absorbance vs. wavelength plots were generated for these reaction mixtures, recording spectrophotometric data at a regular time interval of 5 min in the range 300–700 nm. To determine the substrate concentration dependence of the rate and various kinetic parameters, 1 μM solutions of catalyst was treated with 100, 200, 300, 500, 600, 700, 800 molar equivalents of DTBC and the absorbance monitored as mentioned above (Fig. S1). The kinetic parameters were determined by using Lineweaver-Burk plot as well as Michaelis-Menten plot (Fig. S2). The product (DTBQ) was also characterized by ESI-MS and NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.93 (d, 1H, J = 2.28 Hz), 6.21 (d, 1H, J = 1.52 Hz), 1.26 (s, 9H), 1.22 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.26 (C-1), 180.17 (C-2), 163.46 (C-3), 150.07 (C-4), 133.60 (C-5), 122.22 (C-6), 36.16 (C-7), 35.61 (C-8), 29.34 (C-9), 28.01 (C-10) ppm. ESI-MS (+ve ion mode): m/z = 243.14 [(DTBC + Na^+)]$^+$ (calc. 243.14) (Fig. S3–S4).

2.3. Detection of hydrogen peroxide in the catalytic reaction of oxidation of DTBC

Earlier studies indicated that either water or hydrogen peroxide could form as side product in catalytic oxidation of catechol. Formation of hydrogen peroxide was probed by two methods

(i) H_2O_2 can be detected by the generation of characteristic peak at 352 nm for I_3^- ion with potassium iodide. To detect hydrogen peroxide after the oxidation of DTBC, DTBC was oxidized by 1 mol% Mn^{III} acetate for 2 h in acetonitrile and methanol mixture. The formed DTBQ was then extracted three times using dichloromethane. Water part was then acidified to pH 2 using diluted H_2SO_4 and one-third volume of KI solution

(500 mg/10 mL) in water was added to it with 100 nM Horse Radish Peroxidise and the appearance of the band at 352 nm characteristic for I_3^- ion was monitored. Control experiments were performed using only H_2O_2 solution. Since atmospheric oxygen can also oxidize I^- blank experiments (without catalyst or DTBC) were also performed (Fig. S5).

(ii) H_2O_2 formation can also be detected by formation of Ti(IV)-peroxo species using potassium titanium(IV) oxalate. In this experiment the catalytic reaction of DTBC oxidation and extraction procedure was same as that in method (i) stated above. The isolated aqueous part was added 1 mM solution of potassium titanium(IV) oxalate to monitor the band ca. 379 nm, due to the formation of Ti(IV)-peroxo bond [102,103]. Control experiment was also performed using hydrogen peroxide (Fig. S6).

2.4. Catalytic oxidation of 2-aminophenol (synthesis of 2-aminophenoxazinone or APX)

Oxidation of *o*-aminophenol (OAP) was carried out by taking OAP (109.0 mg, 1.0 mmol) in acetonitrile and manganese(III) acetate dihydrate (2.4 mg, 0.01 mmol) in methanol so that final solvent mixture is 90:1 and then the reaction mixture was stirred for 12 h. Product precipitated out of the solution which was filtered, collected and characterized by ESI-MS, ^{1}H NMR and ^{13}C NMR. ESI-MS (+ve ion mode): m/z = 213.08 [(APXH)]$^+$ (calc. 213.07); m/z = 235.05 [(APXNa)]$^+$ (calc. 235.05); m/z = 251.03 [(APXK)]$^+$ (calc. 251.02). ^{1}H NMR (500 MHz, Me_2SO-d_6): δ = 7.71 (dd, 1H, J = 7.5 Hz, ArH), 7.44 (m, 2H, ArH), 7.39 (m, 1H, ArH), 6.80 (br, s, 2H, NH_2), 6.36 (s, 2H, ArH) ppm. ^{13}C NMR (125 MHz, Me_2SO-d_6) δ = 180.2 (C-3), 148.9 (C-10a), 148.2 (C-4a), 147.3 (C-2), 141.9 (C-5a), 133.7 (C-9a), 128.8 (C-7), 127.9 (C-9), 125.3 (C-8), 115.9 (C-6), 103.4 (C-1), and 98.3 (C-4) ppm (Fig. S7–S11).

Kinetics of the aerobic oxidation of OAP in the presence of Mn^{III} acetate were measured by monitoring the change in absorbance as a function of time at 430 nm ($\varepsilon = 22 \times 10^3$ M^{-1} cm^{-1}), which is characteristic of 2-aminophenoxazin-3-one in methanol. All the kinetics measurements were conducted at a constant temperature of 25 °C, monitored with a thermostat. Initially, 100 molar equiv of OAP in acetonitrile were added to 5 μM solutions of Mn^{III} acetate in methanol under aerobic condition at room temperature (25 °C). The final ratio of acetonitrile:methanol in cuvette was 90:1 v/v. Absorbance vs. wavelength plots were generated for these reaction mixtures, recording spectrophotometric data at a regular time interval of 5 min in the range 300−700 nm. To determine the substrate concentration dependence on the rate and various kinetic parameters, 5 μM solutions of catalyst was treated with 800, 1200, 1500, 1800, 2600, 3200 and 3600 molar equivalents of OAP and the absorbances monitored as mentioned above. The completion of the reactions was determined spectrophotometrically by monitoring the increase in absorbance at 430 nm as a function of time. The kinetic parameters were determined by using Lineweaver-Burk plot.

