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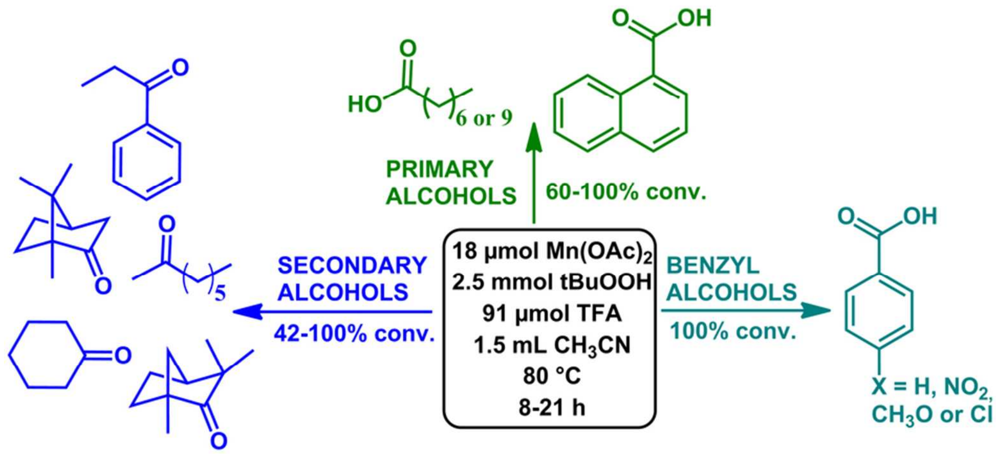

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Mn(II) acetate: An efficient and versatile oxidation catalyst for alcohols†

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ABSTRACT

A homogeneous catalytic system consisting of Mn(II) acetate (18 µmol), *tert*-butylhydroperoxide (2.5 mmol), acetonitrile (1.5 mL) and trifluoroacetic acid (91 µmol) was developed for efficient and selective oxidation of various alcohols (1 mmol). The system yielded good to quantitative conversions (42-100%) of various secondary alcohols, such as 2-octanol, fenchyl alcohol and borneol, to their corresponding ketones. Primary alcohols, for example 1-octanol and differently substituted benzyl alcohols, were mainly converted to their corresponding carboxylic acids. Studies with a selection of hydrocarbons, tertiary amines and a cyclic ether isochroman showed that besides alcohols, other substrates can be oxidised as well.

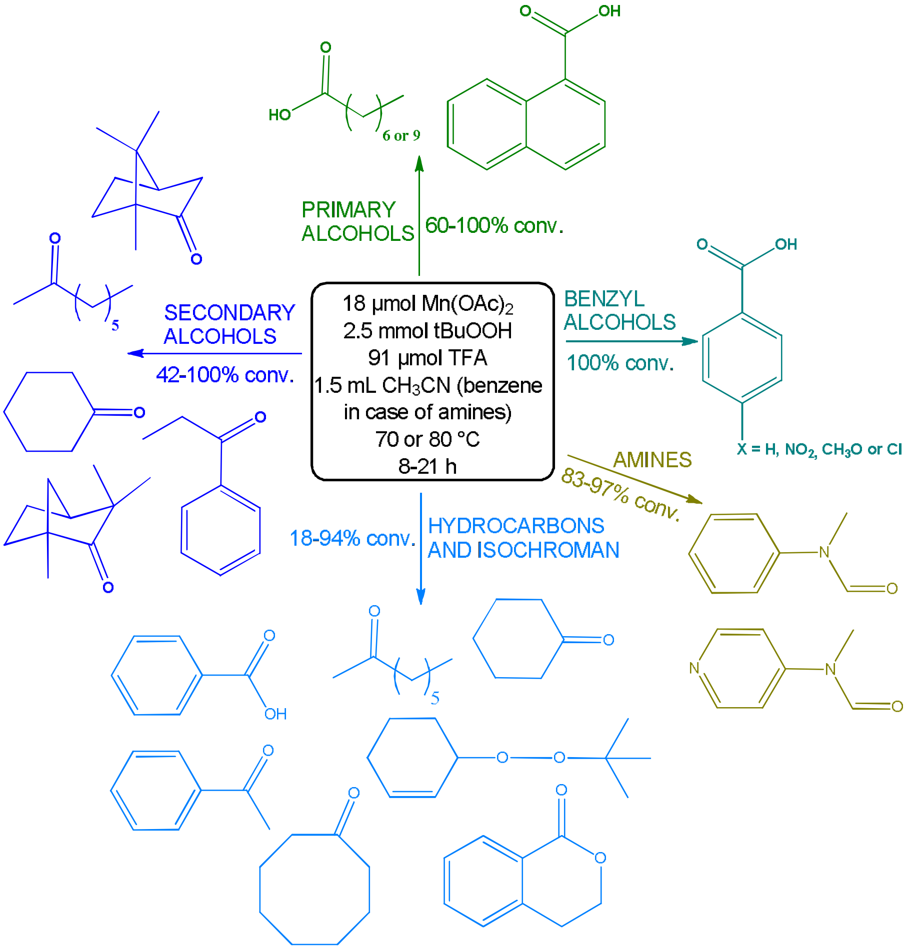
† Electronic supplementary information (ESI) available: Tables S1-S8 and Figs. S1-S6 for additional information. See DOI: x.

1. Introduction

Efficient and selective catalytic systems for oxidation of alcohols, hydrocarbons and amines to valuable products are continuously sought after.[1-10] In nature, several enzymes capable of catalysing oxidation reactions contain first row transition metal centres such as Mn, Fe, Co and Cu.[11] The enzymes have been the stepping stone for the development of synthetic catalysts for oxidative reactions in general and less toxic Mn and Fe complexes, including Mn Schiff base complexes, are under intense study.[2-4,12-20]

The approach we have adopted herein involves the use of manganese acetate, in a catalytic amount, for homogeneous oxidation reactions. Back in the 1960's and 1970's, stoichiometric amount of manganese(III) acetate ($Mn_3O(OAc)_9$) has been used to oxidise various hydrocarbons in acetic acid, the major oxidation products mostly being acetates of the substrates.[21-24] Reactions which require $Mn_3O(OAc)_9$ in equivalent amounts are alcohol oxidations with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone oxidant,[25] oxidative free-radical cyclizations,[26-30] conversion of oximes to ketones and aldehydes[31] as well as radical reactions of C_{60} with various esters and ketones.[32-34] Studies on manganese salt catalysed reactions are much scarcer including $Mn_3O(OAc)_9$ in oxidation of alkenes with *tert*-butylhydroperoxide (*t*BuOOH)[35] and sulfides with H_2O_2.[36] $MnCl_2{\cdot}4H_2O$ and $Mn(CH_3COO)_2{\cdot}4H_2O$ ($Mn(OAc)_2$) also catalyse alcohol oxidations, though with very moderate conversions (20-29%).[37] It has been reported that catalytic species which are able to oxidise for example cyclohexane with *t*BuOOH oxidant are generated when manganese(II) salts are reacted with nitrogen containing coordinating ligands, such as 2,2´-bipyridine.[38-40]

As a continuation to our recent oxidation studies on various homogeneous catalysts,[41,42] we report herein an efficient catalyst based on $Mn(OAc)_2$ and *t*BuOOH for oxidation of various alcohols. The versatility of the system is further demonstrated with selected hydrocarbons, amines and cyclic ether (Scheme 1).



