Elucidation of mechanisms in manganese and iron based oxidation catalysis

Angelone, Davide

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2016

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Mechanistic links in the \textit{in situ} formation of dinuclear manganese catalysts, H$_2$O$_2$ disproportionation and alkene oxidation

The oxidation of substrates, such as alkenes, with H$_2$O$_2$ with the catalyst [Mn(IV,IV)$_2$(µ-O)$_3$(tmtacn)$_2$]$^{2+}$ (1) is promoted by the addition of carboxylic acids by in situ formation of bis-carboxylato complexes of the type [Mn(III,III)$_2$(µ-O)(µ-RCO$_2$)$_2$(tmtacn)$_2$]$^{2+}$. The conversion of 1 to these complexes requires a complex series of redox reactions coupled with overall exchange of µ-oxido for µ-carboxylato ligands. Here, we show that the mechanism by which this conversion takes place holds implications with regard to the species that is directly engaged in the catalytic oxidation of alkenes. Using a combination of UV/Vis absorption, Raman, resonance Raman and EPR spectroscopies, it is shown that the conversion proceeds via an autocatalytic mechanism and that the species that engages in oxidation of organic substrates also catalyses H$_2$O$_2$ decomposition, with the former process being the faster.

Chapter 4

4.1 Introduction

The intimate connection between coordination mode and redox state that is observed in multinuclear manganese complexes lies at the core of the ability of biological systems to engage in redox catalysis, the most prominent examples being manganese based catalases,\(^\[1\]\) superoxide dismutases\(^\[2\]\) and the oxidation of water to molecular oxygen achieved in the oxygen evolving complex of PSII.\(^\[3\]\) The coordination chemistry of multinuclear \(\mu\)-oxido and \(\mu\)-carboxylato bridged manganese complexes has therefore attracted extensive interest over the last decades due to their bioinorganic relevance\(^\[4,5\]\) and their application in selective catalytic oxidations and in bulk oxidation chemistry.\(^\[6,7,8\]\) In particular, in regard to catalytic activity of dinuclear manganese based enzymes,\(^\[9\]\) there is an intimate connection between the cycle between redox states and changes in coordination mode, not least in regard to switching between \(\mu\)-oxido and terminal hydroxide and aqua ligands and carboxylate shifts.\(^{[1b,10]}\)

Manganese complexes based on the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn), such as [Mn(IV,IV)\(_2\)](\(\mu\)-O\(_3\))\(_2\)(tmtacn)\(_2\)]\(^{2+}\) (1) and [Mn(III,III)\(_2\)](\(\mu\)-O)(\(\mu\)-CH\(_2\)CO\(_2\))\(_2\)(tmtacn)\(_2\)]\(^{2+}\) have received notable attention since the first reports by Wieghardt and coworkers,\(^{[11,12]}\) in part due to their remarkably versatile redox dependent coordination chemistry and the discovery in the mid-1990s of their catalytic activity in the oxidation of organic substrates and stains.\(^{[13]}\) A major drawback faced in using these complexes as oxidation catalysts, however, was the excessive disproportionation of H\(_2\)O\(_2\). In the late 1990s, a fruitful search of potential additives led to the discovery that oxalate/oxalic acid,\(^{[14]}\) ascorbic acid,\(^{[15]}\) and more recently alkyl and aromatic carboxylic acids at co-catalytic levels\(^{[16,17]}\) could suppress H\(_2\)O\(_2\) disproportionation. Indeed, carboxylic acids, such as CCl\(_3\)CO\(_2\)H, enabled near complete efficiency in oxidant.\(^{[18]}\)

Although the actual mechanisms by which oxalic and ascorbic acid enhance the activity of 1 towards selective oxidation of organic substrates remains unclear,\(^{[14,15,19]}\) in the case of aliphatic and aromatic carboxylic acids it is clear that under reaction conditions 1 undergoes quantitative conversion to complexes of the type [Mn(III,III)\(_2\)](\(\mu\)-O)(\(\mu\)-RCO\(_2\))\(_2\)(tmtacn)\(_2\)]\(^{2+}\) through a complex series of redox and ligand exchange reactions (Scheme 1).\(^{[18]}\) The presence of carboxylic acids resulted in suppression of disproportionation of H\(_2\)O\(_2\), presumed to be by acting as a source of protons. Furthermore, it is apparent from the dependence of the selectivity of 1 (in regard to the epoxidation vs. cis-dihydroxylation of alkenes) on the steric of the carboxylic acids\(^{[15]}\) used and the observation of enantioselective oxidation with chiral carboxylic acids,\(^{[20]}\) that the active catalytic species bears carboxylato ligands.
Identification of the species that actually engages in oxygen transfer to the organic substrates, however, is challenging since the dominant species (>95%) present under reaction conditions are of the type \([\text{Mn(III,III)}_2(\mu-\text{O})(\mu-\text{RCO}_2)(\text{tmtacn})]^{2+}\) with catalytically inactive Mn\(^{2+}\) ions present also. A key feature of the reactions involving \(\mathbf{1}\) with carboxylic acids is that there is a substantial delay between the addition of H\(_2\)O\(_2\) and the initiation of the conversion of \(\mathbf{1}\) to, for example, \([\text{Mn(III,III)}_2(\mu-\text{O})(\mu-\text{CCl}_3\text{CO}_2)(\text{tmtacn})]^{2+}\) (\(\mathbf{2a}\)). Furthermore, the sigmoidal, rather than exponential, shape of the curve indicated that the reaction is autocatalytic, i.e. an unknown species \(\mathbf{2x}\) formed upon reduction of \(\mathbf{1}\), is itself involved in the further reduction of \(\mathbf{1}\).

