Chapter 6
The effect of additives and pH on Mn-tmtacn catalysed oxidations with H$_2$O$_2$ in water

In this chapter catalysis in single phase reactions is explored. The central question addressed is to understand the effect of additives and other reaction parameters on the activity of the manganese catalysts in the oxidation of substrates and decomposition of H$_2$O$_2$. The epoxidation of styrene sulfonate and oxidation of chrysin in water as model substrates in the pH ranges 6-9 and 10-11, respectively, catalysed by Mn-tmtacn complexes are compared and contrasted. It is found that, although control over solution pH in such systems requires the addition of buffering agents, it is shown commonly used buffers are not innocent in regard to the reactivity of the catalysts. In addition it was demonstrated that the initial structure of the complex has a profound effect on the mode of action of the catalyst.

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**Introduction**

Oxidative transformations, and especially the epoxidation of alkenes, are central chemical processes in both synthetic organic chemistry and the chemical industry. The terminal oxidant \( \text{H}_2\text{O}_2 \) is attractive due to its minimal environmental and economic impact and is applied in a wide range of chemical processes. However, \( \text{H}_2\text{O}_2 \) is generally unreactive and requires activation either as peracids or with catalysts, i.e. heterogeneous catalysts (such as zeolites) or hydrotalcites and polynuclear complexes, e.g., \((\text{R}_2\text{N})_6\text{SiW}_{18}\text{Fe(OH)}_2\text{O}_{38}\) (where \( \text{R} = \text{alkyl} \))

Initial interest in manganese complexes of the facially coordinating ligand tmtacn (trimethyl-1,4,7-triazacyclononane, Figure 1) was focused on functional and structural modelling of the redox active metalloproteins. Manganese complexes containing tacn derivatives catalyse a wide variety of substrate conversions both in aqueous and non-aqueous media. These include both bleaching of stains and selective oxidation of organic substrates. The use of Mn-tmtacn complexes in the epoxidation of alkenes was reported by Hage et al., in the context of their use as detergent additives to oxidise organic stains.

Over the last several decades, mechanistic studies into manganese catalysed oxidation has focused on organic solvents and has provided a considerable body of data as to the active form of the catalysts as well as a broad understanding of the role that various additives play in such catalysis. Mechanistic studies have shown the formation of carboxylato bridged dinuclear Mn(III) complexes in the catalysed oxidation of alkenes in organic solvents, in which carboxylic acids controlled the selectivity and activity. Three roles were proposed for the carboxylic acid as (a) a proton source to facilitate the reduction of \([\text{Mn}_2^{\text{IV}}(\mu-\text{O})_3(\text{tmtacn})_2][\text{PF}_6]_2\) by \( \text{H}_2\text{O}_2 \) (b) as bridging ligands in carboxylato-bridged dinuclear complexes and (c) to stabilize the Mn\(^{\text{III}}\)/Mn\(^{\text{III}}\) dimers as the precursor to the \( \text{H}_2\text{O}_2 \) activated complex. The involvement of the dinuclearbis(carboxylato) bridged Mn\(^{\text{III}}\)-OH:Mn\(^{\text{III}}\)OH was proposed as a key intermediate in the formation of epoxide or cis-diol products, based on spectroscopic data and \(^{18}\text{O}\)-labeling studies.

The oxidation of cinnamates catalysed by Mn-tmtacn complexes in buffered aqueous acetonitrile was studied by Lindsay-Smith and co-workers using a combination of UV/Vis absorption, EPR spectroscopy and ESI-MS. They noted the formation of mononuclear Mn\(^{\text{IV}}\)=O species based on ESI-MS and suggested that this species reacts with alkenes to form an epoxide and a Mn\(^{\text{III}}\) species, with the latter reacting with a further equivalent of \( \text{H}_2\text{O}_2 \) to reform the high valent manganese species. A similar mechanism was proposed for a manganese Schiff base catalysts in the enantioselective epoxidation of alkenes with hypochlorite as oxidant. The optimum pH for epoxidation was ca. pH 8 while for bleaching of dyes the optimum is ca. pH 10, which suggests that epoxidation and stain bleaching proceeded via different mechanisms. The wide range of applications of this catalyst in laundry stain removal, fine and bulk chemical synthesis, wood pulp and cotton bleaching makes understanding how the catalyst achieves oxidation under such a wide range of conditions an important goal. However, there is a lack of information in regard to the catalysts mode of action in aqueous solutions, especially at high pH.
In this chapter the epoxidation of styrene sulfonate and oxidation of chrysin in water (in the pH ranges 6-9 and 10-11, respectively) catalysed by Mn-tmtacn complexes are compared and contrasted. The alkene styrene sulfonate (SS) and chrysin were chosen as model substrates due to their high solubility in water and lack of sensitivity to pH in the ranges examined (Figure 1). The overall goal of the work described in this chapter is to understand, at a molecular level, how and why factors such as pH and additives, such as sequestrants, affect the activity of Mn-tmtacn based catalysts in aqueous solutions.