Scheme 1 Overview of the reaction conditions, substrate scope and main products from $Mn(OAc)_2$/*t*BuOOH catalysed oxidation reactions.

2. Experimental

2.1. General

All chemicals were obtained from commercial suppliers and used without further purification. Cyclohexene (≥99.0%, Sigma-Aldrich) contained ~0.01% of 2,6-di-*tert*-butyl-4-methylphenol as stabiliser and was used as received. Caution should be taken while using high concentrations of *tert*-butylhydroperoxide (*t*BuOOH). Its vapours are highly flammable and it could undergo homolytic decomposition to afford *tert*-butoxy and *tert*-butyl peroxy radicals which can trigger radical decomposition.

The ^1H NMR spectra were recorded with a Varian Gemini 200 MHz or a Varian Mercury 300 MHz spectrometer and the IR spectra with a Bruker ALPHA. HRMS (ESI-TOF) mass spectra were recorded with a Bruker micrOTOF mass spectrometer using sodium formate as calibrant. Elemental analyses (CHN) were performed with a vario MICRO instrument. An Oxford INCA 350 energy-dispersive X-ray microanalysis system connected with the Hitachi S-4800 Field emission scanning electron microscope was used for the energy-dispersive X-ray spectrometry (EDS) measurements. Substrate conversions were determined by a gas chromatography-mass spectrometry (GC-MS). GC-MS analyses were performed with a Agilent 6890N Network GC system equipped with DB-1MS column (30 m × 0.250 mm) and Agilent 5973 Network MS detector (1,2-dichlorobenzene used as an internal standard). Calibration curves were obtained from commercial products purchased from Aldrich or TCI when available or from pure isolated products from catalytic reactions. The concentrations of each organic product were calibrated relative to that of an internal standard (1,2-dichlorobenzene).

2.2. Ligand synthesis

2-Hydroxy-4-[2-(ethylthio)ethoxy]benzaldehyde was synthesised by modifying a literature procedure.[43] 2,4-Dihydroxybenzaldehyde (4.500 g, 33 mmol) was dissolved in acetone (40 mL) and K_2CO_3 (4.500 g, 33 mmol) and 2-chloroethyl ethyl sulfide (3.8 mL, 33 mmol) were added. The mixture was refluxed at 65 ºC for 49 h to obtain a brown suspension. It contained the product together with unreacted 2,4-dihydroxybenzaldehyde and 2,4-bis[2-(ethylthio)ethoxy]benzaldehyde as a side product. The product was purified by a column chromatography using *n*-hexane/ethyl acetate (9:1, v/v) as an eluent. After solvent removal the product was obtained as colourless liquid (yield 3.548 g, 46%). ^{1}H NMR (200 MHz, $CDCl_3$, TMS, 25 °C): δ = 1.29 (t, J_{HH} = 7.4 Hz, 3H, CH_3), 2.65 (q, J_{HH} = 7.2 Hz, 2H, CH_2), 2.91 (t, J_{HH} = 6.4 Hz, 2H, CH_2), 4.17 (t, J_{HH} = 6.4 Hz, 2H, OCH_2), 6.41 (s, 1H, H–Ar), 6.53 (dd, J_{HH} = 8.8 and 2.0 Hz, 1H, H–Ar), 7.42 (d, J_{HH} = 8.6 Hz, 1H, H–Ar), 9.70 (s, 1H, HC=O), 11.46 (s, 1H, OH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, TMS, 25 °C): δ = 14.93, 26.64, 30.26, 68.25, 101.18, 108.47, 115.34, 135.35, 164.37, 165.63, 194.38 ppm. ^{13}C NMR spectrum is presented in the ESI (Fig. S1). Selected IR data: ν = 3075 (O–H), 2968-2750 (aliphatic C–H), 1624 (C=O), 1575 (C=C), 1287 (C–O) cm^{-1}. HRMS (ESI+): $C_{11}H_{14}O_3S_1Na$ $[M+Na]^+$ obs. *m/z* 249.0562, calc. 249.0556, error -2.628 ppm.

For synthesis of *N*,*N′*-(Ethylene)bis(4-[2-(ethylthio)ethoxy]salicylideneimine) a methanol (2 mL) solution of 2-hydroxy-4-[2-(ethylthio)ethoxy]benzaldehyde (0.400 g, 1.8 mmol) and 1,2-ethylenediamine (60 μL, 0.9 mmol) was stirred at room temperature for 15 h. The resulted yellow suspension was filtered and the product was obtained as a yellow powder after drying in vacuum (yield 0.346 g, 82%). $C_{24}H_{32}N_2O_4S_2$ (476.65): calcd. C 60.48, H 6.77, N 5.88%; found C 60.43, H 6.77, N 5.87%. ^{1}H NMR (200 MHz, $CDCl_3$, TMS, 25 °C): δ = 1.29 (t, J_{HH} = 7.4 Hz, 6H, CH_3), 2.48 (q, J_{HH} = 7.4 Hz, 4H, CH_2), 2.90 (t, J_{HH} = 6.8 Hz, 4H, CH_2), 3.85 (s, 4H, CH_2), 4.13 (t, J_{HH} = 6.8 Hz, 4H, OCH_2), 6.36-6.40 (m, 4H, H–Ar), 7.09 (d, J_{HH} = 8.4 Hz, 2H, H–Ar), 8.20 (s, 2H , HC=N), 13.73 (br s, 2H, OH) ppm. Selected IR data: ν = 3072 (O–H), 2972-2868 (aliphatic C–H), 1615 (C=N), 1580 (C=C), 1287 (C–O) cm^{-1}. HRMS (ESI+): $C_{24}H_{33}N_2O_4S_2$ $[M+H]^+$ obs. *m/z* 477.1880, calc. 477.1876, error -0.880 ppm.