In addition to the processes involved in the conversion of \(\mathbf{1}\) to \(\mathbf{2a}\), an open question remains as to the initiation of the reaction. Since the species \(\mathbf{2x}\), which is responsible for the autocatalysis, is formed only upon reduction of \(\mathbf{1}\) then it is probable that the initiation step is either a spontaneous reduction event or triggered by other species. In this contribution, we explore the conversion of \(\mathbf{1}\) to \(\mathbf{2a}\) in detail using a combination of UV/Vis absorption, EPR, Raman and resonance Raman (rR) spectroscopies with the aim of elucidating the series of reactions that convert \(\mathbf{1}\) to \(\mathbf{2a}\) and in establishing whether or not the species involved during this process are of relevance to the catalysed oxidation of organic substrates also.
Chapter 4

4.2 Results
UV/Vis absorption, FTIR, Raman and resonance Raman spectroscopy of 1 and 2
The synthesis and characterization of complexes 1, 2a and 2b were described earlier.\textsuperscript{[11,12]} The Mn(II,II)\textsubscript{2} complex 2b does not show substantial UV/Vis absorption.\textsuperscript{[13]} The Mn(III,III)\textsubscript{2} complex 2a\textsuperscript{[12]} and Mn(IV,IV)\textsubscript{2} complex 1\textsuperscript{[11]} both show strong absorption in the UV and visible regions (Figure 1). The visible absorption bands of 1 and 2a are assigned to metal centred transitions, while the bands < 450 nm are assigned to ligand to metal charge transfer bands (vide infra).

Assignment of the FTIR and Raman spectra of complexes 1, 2a and 2b is facilitated by comparison with DFT calculated spectra (see supporting information) and, as expected, are similar with respect to bands associated with the tmtacn ligand but differ substantially in the low wavenumber region (Figures S1-3). Indeed, the modes associated with the Mn(IV)(μ-O)\textsubscript{3}Mn(IV) and Mn(III)(μ-O)(μ-RCO\textsubscript{2})\textsubscript{2}Mn(III) cores of 1 and 2a, respectively, dominate the resonance Raman spectra recorded at λ\textsubscript{exc} 355 nm (Figure S4 and S5) and 457 nm at the same concentrations (1 mM) as employed\textsuperscript{[12,13]} in the catalytic oxidation of alkenes (vide infra). The resonance Raman spectrum of 1 was reported earlier (in the solid state, λ\textsubscript{exc} 457 nm) by Hage \textit{et al.}\textsuperscript{[21]} and showed enhancement of a band at 700 cm\textsuperscript{-1} assigned to the ν\textsubscript{sym}(Mn-O-Mn) mode based on \textsuperscript{18}O labelling. Raman spectra of 1 recorded in CH\textsubscript{3}CN at λ\textsubscript{exc} 355 nm and 457 nm show resonance enhancement primarily of low wavenumber modes (< 900 cm\textsuperscript{-1}) consistent with a μ-oxido to Mn\textsuperscript{IV} LMCT band. DFT and TD-DFT calculations on 1 confirm that the enhanced band at 700 cm\textsuperscript{-1} is due to a symmetric Mn-(μ-O)\textsubscript{3}-Mn stretching mode. Assignment of the band at 799 cm\textsuperscript{-1} is less straightforward, however, but is likely to be due to Mn-N stretching modes or tmtacn ring breathing. For 2a, significant resonance enhancement was observed, at 355 nm only, with a carboxylato bending mode at 790 cm\textsuperscript{-1} and additional weaker bands at 743 cm\textsuperscript{-1} (which overlaps with a band of acetonitrile, Figure 2) 1002, 1138, 1162, 1261 and 1293 cm\textsuperscript{-1} assigned to tmtacn
Manganese oxidation catalysis in acetonitrile

ligand modes. The latter bands are similar to those observed for 1. In addition to the carboxylato based modes, relatively intense bands are observed between 420 and 520 cm$^{-1}$, which are assigned, based on DFT calculations, to symmetric and asymmetric breathing modes, respectively, involving the entire \( \text{Mn}(\text{III,III})_2(\mu\text{-oxido})(\mu\text{-carboxylato}) \) structure. The enhancement of predominantly carboxylato modes indicates that the absorption band at 350 nm is a carboxylato to \( \text{Mn}(\text{III}) \) charge transfer band. The UV/Vis absorption and resonance Raman spectra of 1 and 2a (Figures S4 and S5, respectively) are unaffected by the addition of \( \text{CCl}_3\text{CO}_2\text{H} \).