2.5. Oxidative C–C coupling of 2,6-di-tert-butylphenol (conversion of 2,6-di-tert-butylphenol to 3,3′-5,5′-tetra-tert-butyldiphenoquinone)

Oxidative coupling of 2,6-di-*tert*-butylphenol (2,6-DTBP) was performed by taking 2,6-DTBP in acetonitrile, sodium hydroxide in water was added to it such that the overall concentration is 10 mol%. To the above solution Mn^{III} acetate (1 mol%) in methanol was added and the mixture was stirred at 25 °C for 4–12 h. Product started forming immediately after addition of Mn^{III} acetate solution. Reaction mixture was stirred for 4–12 h. Then the product was collected by filtration, washed by methanol and dried. The dried product was analyzed by ESI-MS and ^{1}H NMR spectroscopy. ESI-MS (+ve ion mode): m/z = 409.30 [(BDPH)]$^+$ (calc. 409.31); m/z = 431.29 [(BDPNa)]$^+$ (calc. 431.29). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (s, 4H), 1.36 (s, 36H) ppm (Fig. S12–S13).

2.6. Oxidative C–C coupling of 2,4-di-tert-butylphenol (conversion of 2,4-di-tert-butylphenol to 2,2′-dihydroxy-3,3′-5,5′-tetra-tert-butylbiphenyl (BP)

Oxidative coupling of 2,4-di-*tert*-butylphenol (2,4-DTBP) was performed by taking 2,4-DTBP in acetonitrile, Mn^{III} acetate (1 mol%) in methanol and NaOH (10 mol%) in water, similar to above and the mixture was stirred at 25 °C for 12 h. Product was analyzed by ESI-MS and isolated by evaporating the reaction mixture and extracting with water and dichloromethane. Combined organic layers were then dried and collected. ^{1}H-NMR of the dried product indicates partial conversion (65%) of 2,4-di-*tert*-butylphenol to 2,2′-dihydroxy-3,3′-5,5′-tetra-*tert*-butylbiphenyl with unreacted reactant. ESI-MS (+ve ion mode): m/z = 433.32 [(BPNa)]$^+$ (calc. 433.31). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, 2H), 7.11 (d, 2H), 5.21 (br, s, 2H), 1.45 (s, 18 H), 1.32 (s, 18 H) ppm (Fig. S14–S15).

2.7. Mass spectrometry

ESI mass spectrometric data were recorded using Waters Q-TOF micro mass spectrometer. The mass spectrometric studies of catechol oxidation were performed using (1:1) methanol: acetonitrile mixture. The ESI-MS was performed with 1:50 mixture of Mn^{III}-acetate dihydrate with DTBC. The ESI-MS data were performed in presence of inhibitors at a molar concentration ratio of 1:10:50 (Mn:inhibitor:substrate). The ESI-MS of the catalytic products were performed with 10 μM stock solutions.

3. Results and discussions

The redox chemistry of Mn^{III}-acetate, using cyclic voltammetry, in methanol and acetonitrile showed no significant redox events in the range of −1.0 to +1.0 V. However, the oxidation of DTBC to DTBQ by Mn^{III}-acetate was observed with quite high k_{cat} compared to many catechol oxidase mimics (Table 1). Detailed kinetic experiments to understand the effciency of Mn^{III}-acetate using 1 μM solution of Mn^{III}-acetate and upto 800 equivalent of DTBC (substrate) was performed. The experiments were done at a constant temperature of 25 °C under aerobic condition in (90:1) v/v acetonitrile and methanol mixture. The oxidation was monitored by the visible band appearing at 402 nm (ε = 1650 M^{-1}cm^{-1}) due to formation of DTBQ, using a UV–vis spectrophotometer (Fig. 1(A)). Then the differences in absorbance at 402 nm were plotted against time and rate constants of each case were determined by initial rate method. We also calculated the average rate constants of each of those experiments since we found complete conversion of the reactant to product (saturation was observed) (Fig. S1). The plot of rate constants vs. concentration of substrate was analyzed using Lineweaver-Burk plot and all the important kinetic parameters (V_{max}, k_M, k_{cat}) were obtained (Fig. 2). The k_{cat} value was found to be 1.72 (2) × 10^3 h^{-1}. It should be noted here that such a high turnover is obtained by a commercially available compound which is relatively cheap and is active at a lower concentration than reported for other functional mimics except the Mn complex of 9-hydroxy phenalenone reported by us earlier [87].