2.3. Oxidation experiments

Each catalytic experiment was done at least twice and the stated conversion is the average value. A general procedure for the oxidation experiments: Magnetic stirring bar, metal salt (18 µmol), 1.5 mL of CH_3CN (in case of alcohol and hydrocarbon substrates) or benzene (in case of amine substrates), TFA (7 µL, 91 µmol), 313 µL of *t*BuOOH (80% in water, 2.5 mmol, 2.5 equivalents with respect to the substrate) and substrate (1 mmol) were placed in a microwave vial (volume 10 mL). The vial was sealed with a vial cap (equipped with a septum). These vials are designed to withstand pressures below 20 bar so the reactions could be safely performed in a closed system and possible evaporation from the solutions could be avoided. It is noteworthy that most of the oxidation reactions, fenchyl alcohol, cyclohexane, toluene and cyclohexene substrates being the exceptions, can also be carried out in a regular test tube (volume 14 mL) which is sealed with a septum. In this case a needle (0.4 mm in diameter and 19 mm in length) is inserted through the septum to avoid pressure formation inside the test tube. One must also take care that concentration of the solution is constant during the reaction. Reaction mixture was stirred at 80 °C (alcohol substrates) or 70 °C (hydrocarbon and amine substrates) for the designated time (see Tables 1 and 2). Sodium thiosulphate (*ca.* 400 mg, 2.5 mmol) was then added to the reaction mixture to quench further oxidation. The reaction mixtures were filtered through silica gel column with CH_3CN as an eluent prior to GC-MS analysis. The GC-MS samples from hydrocarbon oxidation reactions were treated with triphenylphospine (PPh_3) according to the method developed by Shul´pin et al. The method allows to determine the real concentrations of the oxidation products.[44-46] The chromatograms obtained were compared with the chromatograms prepared for the samples untreated with PPh_3. In this study PPh_3 showed no effect on the chromatograms.

Reactions under argon were performed similarly to those done under aerobic conditions except that standard Schlenk techniques were used. An oxidation experiment with an O_2 filled balloon was performed as follows. $Mn(OAc)_2$ (18 µmol), CH_3CN (1.5 mL), TFA (7 µL), *t*BuOOH (2.5 mmol) and 1-phenyl-1-propanol substrate (1 mmol) were placed in a two-neck round-bottom flask (25 mL) fitted with a condenser which had the O_2 filled balloon on top of it. Another neck was sealed with a septum. The reaction was carried out at 80 °C for 2 h prior the GC-MS analysis. Oxidation of 2-octanol with H_2O_2 was performed similarly to the general procedure except H_2O_2 (30%, 2.5 equivalents, 223 µL) was used instead of *t*BuOOH and temperature was 60 ºC to avoid decomposition of H_2O_2. Oxidation of 2-octanol with O_2 (10 bar) as an oxidant was carried out at 80 ºC in a stainless steel autoclave using same amounts of CH_3CN, TFA, $Mn(OAc)_2$ and 2-octanol as in the general procedure. After the reaction, the autoclave was cooled and slowly depressurised.

1-Phenyl-1-propanone was isolated as a yellow oil in 93% (125 mg) yield by a silica gel column using *n*-pentane/ethyl acetate 7:3 v/v as an eluent. ^1H NMR (300 MHz, $CDCl_3$, TMS, 25 °C): δ = 1.19 (t, 3H,

CH_3), 2.96 (q, 2H, CH_2), 7.37 (m, 3H, H–Ar), 7.86 (d, 2H, H–Ar) ppm. Selected IR data: ν = 1685 (C=O) cm^{-1}.

Benzoic acid (109 mg, 89%, white powder) was purified by silica gel column chromatography using *n*-pentane/ethyl acetate as an eluent. ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 7.50 (t, J_{HH} = 7.5 Hz, 2H, H–Ar), 7.62 (t, J_{HH} = 7.5 Hz, 1H, H–Ar), 7.95 (d, J_{HH} = 7.3 Hz, 2H, H–Ar) ppm. Selected IR data: $\bar{\upsilon}$ = 2956 (O–H), 1679 (C=O) cm^{-1}.

1-Naphthoic acid (163 mg, 95%, yellow powder) was purified by silica gel column chromatography using *n*-pentane/ethyl acetate as eluent. ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 7.57-7.67 (m, 3H, H–Ar), 8.02 (d, J_{HH} = 7.9 Hz, 1H, H–Ar), 8.16 (d, J_{HH} = 7.9 Hz, 2H, H–Ar), 8.87 (d, J_{HH} = 8.2 Hz, 1H, H–Ar) ppm. Selected IR data: ν = 2927 (O–H), 1668 (C=O) cm^{-1}.

4-Chlorobenzoic acid (143 mg, 91%, white powder) was purified by silica gel column chromatography using *n*-pentane/ethyl acetate as eluent. ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 7.63 (d, J_{HH} = 8.3 Hz, 2H, H–Ar), 7.92 (d, J_{HH} = 8.3 Hz, 2H, H–Ar) ppm. Selected IR data: ν = 2982 (O–H), 1674 (C=O) cm^{-1}.

4-Nitrobenzoic acid (158 mg, 95%) was isolated as pale yellow microcrystals which formed in the reaction mixture upon cooling. The crystals were filtered off, washed with CH_3CN and dried. ^1H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 8.16 (d, J_{HH} = 8.0 Hz, 2H, H–Ar), 8.31 (d, J_{HH} = 8.3 Hz, 2H, H–Ar), 13.66 (s, 1H, CH=O) ppm. Selected IR data: ν = 3113 (O–H), 1683 (C=O) cm^{-1}.

2.4. Evans' NMR method

The solution containing d_6-benzene (0.5 mL), $Mn(OAc)_2$ (2.4 mg, 9 µmol), TFA (7 µL, 91 µmol), *t*BuOOH (50 µL, 399 µmol) and borneol (0.2 mg, 1.3 µmol) was heated in a NMR tube at 70 °C for 4 h while stirring (conversion to camphor 100% according to GC-MS). The magnetic stirring bar was removed from the cooled solution and a sealed glass capillary containing d_6-benzene was inserted in the NMR tube. The ^1H spectrum was measured with a 300 MHz spectrometer at 27 °C to detect the shift of the d_6-benzene signal (0.42 ppm = 126 Hz). Diamagnetic corrections were calculated using Pascal's constants.

3. Results and discussion

3.1. Oxidation of alcohols by $Mn(OAc)_2$

After initial finding that $Mn_3O(OAc)_9$ catalyses oxidation of 2-octanol in acetonitrile at 80 ºC with *t*BuOOH and trifluoroacetic acid (TFA) additive, various metal salts were studied as catalysts (Fig. 1). 2-Octanol was chosen for a model substrate as aliphatic alcohols are typically challenging to be oxidised. Of the studied metal salts $Mn(OAc)_2$ was chosen for further studies as it gave highest activity (87% conversion).