For 1 and 2a, the redox potentials (in CH$_3$CN vs SCE) for reduction (0.2 V) and oxidation (1.4 V), respectively,[13] indicate that direct electron transfer between these complexes is not thermodynamically feasible. Indeed both in the absence and presence of \( \text{CCl}_3\text{CO}_2\text{H} \), mixtures of these complexes are stable over several hours at room temperature and the UV/Vis absorption and rR spectra of a series of mole fraction mixtures match exactly to the spectra calculated by weighted summation of the individual spectra (Figure 2). Similarly, under reactions conditions, i.e. with 10 mM \( \text{CCl}_3\text{CO}_2\text{H} \) and 100 mM water in CH$_3$CN, 1, 2a and 2c do not react with each other and are stable for several hours after mixing (Figure S6). These data exclude the possibility of direct electron transfer between the complexes.

Reaction monitoring with resonance Raman spectroscopy

The comparable degree of enhancement of the low wavenumber Raman bands of 1 and 2a at 355 nm, at the concentrations employed in the catalytic oxidation of alkenes, allow the conversion from 1 to 2a to be monitored quantitatively concomitant with the change in [\( \text{H}_2\text{O}_2 \)] (at 868 cm$^{-1}$, Figure 3).
Figure 3 Raman spectra ($\lambda_{exc}$ 355 nm) before, 10 s and then at 1000 s intervals after addition of 50 equiv. of $\text{H}_2\text{O}_2$ to a solution of 1 (1 mM) with $\text{CCl}_3\text{CO}_2\text{H}$ (10 mM) in acetonitrile. Arrows indicate the direction of change in band intensity. Spectra have been normalised to the solvent band at 919 cm$^{-1}$ to correct for changes in inner filter effects during the reaction.

Inspection of the time dependence of the changes in Raman intensity reveals an excellent correlation between the changes in intensity of the characteristic Raman bands of $\textbf{1}$, $\textbf{2a}$ and $\text{H}_2\text{O}_2$, showing that the consumption of $\text{H}_2\text{O}_2$ and the conversion of $\textbf{1}$ to $\textbf{2a}$ proceed concomitantly. Notably, although 50 equiv. of $\text{H}_2\text{O}_2$ w.r.t. $\textbf{1}$ were added, the consumption of $\text{H}_2\text{O}_2$ proceeds at a steady rate until $\textbf{1}$ is consumed and continues thereafter until all $\text{H}_2\text{O}_2$ was consumed (Figure 4). The full consumption of the 50 equiv. of $\text{H}_2\text{O}_2$ during the period over which $\textbf{1}$ converts to $\textbf{2a}$ indicates that in that period a species capable of $\text{H}_2\text{O}_2$ disproportionation is present (vide infra).

Figure 4 Change in normalised intensity of Raman scattering ($\lambda_{exc}$ 355 nm) at (i) 868 cm$^{-1}$ ($\text{H}_2\text{O}_2$) (ii) 700 cm$^{-1}$ (1) (iii) 919 cm$^{-1}$ ($\text{CH}_3\text{CN}$, a proxy for absorbance at 363 nm)$^{22}$ and (iv) 786 cm$^{-1}$ ($\textbf{2a}$) after addition of 50 equiv of $\text{H}_2\text{O}_2$ to a solution of 1 (1 mM) with $\text{CCl}_3\text{CO}_2\text{H}$ (10 mM) in acetonitrile.
Reaction monitoring with EPR spectroscopy

Although both complexes \(1\) and \(2a\) are silent to X-band EPR spectroscopy (at 77 K), the presence of complexes in other oxidation states, in particular Mn(II), Mn(IV), Mn(II,II)\(_2\), Mn(II,III)\(_2\) and Mn(III,IV)\(_2\), should be manifested by the appearance of their characteristic EPR signals. The conversion of \(1\) to \(2a\) under standard conditions was monitored by UV/Vis spectroscopy with flash freezing of aliquots of the reaction mixture at specific times (Figure 5). The EPR spectra of the aliquots 1-4 are featureless. In the case of the spectra obtained at points 5 and 6 a very weak signal is observed that can be assigned tentatively to a 16 line species (the hyperfine coupling value \(a\) is ca. 76 G).\(^{[21]}\) Between points 7 and 9 the characteristic 6 line signal of octahedral high spin Mn(II) appears and increases in intensity concomitant with the decrease and recovery in absorbance at 532 nm. Comparison of the EPR spectrum at point 9 with that of Mn(II)(ClO\(_4\))\(_2\) under similar conditions indicates that about 10% of the manganese is present as a mononuclear complex, presumably with loss of the tmtacn ligand, which is consistent with the absorbance at 532 nm, which is ca. 10% below that expected for full conversion of \(1\) to \(2a\). Between points 9 and 10 the intensity of the six-line signal remains essentially constant, however, an additional weak 16 line signal appears also. Notably, the characteristic broad signal of \(2c\)^{[18]} is not observed at any stage, indicating that it is not present in significant amounts.

**Figure 5** (a) Change in absorbance with time at 532 nm following the conversion of \(1\) to \(2a\) and X-band EPR spectra (at 77 K) of aliquots of the reaction mixture flash frozen to 77 K at the time points (b) 1-7, (c) 6-9 and (d) 6, 9 and 10, as indicated in (a).