As shown in chapter 2, styrene sulfonate is highly water soluble and can undergo oxidation with catalysts such as 1. Importantly, reaction progress can be monitored by Raman spectroscopy. In chapters 3 and 4 the suitability of chrysin as a model compound for the study of the mechanism by which catalysts engage in the bleaching of raw cotton was demonstrated. This flavonoid is a stable compound with regard to acid/base chemistry in the pH window of interest, oxidation by oxygen and photochemically induced oxidation, allowing for the bleaching activity of 1 with H₂O₂ to be probed.

Results

The reaction shown in scheme 1 was performed under various conditions. The activity of \([\text{Mn}^{IV,IV}_2(\mu-O)_3(\text{tmtacn})_2](\text{PF}_6)_2\) (1) and \([\text{Mn}^{III,III}_2(\mu-O)(\mu-\text{CH}_3\text{CO}_2)_2(\text{tmtacn})_2](\text{PF}_6)_2\) (2) in the absence and presence of acetate, citrate, borate, bicarbonate (common additives employed in bleaching studies) was investigated and compared with the activity of Mn⁺⁺ salts under the same conditions. The epoxidation of SS in aqueous solutions with H₂O₂ catalysed by 1 (Mn²⁺⁺) and 2 (Mn²⁺⁺⁺) (Scheme 1) was described in chapter 2. Raman spectroscopy was demonstrated to be a suitable method to monitor changes in the concentration of styrene sulfonate and its epoxide product. The bands in the range 1600–1650 cm⁻¹ are characteristic of C=C stretching vibrations of vinyl and aryl groups and in particular the band at 1630 cm⁻¹ is useful in monitoring reaction progress.
Scheme 1 Catalysed oxidation of styrene sulfonate (SS) with H$_2$O$_2$.

Figure 2 Raman spectra ($\lambda_{exc} = 785$ nm) of (a) SS and (b) its epoxide product OSS

Epoxidation of styrene sulfonate in the presence of citrate, borate, acetate and bicarbonate

In chapter 2, the oxidation of styrene sulfonate in aqueous bicarbonate with 1 was monitored by both inline analysis and the DCDR method. In aqueous solution at pH 8, almost full conversion of SS was obtained with 2 ($\text{Mn}^{II,III}$), whereas with 1 only ca. 18% conversion was obtained. No conversion was observed with $\text{Mn}^{II}(\text{SO}_4)_2$. The activity of the catalysts in water was used as a basis for comparison with the oxidation of SS in the presence of citrate, acetate, borate and carbonate (Figure 3).

Conversion of SS is not observed with $\text{Mn}^{II}(\text{SO}_4)_2$ in water, neither in the presence of borate, citrate nor acetate, however, as will be discussed in more detail below, conversion was observed in aqueous bicarbonate.
Effect of additives and pH on the reactivity of Manganese catalysts

In the presence of sodium citrate and sodium borate, the conversion of SS was reduced to ca. 20% and 50%, respectively, for 2 while conversion was not observed with 1. Oxidation of styrene sulfonate with 1 and 2 in the presence of acetate showed ca. 15% and ca. 80% conversion, respectively. Notably, although citrate, borate and to a lesser extent acetate, decrease the activity of 1 in the oxidation of SS, they also suppress decomposition of H$_2$O$_2$. In the presence of bicarbonate, however, good conversion was observed with 1 in contrast to 2 which showed reduced conversion.

In summary, for 1 the presence of borate and citrate and for 2 in the presence of all additives, a loss in activity compared to water alone is observed. The activity of 1 shows a several fold increase in the presence of bicarbonate compared to water.

**Catalytic activity in water and bicarbonate**

Due to the unusual behaviour of the catalysts in bicarbonate solution, the time dependence of oxidation of SS was studied in the pH range 6-9 in both water and in the presence of bicarbonate, with 1 and Mn$^{II}$\(_{\text{S}}\).

**pH dependence of the catalytic activity of Mn$^{II}$ in water and bicarbonate (0.1 M)**

The activity of the Mn$^{II}$ in the oxidation of styrene sulfonate in water was studied over the pH range 6-9, with reaction progress monitored by Raman spectroscopy at $\lambda_{\text{exc}}$ 785 nm and 532 nm. Monitoring the decrease in the intensity of the band at 1630 cm$^{-1}$ (Figure 2) showed that, at all pHs examined, SS does not undergo conversion. Notably, complete decomposition of H$_2$O$_2$ (band at 870 cm$^{-1}$) along with an increase in pH is only observed when the initial pH is 9. At an initial pH of 7.45 and 8.6, only a decrease in pH is observed.
Figure 4 Conversion of SS (0.1 M, blue), H₂O₂ consumption (red) and changes in pH (green arrows), in the oxidation of SS with Mn²⁺(SO₄) (0.2 mM) in water.