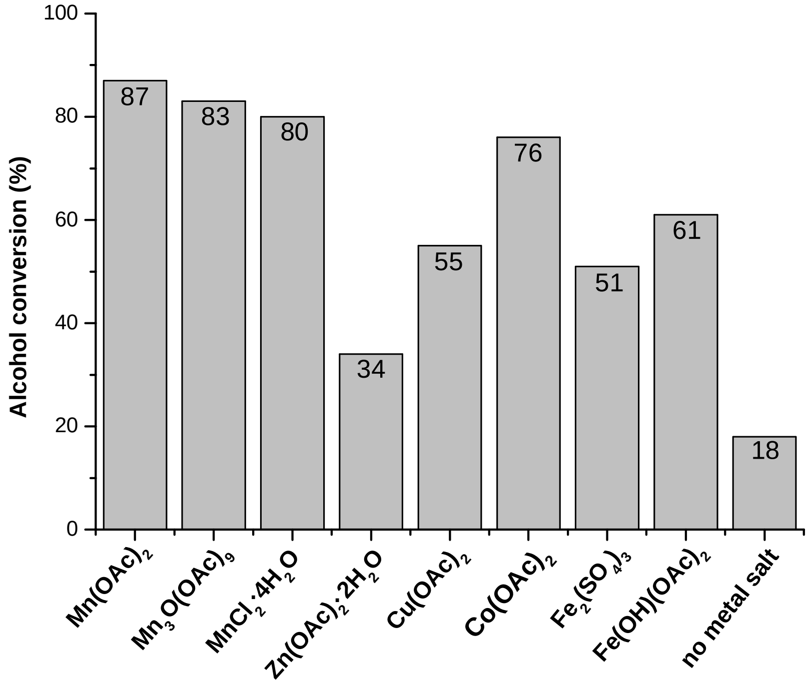


Fig. 1 Oxidation of 2-octanol catalysed by different metal salts with *t*BuOOH. 2-Octanone was obtained as sole product. Reaction conditions: 1 mmol of substrate, 1.8 mol% of metal salt, 2.5 equivalents of *t*BuOOH (313 µL), 7 µL of TFA, 1.5 mL of CH_3CN, 80 °C, 21 h.

Oxidation of 2-octanol was further optimised with respect to TFA acid additive, solvent, oxidant, reaction temperature and the amount of $Mn(OAc)_2$ (the effect of latter is discussed in section 3.3). Previous studies have shown the benefit of carboxylic acid addition for the oxidation activity of a Mn catalyst. The most often used acid for this purpose has been acetic acid and the oxidant has typically been H_2O_2.[13,47] In case of oxidative cyclizations with $Mn_3O(OAc)_9$, it has been found that when TFA is used as an additive, reactions typically proceed faster but the obtained yields of the products are decreased.[27] Our studies with 2-octanol show that TFA additive has a significant effect both on the conversion and the selectivity of the oxidation reaction (Table S1 and Fig. S2 in ESI). When the amount of TFA is varied between 0 and 50 µL (650 µmol), the optimal amount is found to be 7 µL (91 µmol, in comparison to the used catalyst amount of 18 µmol). When less or more carboxylic acid is used, the catalytic system gives lower conversions. Similar trend has been reported previously in oxidation of cyclohexane with Mn(IV) salt catalyst.[13] Larger TFA amounts also decrease selectivity as other oxidation products, such as heptanoic acid and hexanoic acid, are formed (Table S1, ESI). We also noticed herein that TFA esters of primary alcohols, such as 1-octanol, are formed with larger TFA amounts, which as a consequence lowers the alcohol conversion to carboxylic acid. However, the ester formation can be avoided altogether with the chosen TFA amount of 7 µL. When TFA is replaced by acetic acid (400 µL) in oxidation of 2-octanol, lower conversion (66%) and selectivity (87%) are obtained (Table S2 in ESI). Shul´pin et al.[12,48-51] have reported previously about a dinuclear Mn(IV) complex enabling efficient catalysis of various oxidation reactions with H_2O_2 or *t*BuOOH oxidant. The system requires use of carboxylic acid co-catalyst, preferably oxalic acid.[12,48-51] In our catalytic system TFA has an important role in controlling the solubility and the oxidation state of the Mn species (see section 3.4).

Oxidation of 2-octanol was performed in three different solvents. The highest conversion (87%) and selectivity (>99.9%) is obtained in acetonitrile, whereas in both ethyl acetate and toluene they are significantly lower (conversions 38%, selectivities 43 and >99.9%, see Table S3 in ESI). $Mn(OAc)_2$ catalysed oxidation of 2-octanol can be conducted also at 60 °C but the conversion to 2-octanone is somewhat lower than obtained at 80 °C, 67% vs. 87%. However, choice of oxidant is crucial for the catalytic performance of $Mn(OAc)_2$ as H_2O_2 and O_2 (10 bar) gave only very low conversions to 2-octanone (6-7%) during 21 h reactions.

Secondary alcohols, including sterically hindered 1-phenyl-1-propanol, fenchyl alcohol and *endo*-1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-ol (borneol) as well as aliphatic 2-octanol, are converted with $Mn(OAc)_2$/*t*BuOOH to their respective ketones in good to excellent conversions (42-100%, Table 1 entries 1-4). 1-Octanol and 1-undecanol, which as primary aliphatic alcohols are generally considered to be challenging to be oxidised, are selectively converted to their carboxylic acids in a good *ca.* 60% conversion (entries 5 and 6) whereas in case of benzylic alcohols conversion to the corresponding carboxylic acid is high (74-100%) with a selectivity of 80-99.9% (entries 7-11). 1-Naphthalenemethanol gives a full conversion with a 99% selectivity to 1-naphthoic acid. During the oxidation reactions of 2-thiophenemethanol and cinnamyl alcohol various side products are observed (entries 12 and 13), thus showing the limitations of the catalytic system with heterocyclic and allylic alcohols. Cyclohexanol was converted to cyclohexanone in a 66% conversion and >99.9% selectivity (entry 14).