Origin of the lag time observed in the conversion of \(1\) to \(2a\)

Although the duration of the lag-time observed in the conversion of \(1\) to \(2a\) is reproducible, i.e. the duration under standard conditions is 350 s +/- 15 s, it is highly sensitive to impurities and the presence of other metal ions and complexes.\(^{[23]}\) Indeed, with a sample of \(1\) that had not
been recrystallized prior to use, a decrease in lag-time of 200 s was observed.\textsuperscript{[24]} Addition of 2a, the ultimate product, prior to addition of \( \text{H}_2\text{O}_2 \) results in only a marginal reduction in the lag-time even when present at a mole fraction of 0.5 and has relatively little effect on the reaction rate either (Figure 6).

![Figure 6 Absorbance at 532 nm over time after addition of 50 equiv. of \( \text{H}_2\text{O}_2 \) to 1 and 2a in acetonitrile with \( \text{CCl}_3\text{CO}_2\text{H} \) (10 mM). \([1]+[2a]\) = 1 mM, mole fraction of 2a was (i) 0, (ii) 0.05, (iii) 0.1, (iv) 0.2, (v) 0.3, (vi) 0.4 and (vii) 0.5.]

In contrast, even 0.01 equiv. of the Mn(II)Mn(II) complex 2b, or a Mn(II) or Mn(III) salt results in a substantial decrease in the lag-time. It is clear, however, that regardless of the duration of the lag-time and the effect impurities or other complexes have on its duration, once initiated the reaction proceeds with almost identical kinetics (Figure 7). The disconnection between the lag-time and reaction kinetics once initiated\textsuperscript{[18]} indicates that, regardless of the event that triggers the initial reduction of H1\(^+\), the species formed upon reduction is much more effective at catalysing the further reduction of H1\(^+\).

![Figure 7 Absorbance at 532 nm over time after addition of 50 equiv. of \( \text{H}_2\text{O}_2 \) to a solution of (i) 1 (1 mM) with \( \text{CCl}_3\text{CO}_2\text{H} \) (10 mM) in acetonitrile and 1 with (ii) 2b (10 \( \mu \)M) (iii) Mn(ClO\(_4\))\(_2\) (20 \( \mu \)M) and (iv) Mn(CH\(_3\)CO\(_2\))\(_3\) (20 \( \mu \)M). Inset: overlay of curves with time offset to when the absorbance was 0.45.]

Dependence of reaction rate on concentration of \( \text{H}_2\text{O}_2 \)

Variation in the number of equiv. of \( \text{H}_2\text{O}_2 \) (5-100 equiv.) added \textit{w.r.t.} 1 has a pronounced effect on the lag time, especially with less than 75 equiv. (Figure 8). The effect on lag time, however, is likely to be due to the concomitant variation in the amount of water added (vide infra). Notably,
Manganese oxidation catalysis in acetonitrile

however, once initiated, the reaction rate is relatively constant, indicating that the reaction is essentially zero order in H$_2$O$_2$, i.e. that the reaction of H$_2$O$_2$ with the species responsible for reducing H1' is a prior rapid equilibrium to the reduction of 1. Furthermore, although complete consumption of the H$_2$O$_2$ present was observed in all cases (as determined by Raman spectroscopy), the conversion of 1 was essentially complete even with 10 equiv. of H$_2$O$_2$ (Figure 9).

![Figure 8 Absorbance at 532 nm over time after addition of (i) 5, (ii) 10, (iii) 25, (iv) 50, (v) 60, (vi) 75, (vii) 90 and (viii) 100 equiv. of H$_2$O$_2$ to a solution of 1 (1 mM) with CCl$_3$CO$_2$H (10 mM) in acetonitrile.](image)

![Figure 9 Intensity of the Raman band ($\lambda_{exc}$ 355 nm) of 1 at 700 cm$^{-1}$ over time after addition of (i) 5, (ii) 10, (iii) 25, (iv) 40 and (v) 50 equiv. of H$_2$O$_2$ to a solution of 1 (1 mM) with CCl$_3$CO$_2$H (10 mM) in acetonitrile.](image)

It is notable that all of the H$_2$O$_2$ added initially is consumed during the conversion of 1 to 2a but not before or after this process occurs. This correlation indicates that the species (2x) formed upon reduction of 1, could be responsible for both the reduction of 1 and the disproportionation of H$_2$O$_2$. Previously,$^{[18]}$ it was demonstrated that whereas when 2a is used directly in the catalytic oxidation of cyclooctene the efficiency in usage of H$_2$O$_2$ toward alkene oxidation was essentially complete, when 1 is used the reaction is systematically less efficient.$^{[18]}$ The systematic difference observed being the H$_2$O$_2$ that is disproportionated during the short period in which 1 undergoes conversion to 2a.


Chapter 4

Dependence of reaction on concentration of H$_2$O

The addition of excess water to the reaction (up to 150 mM) has relatively little influence on both the lag-time, the reaction rate and final yield of 2a (Figure 10). Above 150 mM, an increase in the lag-time and a decrease in reaction rate was observed together with a decrease in the maximum absorbance at 532 nm, indicating that formation of 2a is incomplete under these conditions. Notably, however, the absorbance reaches the same maximum at 650 nm under all conditions except where a large excess of CCl$_3$CO$_2$H and water is present, which could indicate the formation of the non-$\mu$-oxido bridged Mn(III)Mn(III) complexes, i.e. 2d.$^{[18]}$

![Figure 10 Absorbance at 532 nm and 650 nm over time after addition of 50 equiv. of H$_2$O$_2$ to a solution of 1 (1 mM) in acetonitrile with (i) 100 (i.e. that which is present in the 50 equiv. of H$_2$O$_2$ added), (ii) 120, (iii) 150, (iv) 180, (v) 200, (vi) 1000, (vii) 1500 and (viii) 1900 mM H$_2$O with CCl$_3$CO$_2$H (10 mM) and (ix) with 400 mM of H$_2$O and CCl$_3$CO$_2$H (100 mM).