The literature shows that even transition metal salts of copper [84] and cobalt [85] are capable to oxidize OAP to APX in higher mol%. Hence when we obtained excellent k_{cat} value for oxidation of DTBC (Table 1) using $Mn^{III}(OAc)_3{\cdot}2H_2O$ it prompted us to study the oxidative conversion of o-aminophenol (OAP) to 2-aminophenoxazinone (2-Amino-3H-phenoxazine-3-one or APX) due to its biological and industrial relevance. We found that the

Table 1
Comparison of DTBC oxidation parameters of Manganese(III) acetate with the earlier known Mn model complexes and the best dinuclear copper(II) model complex of catechol oxidase.

Complexes[a]	k_{cat} (10^3 h^{-1})	K_M (10^{-4} M)	V_{max} (10^{-5} M s^{-1})	Solvent [ref]
$[Cu_2(H_2L1)(OH)(H_2O)(NO_3)]^{3+}$	32.4	23	90	b [19]
$Mn^{III}(L2)_2(OAc)(AcOH)$	1320	–	18.3	e [87]
$[Mn(L3)(H_2O)_3]^{2+}$	21.6	18	60	b[44]
Mn(L4)Cl	18.0	83	50.0	c [45]
$[Mn(L3)(SCN)_2(H_2O)]$	14.4	13	40	b [44]
Mn(L5)Cl	10.8	60	30.0	c [45]
Mn(L4)Cl	7.20	42	20.0	b [45]
$[Mn(L3)\,(H_2O)_2]^{+}$	7.2	67	20	b [44]
Mn(L6)Cl	3.60	65	10.0	c [45]
Mn(L5)Cl	3.60	19.0	10.0	b [45]
Mn_2L8Cl_4	3.60	9	10.0	c [45]
Mn_2L9Cl_4	3.31	22	9.19	c [45]
$[Mn^{II}{}_4Mn^{III}{}_4O_2(pyz)_2(C_6H_5CH_2COO)_{10}]$	2.56	1.76	0.12	c [104]
Mn(L6)Cl	2.47	1.00	6.85	b [45]
$Mn_2(L10)Cl_4$	2.44	37	6.79	c [45]
$Mn_2(L11)Cl_4$	2.41	24	6.70	c [45]
Mn(L7)Cl	1.79	7.00	4.97	c [45]
$(Ph_4P)_4[Mn_2O_2(L12)_2]$	1.6(2)	20	0.45	c [49]
$(Ph_4P)_4[Mn_2O_2(L13)_2]$	1.5(2)	24	0.43	c [49]
$(Ph_4P)_4[Mn_2O_2(L14)_2]$	0.9(1)	31	0.26	c [49]
$[Mn^{III}{}_2(\mu\text{-oxo})_2(L15)_2]$	0.336	5	–	c [50]
$[Mn_6(L16)_6(CH_3OH)_3(H_2O)_3]$	0.27	7.0	0.075	d [48]
$[Mn(L17)(Cl)_2]^{+}$	0.23	13	0.639	b [52]
$[Mn_2(L18)_2Cl_4]$	0.168	64	0.427	d [47]
$[Mn(L19)(Cl)_2]^{+}$	0.13	80	0.361	b [52]
$[(Ni(L20))_2Mn(NCS)_2]$	0.105	27.8	0.290	b [43]
$[Mn(L19)(OAc)(OCH_3)]^{+}$	0.101	12	0.281	b [52]
$[Mn(L17)(OAc)(OCH_3)]^{+}$	0.086	15	0.239	b [52]
$[(\{Ni(L20)\}_2Mn(NCO)_2]$	0.077	23.2	0.213	b [43]
$[\{Mn^{III}Mn^{II}(L21)(\mu\text{-}O_2CEt)(EtOH)\}_2(\mu\text{-}O_2CEt)]^{3+}$	0.065	1.149	0.0180	c [42]
$[Mn(L22)(H_2O)_2(CH_3CN)]^{2+}$	0.049	127	0.23	d [46]
$[\{Mn^{III}Mn^{II}(L21)(\mu\text{-}O_2CEt)(EtOH)\}_2(\mu\text{-}O_2CEt)]^{3+}$	0.045	4.170	0.0124	b [42]
$[\{Ni(L20)(EtOH)\}_2Mn(NO_2)_2]$	0.026	49.9	0.0717	b [43]
$[Mn^{III}Mn^{II}(L21)(\mu\text{-}O_2CMe)(H_2O)_2]^{2+}$	0.021	0.826	0.0057	c [42]
$[Mn^{III}Mn^{II}(L21)(\mu\text{-}O_2CPh)(MeOH)(ClO_4)]^{+}$	0.016	6.265	0.0043	c [42]
$[Mn^{III}Mn^{II}(L21)(\mu\text{-}O_2CMe)(H_2O)_2]^{2+}$	0.012	1.57	0.0032	b [42]
$[Mn^{III}Mn^{II}(L21)(\mu\text{-}O_2CPh)(MeOH)(ClO_4)]^{+}$	0.008	1.370	0.0021	b [42]
Mn^{III} acetate dihydrate	1.72	6.38	0.0477	[f]