Table 1

Oxidation of various alcohols with the homogeneous $Mn(OAc)_2$/*t*BuOOH system.[a]

Entry	Substrate	Main product	Time (h)	Alc. conv. (%) / Isolated yield (%)	Select. (%)
1	2-octanol	ketone	21	87[b]	>99.9
2	1-Ph-1-propanol	ketone	2	40[c]	>99.9
		ketone	5	84	>99.9
		ketone	8	100[c] /93	>99.9
3	fenchyl alc.	ketone	21	42	>99.9
4	borneol	ketone	21	98	>99.9
5	1-octanol	acid	21	60	>99.9
6	1-undecanol	acid	21	61	>99.9
7	benzyl alc.	aldehyde	8	67[d]	52
		acid	21	100[d] /89	>99.9
8	4-NO_2-benzyl alc.	acid	13	100 /95	99
9	4-MeO-benzyl alc.	acid	8	93[e]	60
		acid	21	100[e]	89
10	1-naphthalenemeth.	acid	13	100 /95	99
11	4-Cl-benzyl alc.	acid	8	90[f]	58
		acid	21	100[f] /91	87
12	2-thiophenemeth.	aldehyde	15	93[g]	67
13	cinnamyl alc.	acid	21	100[h]	40
14	cyclohexanol	ketone	21	66	>99.9

[a] See section 2.3. for reaction conditions. [b] $Mn(OAc)_2$ (18 µmol) used with SB ligand (18 µmol): 65% conv. and >99.9% select. to 2-octanone in 21 h. [c] $Mn(OAc)_2$ (18 µmol) used with Schiff base ligand (18 µmol): 64% conv. and 100% select. to 1-phenyl-1-propanone in 2 h; 100% conv. and >99.9% select. in 8 h. [d] $Mn(OAc)_2$ (18 µmol) used with Schiff base ligand (18 µmol): 72% conv. and 64% select. to benzoic acid in 8 h; 84% conv. and 80% select. to benzoic acid in 21 h. [e] Side products: 4-methoxybenzaldehyde (32% in 8 h, 9% in 21 h), 4-methoxyphenol (2% in 8 h, 1% in 21 h), *N*-(4-methoxybenzyl)acetamide (2% in 8 h, 1% in 21 h). [f] 12% of chlorobenzene side product. [g] Side products: 21% 2-thiophenecarboxylic acid, 3% 2,2'-methylenedithiophene, 7% 2-methylthiophene. [h] Side products: 40% benzoic acid, 12% benzaldehyde, 5% acetophenone, 5% 1-phenyl-1-propanone.

Formation of oxidation products as a function of reaction time was studied with 1-phenyl-1-propanol, 1-octanol and 2-octanol (Fig. 2). As predicted, the secondary alcohols are oxidised clearly faster than the primary alcohol which produced 1-octanoic acid as the sole product. When a mixture of 1-octanol (0.5 mol) and 2-octanol (0.5 mol) was oxidised under the typical reaction conditions, the catalytic system showed no chemoselectivity. 2-Octanol gave 2-octanone with a 89% conversion and 1-octanol yielded 70% of 1-octanoic acid and 9% of the corresponding TFA ester.

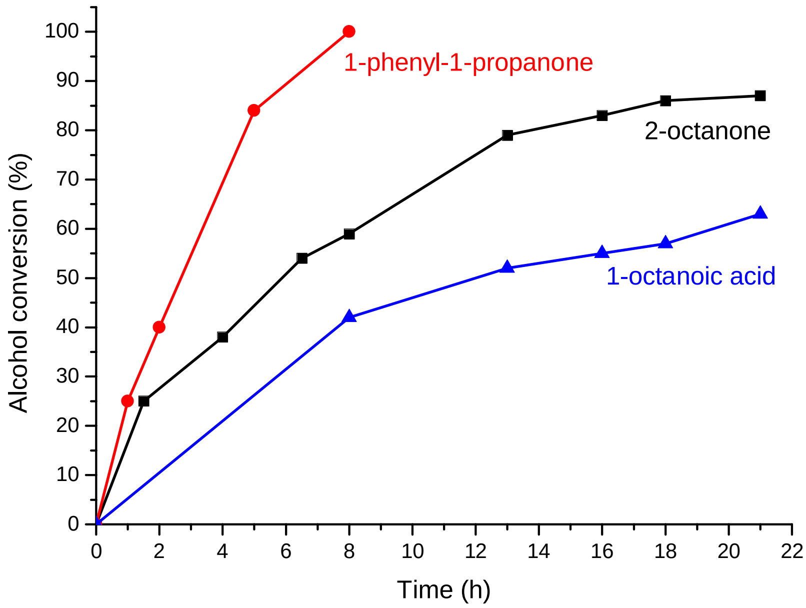


Fig. 2 Selective formation of 1-phenyl-1-propanone, 2-octanone and 1-octanoic acid oxidation products as a function of reaction time. Reaction conditions: 1 mmol of alcohol substrate, 18 µmol of $Mn(OAc)_2$, 313 µL of *t*BuOOH (2.5 equivalents), 7 µL of TFA, 1.5 mL of CH_3CN, 80 °C.

Manganese Schiff bases are often used as homogeneous alcohol oxidation catalysts[13-20] but only in a few cases the oxidant has been *t*BuOOH.[19,20] For this reason, we wanted to study how the addition of synthesised *N*,*N′*-(ethylene)bis(4-[2-(ethylthio)ethoxy]salicylideneimine) Schiff base (SB) ligand affects the oxidation of 1-phenyl-1-propanol, benzyl alcohol and 2-octanol by $Mn(OAc)_2$/*t*BuOOH. These substrates were chosen since without SB ligand two of the former alcohols are oxidised surprisingly slowly (8 or 21 h) in relation to 2-octanol (21 h) which generally requires the longest reaction time. 1-Phenyl-1-propanol is selectively oxidised to the corresponding ketone in 64% conversion in 2 h time with SB ligand/$Mn(OAc)_2$ in comparison to the 40% conversion obtained when only $Mn(OAc)_2$ is used (Table 1, entry 2). In case of benzyl alcohol oxidation, addition of SB ligand enhances slightly both the conversion (72% vs. 67% with solely $Mn(OAc)_2$) and the selectivity (64% benzoic acid vs. 52% benzaldehyde with solely $Mn(OAc)_2$) during the first eight hours of the reaction. However, in 21 hours $Mn(OAc)_2$ catalysed reaction reaches selective 100% conversion to benzoic acid whereas the SB ligand/$Mn(OAc)_2$ catalysed reaction results to 84% conversion to benzoic acid with 80% selectivity (Table 1, entry 7). 2-Octanol is oxidised in 87% conversion with $Mn(OAc)_2$ catalyst after 21 h reaction time whereas with SB ligand/$Mn(OAc)_2$ the conversion is significantly lower being 65% at its highest (Table 1, entry 1). Of the studied alcohols, only with 1-phenyl-1-propanol the oxidation reaction proceeded faster in the presence of the SB ligand.