Dependence of reaction on the concentration of CCl$_3$CO$_2$H

Typically 10 equiv. of carboxylic acid were employed for catalysis with 1, however, it was noted earlier$^{[18]}$ that the concentration of carboxylic acid had only a modest effect on the catalytic oxidation of cyclooctene with 1. Specifically, even two equiv. of CCl$_3$CO$_2$H were sufficient to achieve full activity initially, albeit with a loss of activity at later stages in the reaction. The lag time is affected only modestly with increasing acid concentration and notably the rate of reaction, once it has initiated, is essentially the same in all cases (Figure 11). The decrease in absorbance after the initial maximum is reached is noticeable in all cases and becomes especially pronounced at higher concentrations of CCl$_3$CO$_2$H. The dip and subsequent further recovery at higher concentration indicate that initial formation of a less coloured species, e.g., [Mn(III,III)$_2$(OH)$_2$(μ-Cl$_3$CO$_2$)$_2$(tmtacn)$_2$]$_{2+}$ (2d) occurs initially, which subsequently converts to 2a (vide infra). The rate of exchange of $^{18}$O in 2a has been determined by ESI-MS to be on the min time scale,$^{[18]}$ which is consistent with an equilibrium being established between 2a and 2d.
Figure 11 Absorbance at 532 nm over time after addition of 50 equiv. of H$_2$O$_2$ to a solution of 1 (1 mM) with (i) 1, (ii) 2, (iii) 5, (iv) 10, (v) 20, (vi) 50, (vii) 80 and (viii) 100 mM CCl$_3$CO$_2$H in acetonitrile.

When 1 was used with only 1 equiv. of CCl$_3$CO$_2$H, the conversion of cyclooctene (9%) was significantly less than when 2 equiv. of CCl$_3$CO$_2$H (59%) were present.[17] The large difference in the extent of alkene oxidation observed is surprising since even in the absence of CCl$_3$CO$_2$H, reasonable conversion (44%) of cyclooctene to its cis-diol and epoxide products were observed when 2a was used as catalyst directly.[18]

When only 1 equiv. of CCl$_3$CO$_2$H w.r.t. 1 is available, only 50% conversion to 2a is observed by both Raman (Figure 12b) and UV/Vis absorption spectroscopy (Figure 12a). Given that 2a forms under these conditions, albeit with incomplete conversion of 1, the limited conversion of the alkene is likely to be due, at least partly, to the decomposition of H$_2$O$_2$ (determined by Raman spectroscopy) catalyzed by reduction products of 1 in the absence of acid (note that all of the acid is consumed to form 2a). Indeed, addition of a further 590 equiv. of H$_2$O$_2$ resulted in rapid disproportionation (monitored through the Raman band at 868 cm$^{-1}$) and ultimately the decomposition of 2a (Figure 12). It is notable, however, that although excess H$_2$O$_2$ leads to destruction of 2a, no further change in the concentration of 1 was observed.

Figure 12 (a) UV/Vis absorption spectra of (solid line) 1 (1 mM) with CCl$_3$CO$_2$H (1 mM) in acetonitrile, (dashed line) 30 min after addition of 50 equiv. of H$_2$O$_2$ and (dash-dot line) 30 min after addition of 590 equiv. of H$_2$O$_2$. For comparison (dash-double dot), the spectrum 30 min after addition of 50 equiv. of H$_2$O$_2$ to 1 (1 mM) with CCl$_3$CO$_2$H (10 mM) in acetonitrile. (b) Raman spectrum ($\lambda_{exc}$ 355 nm) of 1 (1 mM) with CCl$_3$CO$_2$H (10 mM) in acetonitrile at various times after addition of 50 equiv. of H$_2$O$_2$. 

55
Inhibition of the conversion of 1 to 2a by cyclooctene

The lag time before conversion of 1 to 2a begins is affected to a minor extent (< double) even with 0.5 M cyclooctene present. The observed rate of conversion of 1 to 2a, however, is decreased dramatically and takes on the appearance of a 1st order rather than autocatalytic reaction (Figure 13). The retardation in reaction rate is not linearly dependent on cyclooctene concentration and indeed gives the appearance of saturation kinetics at higher concentrations. A further effect of addition of even only 10 equiv. of cyclooctene is that the overall yield of 2a is higher (essentially full conversion to 2a) and the additional process observed between 1000 and 2000 s (i.e. the decrease and then increase in absorbance is not observed with 50 or more equivalents of H₂O₂).