[a] Structure of the ligands L1–L22 are shown in Scheme S2; pyz = pyrazine; Solvent system [b] CH_3OH; [c] CH_3CN; [d] DMF; [e] CH_3CN:DMF (90:1); [f] this work, CH_3CN:CH_3OH (90:1) mixture used as solvent.

relatively cost effective catalyst Mn^{III} acetate, at only 1 mol%, can catalyze the reaction in presence of molecular oxygen with quantitative yield and selectively form APX from OAP in 5 h. In addition no polymeric product could be detected in solution showing the reaction selectively gives one product. Detailed kinetic studies of the OAP oxidation reveal first order kinetics with respect to substrate and show that only 5 μM of Mn^{III}-acetate can catalyze conversion of upto 3600 molar equivalent of OAP to APX. The formation of APX was confirmed by NMR and ESI-MS studies (Fig. S7–S11). The UV–vis spectroscopic studies were done in 90:1 v/v acetonitrile:methanol mixture. The kinetic parameters of oxidation of OAP to APX have been derived from the Lineweaver Burk plot (Fig. 3, Table 2). The results show that OAP can be converted to APX with a k_{cat} value of 0.078 s^{-1}. The k_{cat} value of 0.078 s^{-1} is the highest among the reported mimics of PHS.

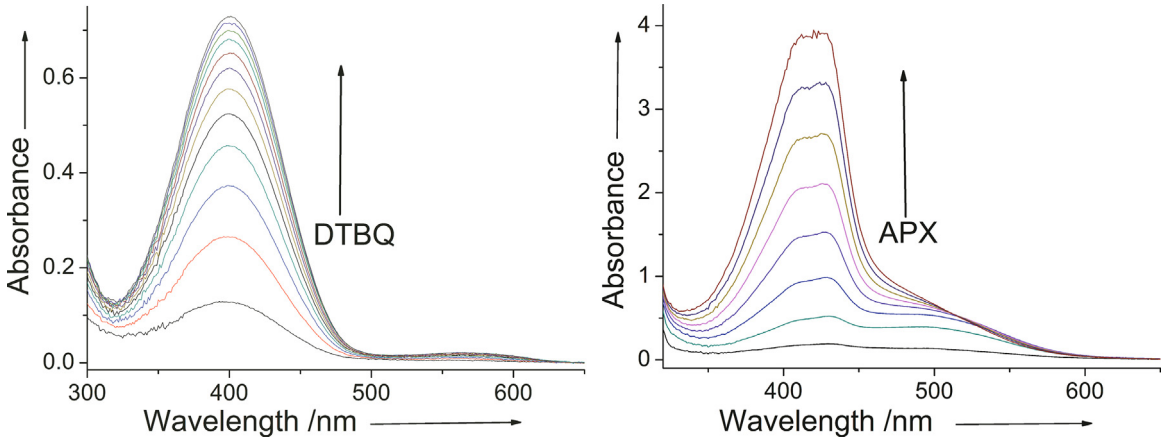


Fig. 1. (A) Increase in absorbance around 402 nm, after addition of 400 equivalent of DTBC to a 1 μM solution of Mn^{III}-acetate. (B) Increase in absorbance around 430 nm, after addition of 3200 equivalent of OAP to a 5 μM solution of Mn^{III}-acetate. Spectra were recorded every 5 min.

Table 2
A comparison of selected literature on conversion of 2-aminophenols to the corresponding phenoxazinones.

Catalyst [a]	k_{cat} (s^{-1})	K_M (mM)	k_{cat}/K_M ($mM^{-1}\,s^{-1}$)	V_{max} ($M\,s^{-1}$)	[ref]
$[Co_2(L23)_2(\mu\text{-}L23')_2Cl_2]^{2+}$	0.00382	1.57	0.0024	1.91×10^{-7}	[56]
$[Co(L24)(N_3)_3]$	0.0056	7.12 ± 0.72	0.0008	5.66×10^{-8}	[75]
$[Co(L25)(N_3)_3]$	0.0092	8.58 ± 0.96	0.0011	9.24×10^{-8}	[75]
$[Co_2(L26)_2(\mu\text{-}O_2)]^{4+}$	0.0084	10.1	0.0008	8.60×10^{-8}	[76]
$[Co_2(L27)_2(\mu\text{-}O_2)]^{4+}$	0.0064	14.7	0.0004	6.40×10^{-8}	[76]
$[Co(L28)(CH_3CN)]^{2+}$	0.00093	10.1	0.00009	1.87×10^{-8}	[76]
$[Co(L29)(H_2O)]^{2+}$	0.0018	12.8	0.0001	3.54×10^{-8}	[76]
$[Co(L30)(H_2O)]^{2+}$	0.0028	13.2	0.0002	4.60×10^{-8}	[76]
H_2O_2 with modified cyclodextrin	0.00061	10.7 ± 1.1	–	–	[58]
[Cu(L31)2]	0.00825	–	–	–	[59]
PS-$[Cu(L31)_2]$	0.0365	–	–	–	[59]
$[Mn(L22)(H_2O)_2(CH_3CN)]^{2+}$	0.00081	5.13	0.00016	1.34×10^{-7}	[46]
Mn^{III}-acetate dihydrate	0.078	55.3	0.0014	3.9×10^{-7}	[b]

[a] Structure of the ligands L23–L31 are shown in Scheme S3; [b] This work.