3.2. Oxidation of hydrocarbons, amines and isochroman by Mn(OAc)$_2$ catalyst using tBuOOH oxidant

Our alcohol oxidation studies carried out in different solvents showed that Mn(OAc)$_2$ catalyst is able to oxidise toluene with *t*BuOOH oxidant (Table S3 in ESI). Catalytic amounts of manganese salts have been only rarely reported to function as oxidation catalysts.[35-37] In one of the studies, $Mn_3O(OAc)_9$ has been shown to oxidise a variety of alkenes with *t*BuOOH oxidant in O_2 atmosphere at room temperature during 48 h reactions.[35] The oxidation capacity of the Mn(OAc)$_2$/*t*BuOOH system was experimented herein with a selection of different types of alkanes, cyclohexene and cyclic ether isochroman (Table 2, entries 1-8). All these reactions were performed in air at 70 °C for 16 h except oxidations of *n*-octane and *n*-decane which were continued for 18 h.

Isochroman is oxidised selectively to the corresponding ketone in a high conversion (94%) and also in case of ethylbenzene (53%) and cyclooctane (48%) the corresponding ketones are the major products. Linear *n*-octane and *n*-decane are more challenging substrates to be oxidised than the previous ones. Surprisingly, they have a high preference for the oxidation of C(2) methylene site and are oxidised mainly to the corresponding ketones in good conversions (46%). The normalised selectivity parameters C(2):C(3):C(4) for the obtained ketone products in the oxidation of *n*-octane and *n*-decane are approximately 9:4:2 and 6:2:4 respectively. Previously in the literature for example Fe porphyrin, Cu(II), Mn(III) and Mn(IV) complexes have been reported to oxidise linear alkanes with good regioselectivity.[52-54] Toluene, on the other hand, is oxygenated here mainly to benzoic acid (selectivity 87%, overall conversion 23%). Oxidation of cyclohexane yields cyclohexanone and cyclohexanol in a 2.6:1 ratio with a total conversion of 18%. In a previous study approximately the same ratio of products has been obtained at room temperature using Mn(II) salen catalyst with *t*BuOOH.[55] The same study also reported that Mn(OAc)$_2$ (0.04 mmol) itself with *t*BuOOH (4 mmol) is not able to oxidise cyclohexane (40 mmol) at room temperature.[55] This, together with our results from the oxidation of 2-octanol performed both at 60 and 80 °C (see section 3.1.), seems to prove the importance of elevated temperature for the catalytic activity of Mn(OAc)$_2$ in the current system. The alkane and isochroman oxidation reactions are considered to proceed to ketones/carboxylic acid via formation of alcohols, even though only in case of cyclohexane alcohol product was observed in the GC-MS analysis. It is noteworthy that no alkyl peroxide species were detected in these oxidations reactions by GC-MS analysis.

Alkenes oxidise easier than alkanes and the results obtained herein with cyclohexene (40% total conversion) and cyclohexane (18% total conversion) are in accordance with this. In the reaction with cyclohexene, the products formed are 3-(*tert*-butylperoxy)cyclohexene (24%) and 2-cyclohexen-1-one (16%). 3-(*tert*-Butylperoxy)cyclohexene is considered to be the primary oxidation product which is further decomposed to the ketone. Addition of excess of solid PPh_3 into the GC-MS sample prior to the analysis[44-46] had no effect on concentrations of the observed products. The oxidation of cyclohexene to the allylic ketone and the fact that no epoxide product was observed strongly implicate that the system involves a radical oxidant via one-electron oxidation (see section 3.3. for a more detailed discussion).[9]

The ability of $Mn(OAc)_2$/*t*BuOOH system to oxidise tertiary amines was tested with *N*,*N*-dimethylaniline (DMA) and *N*,*N*-dimethylaminopyridine (DMAP) (Table 2, entries 9 and 10). In both cases, the substrate is almost fully converted and one major oxidation product is obtained. Reaction of DMA yields *N*-methyl-*N*-phenylformamide (57% conversion) as an oxidation product and small amounts of various side products (see Table 2) whereas DMAP yields mainly *N*-methyl-*N*-(pyridin-4-yl)formamide (50%) and *N*-methylpyridin-4-amine (26%). Demethylation of tertiary amines, as was observed to occur herein for both of the amines used, is well reported in the literature.[8-10,56]

Table 2

Oxidation of hydrocarbons, isochroman and amines with the homogeneous $Mn(OAc)_2$/*t*BuOOH system.[a]

Entry	Substrate	Main product[b]	Substrate conversion (%)	Selectivity (%)
1	*n*-octane	2-octanone	46	59
2	*n*-decane	2-decanone	46	52
3	cyclooctane	cyclooctanone	48	71
4	cyclohexane	cyclohexanone	18	72
5	cyclohexene	3-(*t*Bu-peroxy)cyclohexene	40	60
6	isochroman	isochroman-1-one	94	>99.9
7	ethylbenzene	acetophenone	53	74
8	toluene	benzoic acid	23	87
9	DMA	*N*-Me-*N*-phenylformamide	97	59
10	DMAP	*N*-Me-*N*-(pyridin-4-yl)formamide	83	60

[a] Reactions were performed at 70 °C for 16 h except in case of entries 1 and 2 for 18 h. See section 2.3. for detailed reaction conditions. [b] Side products. Entry 1: 13% 3-octanone, 6% 4-octanone. Entry 2: 8% 3-decanone, 14% 4-decanone. Entry 3: 2% cyclooctene, 2% 9-oxabicyclo[6.1.0]nonane, 3% 1,4-cyclooctanedione, 7% unidentified compound. Entry 4: 5% cyclohexanol. Entry 5: 16% 2-cyclohexen-1-one. Entry 7: 6% benzaldehyde, 8% 1,1'-(oxydiethylidene)bisbenzene. Entry 8: 3% benzaldehyde. Entry 9: 12% 4-(methylamino)benzaldehyde, 9% *N*-(4-formylphenyl)-*N*-methylformamide, 7% 4-(dimethylamino)benzaldehyde, 5% *N*-methylaniline, 5% 1,2-diphenyldiazene, 2% *N*-phenylformamide. Entry 10: 26% *N*-methylpyridin-4-amine, 4% *N*-(pyridin-4-yl)formamide, 3% 4-aminopyridine.