![Figure 13 Absorbance at 532 nm over time after addition of 50 equiv. of H₂O₂ to a solution of 1 (1 mM) with CCl₃CO₂H (10 mM) in acetonitrile with (i) 0, (ii) 10, (iii) 50, (iv) 100 and (v) 500 mM cyclooctene.](image)

Importantly, the full conversion of 1 to 2a even with high concentrations of cyclooctene, which slows down the reaction significantly, suggests that H₂O₂ disproportionation is retarded also. The decrease in H₂O₂ disproportionation in the presence of cyclooctene is consistent with the involvement of species 2x in both H₂O₂ disproportionation as well as alkene oxidation. It is notable also that addition of H₂O₂ to the Mn(II)Mn(II) complex 2b results in rapid conversion to 2a, the rate of which is retarded by addition of cyclooctene.¹⁸

Disproportionation of H₂O₂ by 2a

Although the efficiency with respect to the use of H₂O₂ to convert organic substrates is near unity,¹⁸ in the absence of organic substrates, 2a engages in relatively efficient H₂O₂ decomposition (Figure 14) at approximately the same rate as seen during the conversion of 1 to 2a (Figure 4). Notably, the absorbance at 532 nm (and hence concentration of 2a) decreases concomitantly with the decomposition of H₂O₂ and subsequently recovers to a limited extent. These data confirm that 2a is capable, albeit with a low turnover frequency, of catalytic disproportionation of H₂O₂.
4.3 Discussion

The conversion of 1 to 2a involves overall two electron reduction and exchange of two μ-oxido ligands for two μ-carboxylato ligands. It is evident that the conversion proceeds through a series of redox and ligand exchange events. The most obvious features of the conversion are that there is a lag-time before the reaction begins and that once initiated, it proceeds in an autocatalytic manner, i.e. a sigmoidal rather than exponential time dependence in the change in absorbance (e.g., Figure 4). In addition, further processes are observed after the conversion of 1 is complete.

The lag-period is highly sensitive to the presence of Mn(II) and Mn(III) ions. Indeed trace impurities can have a dramatic effect on its duration. Nevertheless, the duration of the lag period is highly reproducible provided precautions are taken to ensure that reaction vessels are free of contaminants.

The duration of the lag-period has relatively little, if any, effect on the subsequent kinetics of the conversion of 1 to 2a. Although an excess (at least 10 equiv. w.r.t. 1) of H$_2$O$_2$ is required to achieve full conversion, with the remainder being disproportionated, consumption of H$_2$O$_2$ is only observed once the conversion of 1 to 2a has initiated. Hence, it is apparent that, regardless of the event that initiates conversion, once the reduction of 1 has begun, the species then formed is much more efficient at catalyzing the reduction of 1 with H$_2$O$_2$.

Once initiated, the conversion of 1 to 2a appears to be essentially direct in the sense that EPR active species are not observed until conversion nears completion and the increase in the intensity of the Raman bands of 2a track exactly the decrease in the bands of 1 (Figure 4). Furthermore, the rate of the reaction is relatively insensitive to the concentration of H$_2$O$_2$, water and CCl$_3$CO$_2$H, except when present in gross excess, indicating that the reaction is zero order in all three components. The consequence of this is that the rate determining step must be the reduction of 1 by a relatively stable species (2x). A possible candidate for 2x is the species
formed upon reaction of \(2d\) with \(H_2O_2\) in a prior rapid equilibrium (i.e. \([Mn(III,III)_2(OH)(OOH)CCl_3CO_2]_2(tmtaca)_2\))\(^{2+}\). The subsequent reactions that lead to \(2a\) are much faster than the rate of reduction. A complication that precludes a detailed kinetic analysis is that in addition to the reduction of \(1\), \(2x\) is active in the disproportionation of \(H_2O_2\) at a rate that is several times higher. Importantly, direct electron transfer between \(2a\) or \(2c\) to \(1\) has been excluded.

\(Mn(II)\) ions are formed during the reaction and are apparent especially at later stages (Figure 5). However, it is unlikely that \(Mn(II)\) ions are involved in the reactions observed as neither \(Mn(II)(ClO_4)_2\) nor \(Mn(III)(OAc)_3\) show \(H_2O_2\) decomposition or cyclooctene oxidation in acetonitrile in the presence of excess \(CCl_3CO_2H\). Furthermore \(1\) is unreactive in regard to \(H_2O_2\) decomposition in the presence of an inorganic acid such as \(HPF_6\). Notably, although \(50\%\) conversion of \(1\) to \(2a\) was observed with only \(1\) equiv. of \(CCl_3CO_2H\) (Figure 12), \(H_2O_2\) underwent rapid disproportionation and eventually decomposition of \(2a\) was observed with no further change to \(1\).

The involvement of \(Mn(II)Mn(II)\) complexes, such as complex \(2b\), \(2c\) and \(2e\) can be excluded also for several reasons: \(2b\) undergoes immediate conversion to \(2c\) upon addition of acid and addition of \(H_2O_2\) to \(2c\) in the presence of \(CCl_3CO_2H\) results in fast conversion to \(2a\) (Scheme 2). Notably, however, the conversion from \(2c\) to \(2a\) is retarded by the presence of cyclooctene (Figure 13 and Scheme 2).\(^{[18]}\)
Manganese oxidation catalysis in acetonitrile

(i) Conversion of 1 to 2a/2d

\[
\begin{align*}
\text{1} & \quad \text{2+} + \text{H}^+ \\
\text{H}^+ & \quad \text{2d}
\end{align*}
\]

(ii) Oxidation of cyclooctene by 2x

(iii) Disproportionation of H\text{2}O\text{2}

Although most experimental factors have relatively modest effects on the conversion of 1 to 2a, cyclooctene is an exception. The addition of even 500 equiv. of cyclooctene has only a modest effect on the lag time, but even 10 equiv. impacts the rate of conversion of 1 and the efficiency in regard to the amount of 2a formed. Indeed at above 50 equiv. w.r.t. 1 the change in absorbance is no longer sigmoidal but pseudo-exponential instead. Furthermore, essentially full conversion to 2a is observed even with only 10 equiv. of cyclooctene, which indicates that the processes observed subsequent to full conversion of 1 are suppressed.