Table 3
Oxidation of 2,6-DTBP to DPQ by Mn^{III} acetate.

Entry	[cat] (mol%)	Base (mol%)	Solvent	Time (h)	Yield[a]
1	1	No base	MeOH	12	0
2	1	NaOH(10)	MeOH	04	90
3	0	NaOH(10)	MeOH	12	0
4	0	NaOH(100)[b]	MeOH	12	75
5	1	Et_3N (100)	MeOH	12	0
6	1	Pyridine (100)	MeOH	12	0
7	1	NaOH(10)	CH_3CN	04	94
8	1	NaOH(10)	CH_3CN	0.5	74
9	0	NaOH(10)	CH_3CN	12	05
10	1	Bu_4NOH (100)	CH_3CN	12	0
11	0	NaOH(100)[b]	CH_3CN	12	83
12	1	NaOH(10)	DMSO	12	15

[a] Isolated yield; [b] reaction was perfomed in presence of 2 mol% Na_2EDTA to remove any adventitious Manganese.

We also found that the activity of the catalyst $Mn^{III}(OAc)_3.2H_2O$ decreases on aging of the solution (linearly with time, rate 0.003 h^{-1}. One representative study shown in Fig. S16). Hence, to get best efficiency a fresh solution of the catalyst should be used. We further studied the oxidative C—C bond coupling of sterically hindered phenols [2,6-di-*tert*-butylphenol (2,6-DTBP) and 2,4-di-*tert*-butylphenol (2,4-DTBP)] using Mn^{III} acetate. The catalytic oxidation of 2,6-DTBP to 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (DPQ) was attempted by dissolving 2,6-DTBP in acetonitrile with 10 mol% sodium hydroxide and 1 mol% Mn^{III}-acetate in methanol was added to it. Reaction mixture was then stirred at 25 °C. The product started precipitating out within 5 min after starting the reaction. As the reaction progressed DPQ was visibly witnessed as reddish brown precipitate, which was finally collected by filtration and dried and analyzed for purity by NMR spectroscopy and ESI-MS. The results for several trials are shown in Table 3.

We observed while performing control reaction in presence of stoichiometric amount of base without any catalyst, that alone NaOH/KOH may provide oxidative C-C bond coupling in certain

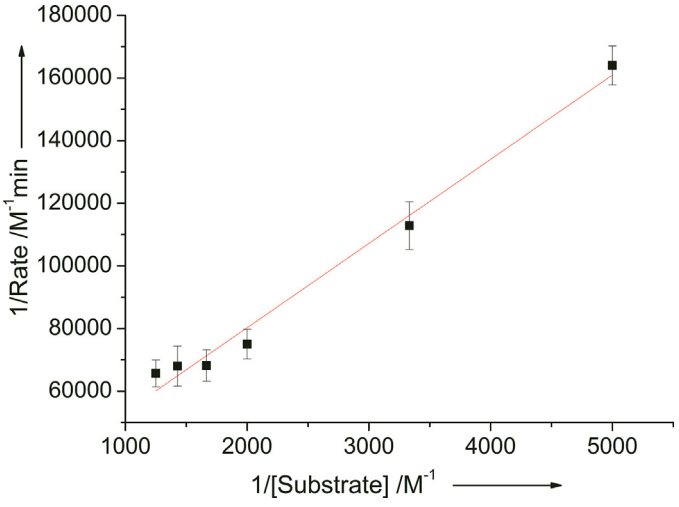


Fig. 2. The Lineweaver-Burk plot for the oxidation of DTBC catalyzed by Mn^{III}-acetate.

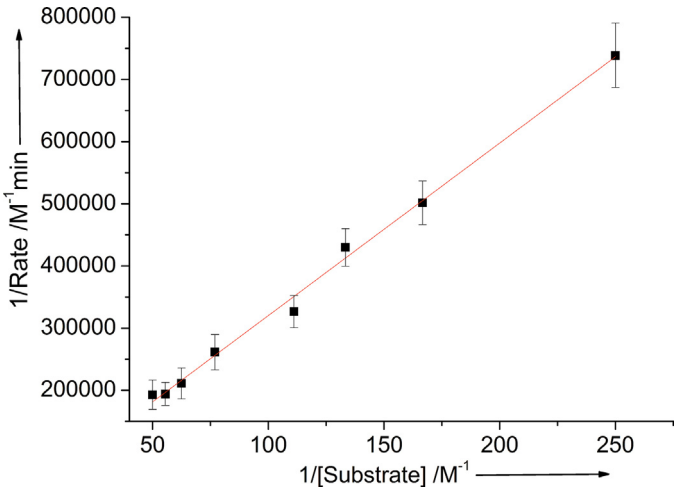


Fig. 3. The Lineweaver-Burk plot for the auto-oxidation of OAP to APX catalyzed by Mn^{III}-acetate.