3.3. Reaction rate study

In the reaction rate study of alcohol oxidation by the $Mn(OAc)_2$/*t*BuOOH based catalytic system, the effects of different initial concentrations of $Mn(OAc)_2$ and 2-octanol were studied using the initial rate method. The kinetic curves of the accumulation of 2-octanone with different concentrations of 2-octanol (0.26, 0.73 and 0.94 M) and $Mn(OAc)_2$ (2.28, 4.55 and 18.21 mM) are presented in Fig. 3 (see also Tables S4 and S5 in ESI). The initial oxidation rate depends linearly on the concentration of substrate as well as on the concentration of $Mn(OAc)_2$ as can be seen from Fig. S3. Dependencies of the reaction rate constants k (obtained from the slopes of the best-fit lines to the plots of [2-octanone] vs. time in Fig. 3a) on the concentrations of 2-octanol and $Mn(OAc)_2$ were next determined to reveal that the reaction is fractional order with respect to the alcohol (Fig. 3b, slope = 0.67) and the $Mn(OAc)_2$ (Fig. 3d, slope = 0.34) concentrations. It seems that the rate of the reaction is dependent on the intermediate $Mn^{(IV)}O$

species which are formed when the metal centre reacts with the oxidant, rather than being directly dependent on the concentration of the $Mn(OAc)_2$ (the suggested reaction mechanism is discussed in detail in the section 3.4).[57]

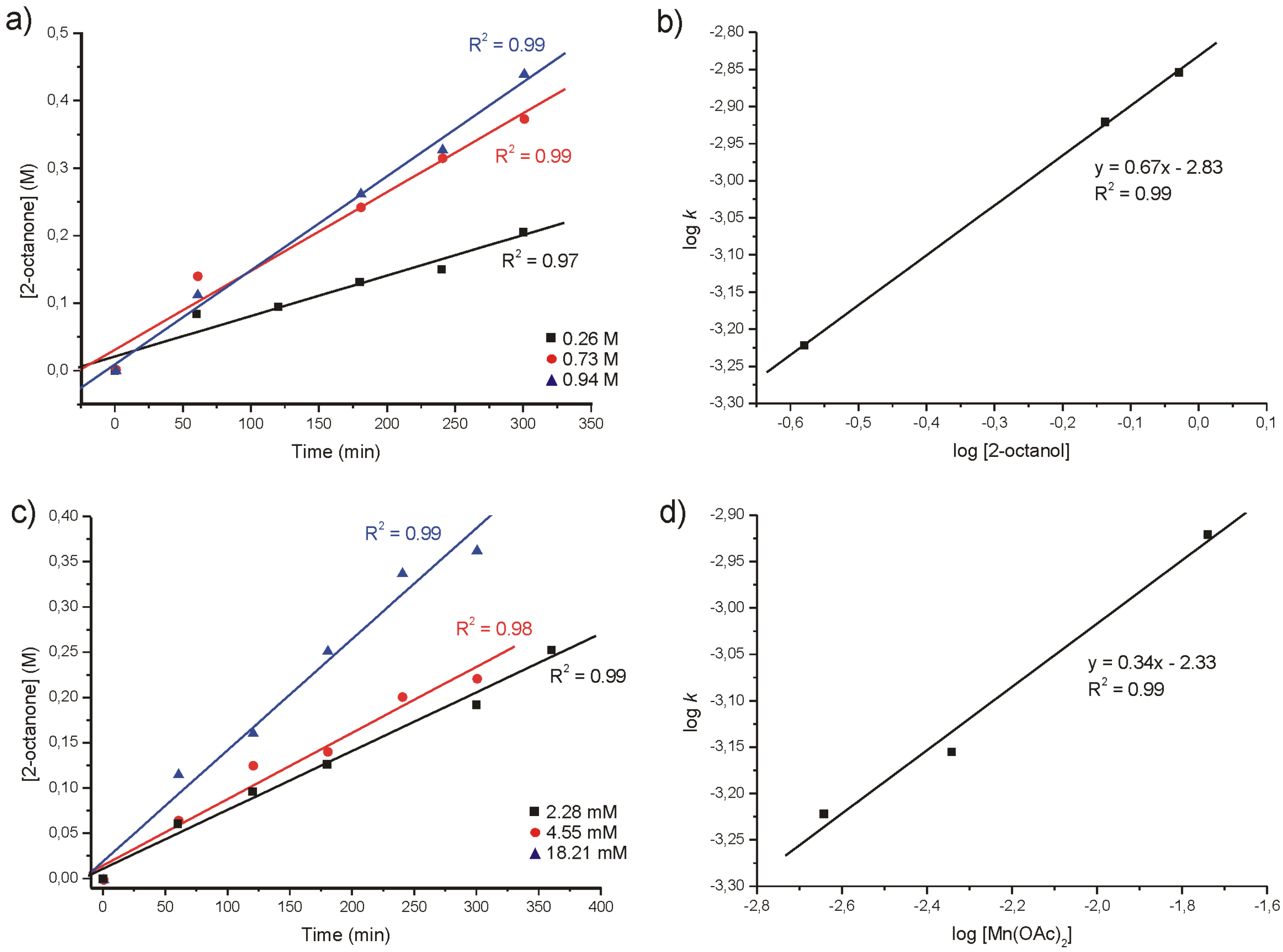


Fig. 3 a) Accumulation of 2-octanone with different concentrations of 2-octanol (0.26, 0.73 and 0.94 M). b) Double logarithmic plot of reaction rate constant *k* vs. initial concentration of 2-octanol. Reaction conditions for graphs a and b: 0.5, 1.5 or 2.0 mmol of 2-octanol, 18 µmol $Mn(OAc)_2$, 1.5 mL of CH_3CN, 7 µL of TFA, 313 µL of *t*BuOOH, 80 °C. c) Accumulation of 2-octanone with different concentrations of $Mn(OAc)_2$ (2.28, 4.55 and 18.21 mM). d) Double logarithmic plot of reaction rate constant *k* vs. initial concentration of $Mn(OAc)_2$. Reaction conditions for graphs c and d: 4.5, 9 or 36 µmol of $Mn(OAc)_2$, 1 mmol of 2-octanol, 1.5 mL of CH_3CN, 7 µL of TFA, 313 µL of *t*BuOOH, 80 °C.

3.4. Reaction mechanism

Mechanism of the oxidation reaction catalysed by the $Mn(OAc)_2$/*t*BuOOH system was studied in various ways. First, we performed experiments with selected alcohols and hydrocarbons under argon atmosphere (Tables S6 and S7 in ESI) in order to reduce the amount of O_2 in the reaction mixtures and thus the radical chain reactions. With all of the studied hydrocarbon substrates, the reactions carried out in air yielded higher conversion which clearly suggests that O_2 is involved in the reactions. However, as also selectivities were higher in the reactions performed in air it is likely that the reaction mechanism is not solely radical chain autoxidation in nature but more controlled.[9,26,58,59] As for the alcohols, the conversions were almost the same or slightly higher for the reactions run in air. The role of dioxygen was then studied further in oxidation of 1-phenyl-1-propanol by carrying out a reaction in dioxygen atmosphere with *t*BuOOH oxidant using an O_2 filled balloon (see section 2.3. for experimental details). During a 2 h reaction, 60% of the corresponding ketone was obtained in comparison to the 40% conversion yielded with *t*BuOOH oxidant in air. These results clearly indicate the significance of O_2 also for the oxidation of alcohols with the used catalytic system. Next, the oxidation studies with amines were conducted in benzene and CH_3CN (see Tables 2 and S8). Conversions of both amines in benzene are slightly lower than in CH_3CN but the selectivities on the contrary are higher. This seems to indicate that benzene is trapping hydroxyl radicals.[9,26,58,59] The observation of the benzene effect and the role of O_2 lead us to the conclusion that at least part of the observed reactivity results from free radical chemistry.