The third stage of the reaction, i.e. after 1 has undergone full conversion, relates to the coordination chemistry of 2a primarily and to its limited ability to disproportionate H\text{2}O\text{2}. It is notable that addition of excess water and/or CCl\text{3}CO\text{2}H to 2a results in the formation of 2d, the
Chapter 4

Mn(III)Mn(III) analogue of 2c.\[18\] Indeed, preparative electrochemical reduction of \(1\) in the presence of \(\text{CCl}_3\text{CO}_2\text{H}\) has been shown earlier to lead to the formation of \(2\text{d}\) rather than \(2\text{a}\).\[18\]

\(2\text{a}\) is relatively stable in the presence of excess \(\text{H}_2\text{O}_2\), i.e. the concentration of \(2\text{a}\) decreases by at most \(15\%\) upon addition of \(50\) equiv. of \(\text{H}_2\text{O}_2\). The disproportionation of \(\text{H}_2\text{O}_2\) by \(2\text{a}\) is relatively slow, even in the absence of cyclooctene, and once complete a partial recovery in absorbance is observed which is consistent with the initial formation of \(2\text{d}\). \(\text{H}_2\text{O}_2\) disproportionation, as proposed for dinuclear manganese catalases,\[1\] involves sequential two electron reduction and subsequent two electron oxidation of the dinuclear manganese unit. It is evident that the \(\text{Mn(II)Mn(II)}\) complex \(2\text{c}\) can undergo oxidation to \(2\text{a}\), tentatively via the non-\(\mu\)-oxido bridged \(\text{Mn(III)Mn(III)}\) analogue \(2\text{d}\). Such a mechanism is analogous to the operation of dinuclear manganese catalases\[1\] in which the redox state is cycled between \(\text{Mn(II)Mn(II)}\) and \(\text{Mn(III)Mn(III)}\) while oxidising and then reducing \(\text{H}_2\text{O}_2\) (Scheme 2(iii)). The relatively slow rate of the reduction of \(2\text{a}\) to \(2\text{c}\) is likely, however, to be due to the equilibrium position between \(2\text{a}\) and \(2\text{d}\) rather than the lack of substantial structural change, since oxidation of \(2\text{c}\) to \(2\text{d}\) results in deprotonation and a decrease in redox potential by 300 mV.\[18\]

The effect of cyclooctene on both the rate of oxidation of \(2\text{c}\) to form \(2\text{a}\) and extent of \(\text{H}_2\text{O}_2\) disproportionation suggests that a competitive inhibition mechanism is operating. The reduction from \(\text{Mn(III)Mn(III)}\) \((2\text{x})\) to \(\text{Mn(II)Mn(II)}\) \((2\text{c})\) with release of dioxygen must therefore be slower than the bimolecular reactions of \(2\text{x}\) with \(\text{H}^+\) and with cyclooctene. The reaction with \(\text{H}^+\), ultimately, yields more \(2\text{d}/2\text{a}\) and accelerates the reaction while the reaction with cyclooctene is likely to produce \(2\text{a}\),\[18\] which then has to undergo opening of the \(\mu\)-oxido bridge before coordination of \(\text{H}_2\text{O}_2\) takes place.

4.4 Conclusions

In summary, it is apparent that the conversion of \(1\) to \(2\text{a}\) involves an initiation step, i.e. the reduction of \(\text{H}^+\), in order to proceed, however, the initial product of the reduction and ligand exchange reactions \((2\text{a}/2\text{d})\) can react readily with \(\text{H}_2\text{O}_2\) to form \(2\text{x}\), which is likely to be the species responsible for the further reduction of \(\text{H}^+\) (Scheme 2(ii)). The rate at which the reaction proceeds is remarkable considering that under the conditions employed, the negative \(p\text{K}_a\) of \(1\) means that relatively little of the reducible complex is available. It is also likely that \(2\text{x}\) is also the species directly responsible for the oxidation of alkenes (Scheme 2(iii)). Indeed, the inhibitory effect of cyclooctene, even with only \(10\) equiv. present, on the rate of conversion of \(1\) to \(2\text{a}\) is expected considering that the reaction between \(2\text{x}\) and the alkene leads to \(2\text{a}\) and the epoxide/cis-diol product. The relative inertness of \(2\text{a}\) towards \(\text{H}_2\text{O}_2\) means that this latter reaction is effectively a termination step in the conversion of \(1\) to \(2\text{a}\).