sterically hindered phenols viz. oxidative C–C coupling of 2,6-DTBP to DPQ. However, strangely this observation has never been reported in literature. An earlier report discussed that after 3 h there is no reaction in presence of KOH which is true [105,106] but when the reaction is allowed to continue longer, than after 6–7 h product formation starts and can be observed by TLC. Using 1 molar equivalent KOH we got 83% isolated yield after 12 h of reaction when we used 2,6-DTBP as the substrate. In case of the relatively tougher substrate 2,4-di-*tert*-butylphenol (2,4-DTBP) 1 mole equivalent KOH or NaOH did not give the desired product 2,2′-dihydroxy-3,3′-5,5′-tetra-*tert*-butylbiphenyl (BP) at room temperature even after 16 h. However, the use of 1 mol% Mn^{III} acetate with 10 mol% NaOH as base gave 65% conversion of 2,4-DTBP to the desired BP in 12 h.

The formation of the phenolate in presence of the base may help the propagation of the reaction. The added base is playing the role to generate the corresponding phenolate anion of the 2,6-DTBP, which is known to be more oxidizable than the original phenol because of the difference between their redox potentials [107]. Yes, that may be one of the reasons. However, the formation of phenolate is not the only activating factor then the similar product would be observed with other bases such as triethylamine (Et_3N) or pyridine but using these bases we do not get any yield of DPQ even after 12 h. During oxidation of 2,6-DTBP there is a possibility of formation of another side product 2,6-di-*tert*-butyl-1,4-benzoquinone (2,6-DTBQ). It was earlier shown that formation of 2,6-DTBQ required peroxide or peroxo intermediates [108]. In our case we have selectively got DPQ as the sole product. Hence, the reaction does not go through any peroxo intermediate. Based on the proposed mechanism the reaction was initiated by the formation of phenoxyl radical from phenoxide via one electro oxidation prompted by Mn^{III} (Scheme S4A). The C–C coupling of a resonance form bearing a high density of unpaired electron at para-position of the phenoxy radical will form an unstable dimer I (Scheme S4A). In our case, the product DPQ can be formed from the dimer I via two different routes as shown earlier [108,109]. First one may be via H_2DPQ intermediate which will form through tautomeric rearrangement (Scheme S4A). Then H_2DPQ will sequentially oxidize to form DPQ. The second route involves direct oxidative dehydrogenation of intermediate I to DPQ and water.

We also performed some initial investigation on the possible reactive oxygen species (ROS) involved with the catechol oxidation reaction using UV-vis spectroscopy. The studies show that there may be involvement of a hydroxyl radical (Fig. 4) since the reaction is inhibited to a large extent (ca.70%) by DMSO but however, the reaction is not much affected by other ROS quenchers like (±)-α-tocopherol or probucol. DMSO is known to react with hydroxyl radical to oxidize itself. Hence hydroxyl radical may be generated from the reaction of molecular oxygen with the metal centre. However, the reaction is not completely quenched by DMSO which we found with our earlier reported Mn^{III} complex (Table 1) when hydroxyl radicals were involved [87]. Hence, formation of alternative carbon centered radicals cannot be ruled out. We found that benzoates and amino acids or esters of amino acids strongly inhibit the oxidation reaction. Complete inhibition was observed by histidine and methyl ester of methionine. Inhibition by amino acid brings in the possibility of Schiff base formation between the product quinone and the amino acid or formation of oxazole after Schiff base condensation but however, we did not observe any such product in the ESI-MS. Such products should be easily detected by ESI-MS since they are pretty stable, easily ionized and hence, very unlikely not to see if they have formed. In addition benzoic acid and amino acids are used in 100 molar equivalents with respect to the catalyst so unless they are deactivating the metal completely through coordination there will be lot of catechol left for oxidation and hence the band at 402 nm should increase after an initial delay. But we see almost complete quenching which strongly suggest