In the following, the oxidation state of Mn will be considered. $Mn(OAc)_2$/*t*BuOOH system oxidises alcohols with and without TFA (see section 3.1, and ESI for Table S1 and Fig. S2) but in the absence of TFA a black precipitate is formed during the oxidation reactions. According to energy-dispersive X-ray spectrometry (EDS) analysis, the precipitate is most likely a mixture of Mn(III) and Mn(IV) oxide (see Fig. S4 in ESI) which is believed to be formed as a result of catalyst poisoning.[60] These results show importantly how the Mn(II) centres of the precatalyst are likely oxidised through one-electron oxidation. The Mn species present in a soluble form in the reaction mixture containing TFA and *t*BuOOH were on the other hand studied by the Evans' NMR method (see section 2.4. for the details).[61,62] The effective magnetic moment of 3.8 B.M. indicates that the main Mn species in the solution is high-spin Mn(IV) (spin-only value 3.9 B.M.). Mass spectrum (ESI^+-TOF) of the acetonitrile solution of $Mn(OAc)_2$, *t*BuOOH and TFA was then recorded to characterise in more detail the Mn species in the solution. The spectrum shows one intense peak at 530 *m/z* which could be identified as a sodium adduct of dinuclear Mn(IV) peroxo species (see Fig. S5 in ESI). Even though it is possible that the dinuclear species is formed during the ionisation process of the MS measurement, both MS and NMR studies indicate the presence of Mn(IV) species in the solution. The acetonitrile solutions of $Mn(OAc)_2$ and $Mn_3O(OAc)_9$ containing TFA and *t*BuOOH were also studied with UV-Vis spectroscopy but unfortunately no absorption bands arising from the Mn species were detected (see Fig. S6 in ESI). There are examples in the literature where the UV-Vis spectra of Mn complexes also lack absorption bands.[63]

In summary, it can be concluded that the catalytic reaction intermediates of *t*BuOOH and $Mn(OAc)_2$ do not react through the heterolysis of the O–O bond which would lead to two-electron oxidation.

Instead, all evidence points to homolytic O–O bond cleavage which yields two radical species (tBuO• and [$Mn^{(IV)}O$]) leading to one-electron oxidants.[9,26,58,59,64] Formation of the tBuO• species is supported by the results from the oxidation of cyclohexene where 3-(*tert*-butylperoxy)cyclohexene was obtained as major product. In the literature, $Mn_3O(OAc)_9$ catalysed reactions have also been reported to proceed via the radical mechanism,[26-29,35] as well as reactions catalysed by dinuclear Mn(IV) complex with oxalic acid co-catalyst and H_2O_2 or tBuOOH oxidant.[49,50] The proposed mechanism for the oxidation reactions catalysed by the $Mn(OAc)_2$/tBuOOH system is presented in Fig. 4. Prior the substrate addition as well as during the oxidation reaction the active species in the solution are Mn(IV) species. Kinetics studies, which show a fractional-order dependency with the $Mn(OAc)_2$ concentration, support the proposed mechanism involving intermediate Mn species.

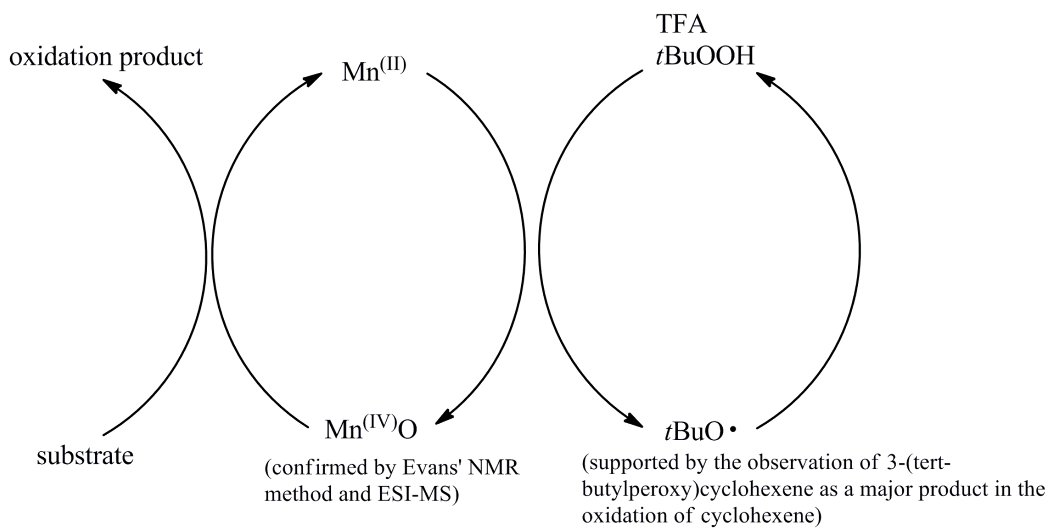


Fig. 4 Proposed mechanism for the oxidation reactions catalysed by the $Mn(OAc)_2$/tBuOOH system.

4. Conclusions

A manganese(II) acetate functions in air as a precatalyst for homogeneous oxidation reactions. The system is based on a catalytic amount of Mn(II) acetate, tBuOOH oxidant, TFA additive and organic solvent. Thorough studies have shown the versatile, efficient and selective nature of the catalytic system. Different alcohols were oxidised in good to high (42-100%) conversions employing the developed catalytic system at 80 °C. Secondary alcohols, such as 2-octanol, fenchyl alcohol and borneol, were converted to their corresponding ketones and primary alcohols, such as 1-octanol and differently substituted benzyl alcohols, were oxidised to carboxylic acids. 2-Thiophenemethanol was an exception giving the corresponding aldehyde as a main product. The catalytic system proved to be applicable also for the oxidation of selected hydrocarbons, tertiary amines and isochroman. For example cyclooctane, isochroman and *N*,*N*-dimethylaniline gave the corresponding main products of cyclooctanone, isochroman-1-one and *N*-methyl-*N*-phenylformamide with good to high conversions. The oxidation reactions proceed likely via a radical pathway that involves *t*BuO• and [$Mn^{(IV)}$O] radical species. The reaction was found to have a fractional-order kinetics dependency with substrate and $Mn(OAc)_2$ concentrations.

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