The identification of an ‘active catalytic species’ and the development of a detailed model (i.e. a series of elementary steps) for a reaction requires an intimate understanding of not only the catalyst and its behavior under reaction conditions but also the factors that influence its reactivity and stability. In the present example the role played by redox state driven changes in coordination is clear in the conversion of \(1\) to the catalytically competent complex \(2\text{a}\). In our search for the structure of the species directly responsible for the oxidation of organic substrates, close examination of the conversion of \(1\) to \(2\text{a}\) is warranted and as is demonstrated
Manganese oxidation catalysis in acetonitrile

in the present study, can reveal direct connections between the reduction of 1 and the oxidation of alkenes. Furthermore, it is clear that it is not the presence of carboxylic acids that suppresses H$_2$O$_2$ disproportionation, but instead the reaction between 2x and substrate, e.g., cyclooctene, to form 2a is faster than release of molecular oxygen to form 2c.

4.5 Experimental Section

All reagents were obtained from commercial sources and used as received unless stated otherwise. H$_2$O$_2$ (50% v/v) in water was obtained from Acros. Complexes 1 ([Mn(IV,IV)$_2$O$_3$(tmtacn)](PF$_6$)$_2$), 2a ([Mn(III,III)$_2$($\mu$-O($\mu$-CCl$_3$CO$_2$)$_2$(tmtacn)](PF$_6$)$_2$), 2b ([Mn(II,II)$_2$($\mu$-OH($\mu$-CCl$_3$CO$_2$)$_2$(tmtacn)](ClO$_4$)] were available from earlier studies. UV/vis absorption spectra were recorded using a Specord S600 UV/vis absorption spectrometer in 1 cm quartz cuvettes unless stated otherwise. X-band EPR spectra (9.47 GHz, Bruker ECS102) were recorded in 3 mm quartz tubes at 77 K with 2 G modulation and 81 ms conversion time. Raman spectra were recorded at 355 nm and 457 nm in backscattering mode as described earlier, and at 785 nm using a Perkin Elmer Ramanstation. ATR-FTIR spectra were recorded using a Perkin Elmer Spectrum400 FTIR spectrometer equipped with a UATR attachment. All experiments were performed at 19 °C unless stated otherwise.

Computational methods

Simulation of Raman and IR spectra were performed using Density Functional Theory (DFT) as implemented in Gaussian 09c using the B3LYP functional and a basis set composed by LANL2TZ+(f) for manganese atoms and 6-311G(d,p) for the remaining atoms after geometry optimization at the same level of theory. Resonance Raman spectra were calculated as implemented in ORCA 3.0.2. Optimization was achieved using the BP86 functional and Def2-TZVP basis set, while the calculation of the Hessian matrices were performed using 6-311G(d,p) for H, C, N, O, Cl elements. The TD-DFT calculations were performed with a BH and HLYP functional and using the same basis set used to calculate the Hessian matrix. See the supporting information for coordinates of calculated structures. Optimized cartesian xyz coordinates for calculations using uB3LYP/6-311G(d,p)/LANL2TZ+(f) (Only For Mn) in Gaussian are available online – in published version of this chapter.

4.6 References

Chapter 4


[22] The possibility of photochemical processes induced by the spectrometers or laser irradiation can be excluded since all complexes (1 and 2) are stable in solution with CCl₃CO₂H even under irradiation at 355 nm (10 mW) for several hours.

[23] It should be noted that rigorous cleaning of cuvettes and glassware (washing with acetone, thrice demi-water, soaking for 10 min in aqua regia (HCl/HNO₃ 1:1 v/v) followed by doubly distilled water and then UVASOL grade acetonitrile) was required to obtain a repeatable lag-time.


4.7 Supporting information

Figure S1 Solid state ATR-FTIR spectra ($\lambda_{\text{exc}}$ 785 nm) of 1 (blue), 2a (red) and 2b (black).

Figure S2 Solid state Raman spectra ($\lambda_{\text{exc}}$ 785 nm) of 1 (black), 2a (red) and 2b (blue).
Figure S3 DFT calculated Raman spectra of 1 (1 mM, black) and 2a (1 mM, blue).

Figure S4 Resonance Raman spectra ($\lambda_{exc}$ 355 nm) in acetonitrile (black line) of 1 (1 mM) without (blue line) and with (red line) CCl$_3$CO$_2$H (10 mM).
Figure S5 Resonance Raman spectra ($\lambda_{exc}$ 355 nm), in acetonitrile (black line), of 2a (1 mM) without (red line) and with (blue line) CCl$_3$CO$_2$H (10 mM).

Figure S6 Absorbance at 532 nm of (i) 2b (1 mM), (ii) 2b (0.5 mM) and 1 (0.5 mM), (iii) 1 (1 mM), (iv) 2a (0.5 mM) and 2b (0.5 mM), (v) 1 (0.5 mM) and 2a (0.5 mM) and (vi) 2a (1 mM), in acetonitrile with CCl$_3$CO$_2$H (10 mM) and water (100 mM).

Figure S7 X-band EPR spectra (at 77 K) of Mn(II)(ClO$_4$)$_2$ (a) 0.2 mM and (b) 2 mM in CH$_3$CN with 10 mM CCl$_3$CO$_2$H and (c) of the aliquot drawn at point 9 in Figure 5.
Manganese oxidation catalysis in acetonitrile