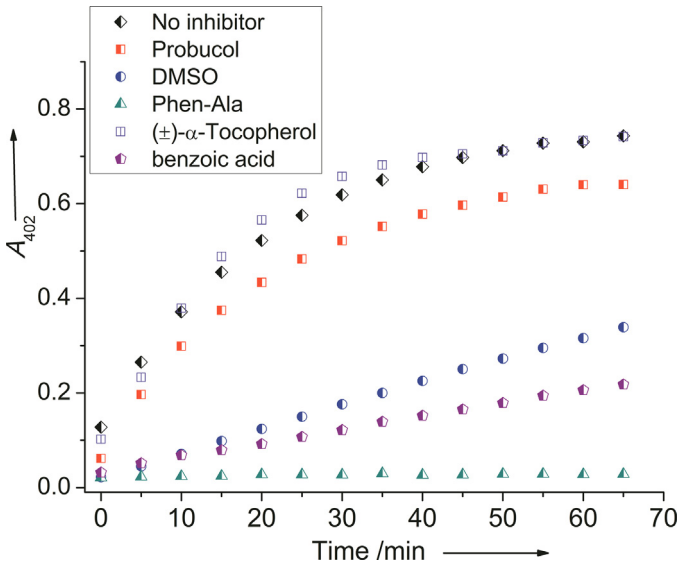
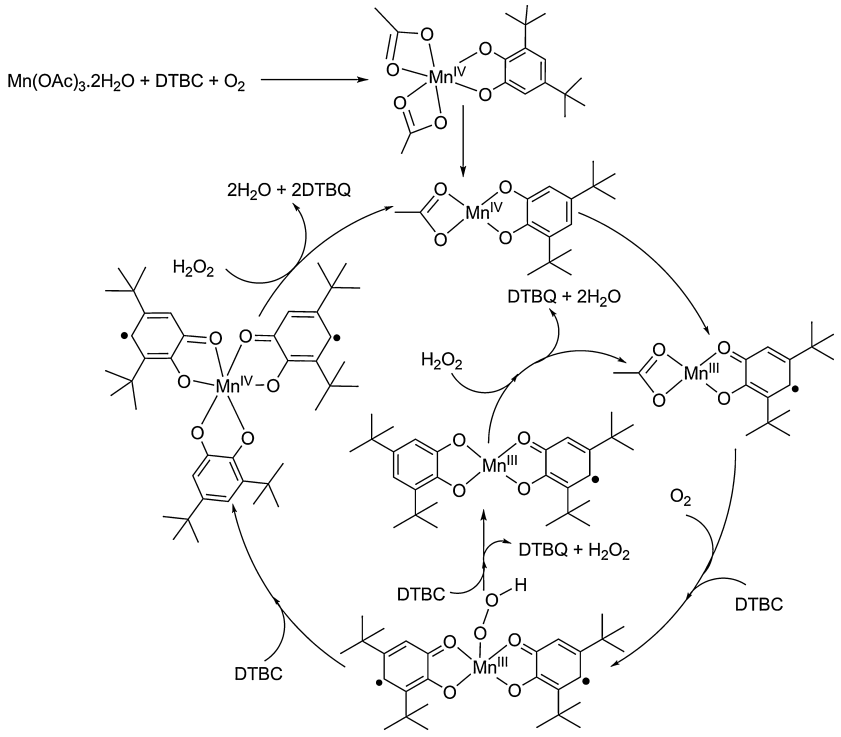


Fig. 4. UV–vis study of the inhibition of catechol oxidation probed by monitoring A_{402}. Reaction condition: 500 molar equivalent of DTBC and 1 μM catalyst in air; 10 molar equivalent of (±)-α-tocopherol and probucol, 100 molar equivalent of methyl ester of D/L-p-chlorophenylalanine, DMSO and benzoic acid with respect to catalyst. Spectra were recorded every 5 min interval and the respective legends are provided in the figure.

that the benzoic acid or the amino acids co-ordinate to the metal centre. The ESI-MS data using histidine as an inhibitor supported the metal histidine co-ordination since we a *m*/*z* of 519.13 which matches very well with the species $[Mn^{III}(His)_2(OAc)_2(H_2O)_2]^+$, (calc. 519.12) (Fig. S20). This strengthens the interpretation that the possible cause of inhibition of the oxidation of DTBC is due to coordination of the amino acid with the metal centre.

The ESI-MS studies were also performed for the reaction mixture of DTBC oxidation by $Mn^{III}(OAc)_3{\cdot}2H_2O$. ESI-MS technique is capable of providing mass spectral data of speciation relevant to the solution condition [110–112]. The results provided us with important insight about the solution speciation and possible mechanism of DTBQ formation. The mass spectrometric data of the reaction mixture of DTBC and $Mn^{III}(OAc)_3$ matches well with four species—Mn^{IV}(OAc)(DTBC-2H), $Mn^{III}(DTSQ)_2$ or Mn^{IV}(DTSQ)(DTBC-2H) and $Mn^{IV}(DTSQ)_3$ (Scheme 2, Fig. S21) most of which may be formed during the catalytic cycle. Although the ESI-MS data repeatedly generates the same features we could not obtain any spectroscopic evidence in support of generation of Mn^{IV}. We attempted to find the semiquinone with X-band EPR at 77 K in CH_3CN and CH_3OH mixture but could not find any evidence of radicals suggesting that perhaps all these processes are faster than EPR time scale (Fig. S18). The EPR spectrum indicates anisotropy and the assignment is not straightforward. However, the g_{iso} is ca. 2.02 and the average A value is ca. 90 G (Fig. S18). Broad unresolved signals of less amplitude at $g = 3.3–4.5$ are also obtained (Fig. S18). The spectrum is suggestive of a Mn(II) species [53,113,114]. It may be that since we used a catalyst to substrate ratio of 1:2 in order to get good signal to noise ratio, the substrate oxidized quickly much before the instrument could be tuned to record data and most of the catalyst disproportionated to Mn(II) and that is what we are observing in the EPR data.

One might argue that the speciation we see in ESI-MS may not be happening under normal solution conditions. However, in literature there exists strong evidences for similar speciation: $Mn^{IV}(DTSQ)_2$(DTBC-2H) or $Mn^{III}(DTSQ)_3$, which was shown individually by Pierpont et al. and Wieghardt et al. [115–117]. Hence our ESI-MS data is in good agreement with the literature. The proposed mechanism shows that in solution the catalytic reaction



Scheme 2. Proposed mechanistic pathway of DTBC oxidation by Mn^{III} acetate.

may initiate through the formation of a $[Mn^{IV}(DTBC)(OAc)]^+$ intermediate, which then is converted to $[Mn^{III}(DTSQ)(OAc)]^+$ (Scheme 2). The *m*/*z* for both the species in ESI-MS would be the same and the data shows a *m*/*z* of 334.10 (calc. 334.10) corresponding to the afore-mentioned species. The $[Mn^{III}(DTSQ)(OAc)]^+$ may further react with another DTBC unit and molecular oxygen to form $[Mn^{III}(DTSQ)_2(O_2H)]^+$ and then convert to $[Mn^{III}(DTBC)(DTSQ)]$. The ESI-MS data corresponds to $[Mn^{IV}(DTBC)(DTSQ)]^+$ *m*/*z* of 495.22 (calc. 495.23) was found which might be forming in mass spectral condition (Scheme 2, Fig. S21).

Further there is coordination of another DTBC unit as shown in Scheme 2 to form $[Mn^{IV}(DTBC)(DTSQ)_2]$ similar to that found in earlier studies [117]. Two quinone molecules are hence produced with two molecules of water and the catalytic cycle continues (Scheme 2). The generation of DTBQ and water as a final product, rather than H_2O_2 is based on the fact that we could hardly detect the presence of any hydrogen peroxide using the Horse Radish peroxidise experiment (details in Experimental section, Fig. S5) [27,118] as well as using potassium titanium(IV) oxalate (Fig. S6) [102,103] which indicates that even if any peroxide was generated was consumed in the reaction and hence cannot be detected in the extracted medium.

Probing the mechanistic pathway of oxidation of OAP to APX the earlier literature described the involvement of organic radical intermediates in their mechanistic pathways [46,56,59,75,78,81,83,84]. Although most of the cases they were unable to detect any organic radical by EPR study, only in two cases organic radical involvement was detected [80,82]. We have also carried out an X-band EPR study to investigate any radial intermediate but similar to most we too have not found any signal which corresponds to organic radical, this may be due to the fact that the stability of the radical intermediate is beyond the EPR time scale in presence of our active catalyst. Hence, our proposed mechanistic pathway is in line with the earlier proposed mechanisms. The OAP may first coordinate to Mn^{III} centre where it was oxidized to OAP radical which generate o-benzoquinone monoamine (BQMI) (Scheme S4B) and the BQMI then couple with OAP to form APX as the final product.

4. Conclusions

We have shown that Manganese(III) acetate can efficiently perform oxidation of DTBC and OAP to DTBQ and APX repsectively. It seems to be a good, cheap, commercially available catalyst capable of producing quinone or phenoxazinone derivatives. It can also form oxidatively coupled biaryls from sterically hindered phenols at room temperature. The studies suggest that there is formation of $[Mn^{IV}(DTBC)(DTSQ)_2]$ during the oxidation of DTBC as per ESI-MS data which is in strong agreement with earlier literature [117]. Oxidation of OAP to APX or DTBC to DTBQ did not show invovlement of any radical in EPR studies. Although ESI-MS data of DTBC oxidation suggests invovlement of semiquinone and Mn^{IV}, the EPR data reveals that the intermediates formed have very short lifetime and hence not detectable by EPR. The oxidative coupling of 2,6-DTBP with only 1 mol% $Mn^{III}(OAc)_3{\cdot}H_2O$ selectively forms DPQ with more than 90% yield in less than 4 h and none of the side product 2,6-DTBQ is observed. Oxidative coupling of 2,4-DTBP is only possible with 1 mol% of $Mn^{III}(OAc)_3{\cdot}H_2O$ and 10 mol% of base and takes longer time (12 h). We have shown that although NaOH or KOH alone without the Mn^{III} catalyst, cannot perform the oxidative coupling of 2,4-DTBP but they perform the oxidative coupling of 2,6-DTBP to the corresponding biaryl (DPQ) with 100 mol% taking a relatively longer period of 12 h which seemed to have gone unnoticed earlier.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.08.014.

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