Figure 5 Decomposition of H₂O₂ at pH 9 monitored by Raman spectroscopy at λ_{exc} 785nm. (see Figure 4 for details)

Decomposition of H₂O₂ was not observed at pH 9 in the presence of Mn²⁺(SO₄) at a concentration of 10 μM and 1 μM, albeit without conversion of SS either. Notably the pH changed to 7.85 and 8.36, respectively. These data confirm that in water Mn²⁺ is active neither in the oxidation of SS, nor in the decomposition of H₂O₂ within the pH range 6-9.

In sharp contrast, full conversion over the pH range of 6-8 is observed with Mn²⁺(SO₄) in aqueous bicarbonate (0.1 M). At pH 9, lower conversion, ca. 20% was obtained. Furthermore, the pH of the solutions, initially at 6.55 and 7.05, increased to ca. 8 and in all cases consumption of H₂O₂ was incomplete (Figure 6).
Effect of additives and pH on the reactivity of Manganese catalysts

Figure 6 Conversion (blue) of SS (0.1 M) with Mn$^{II}$(SO$_4$) (0.2 mM) in NaHCO$_3$(aq) (0.1 M), and consumption of H$_2$O$_2$ (0.5 M)(red). The change in pH between the start and end of the reaction is indicated with green arrows.

Reaction progress monitoring of the oxidation of the SS with Mn$^{II}$(SO$_4$) and H$_2$O$_2$ was studied between pH 6-9 by Raman spectroscopy at $\lambda_{exc}$785 nm. As shown in Figure 7, bands of 1630 cm$^{-1}$, 1252 cm$^{-1}$ and 870 cm$^{-1}$, which are associated with the alkene, epoxide and H$_2$O$_2$, respectively, allow for reaction progress to be monitored over time.

Figure 7 Oxidation of styrene sulfonate (0.1 M) with H$_2$O$_2$ (0.5 M) and Mn$^{II}$ (0.2 mM) in NaHCO$_3$(aq) (0.1 M) at pH 6 (left) monitored by Raman spectroscopy at $\lambda_{exc}$ 785nm. (right) Conversion of alkene (blue) and H$_2$O$_2$ (red) and changes in the pH (green) over time in NaHCO$_3$(aq) at pH 6.

Following the progress of the reaction over time at pH 6 shows that, after a lag phase (ca. 100 min), the reaction rate increases with the consumption of H$_2$O$_2$ concomitant with the conversion of the alkene. The pH increase during the reaction to reach pH 7 after ca. 100 min coincided with the end of the lag phase and the beginning of conversion of SS and H$_2$O$_2$. At pH 7 and 8 a lag phase was not observed with conversion of SS complete over 1 h. In both cases H$_2$O$_2$ consumption occurred concomitant with alkene oxidation (Figure 8).
Chapter 6

Figure 8 Conversion of SS (0.1 M) and H₂O₂ (0.5 M) with Mn⁴⁺(SO₄) (0.2 mM) in NaHCO₃(aq) at an initial pH of (left) 7 and (right) 8.

The conversion of SS and consumption of H₂O₂ at pH 9 showed that the decomposition of H₂O₂ was faster than the oxidation of substrate, which limited conversion of SS compared with that observed at lower pH.

Figure 9 Conversion of SS and H₂O₂ over time in NaHCO₃(aq) with Mn⁴⁺(SO₄) at pH 9.

Addition of the sequestrant DTPA has a pronounced effect on the reactivity observed with Mn⁴⁺(SO₄). Indeed conversion was not observed in the presence of DTPA between pH 6 and 9, in accordance with sequestration of Mn⁴⁺ ions by DTPA (Figure 10).

Figure 10 Oxidation of SS (0.1 M) with Mn⁴⁺(SO₄) (0.2 mM, initial spectrum in blue) after ca. 20 h with DTPA (0.5 mM in red) and without DTPA (green) in NaHCO₃(aq) at pH 8 and H₂O₂ (0.5 M).
Effect of additives and pH on the reactivity of Manganese catalysts

pH dependence of the catalytic activity of 1 in water and bicarbonate

The oxidation of SS with H₂O₂ catalysed by 1 was studied in water and NaHCO₃(aq) between pH 6 and 9. In water at pH 8, along with a decrease in pH over the course of the reaction, 1 was found to be catalytically active in the oxidation of SS. At pH 6 and 7 almost no conversion was observed and at pH 9, all of the H₂O₂ added was decomposed rapidly and the pH increased. At pH 8, ca. 40% and 80% conversion of SS and H₂O₂, respectively, was observed within 20 h. Conversion of SS was observed with 10 μM of 1 but not with 1 μM at pH 9. Notably, decomposition of H₂O₂ was not observed at either concentration and a decrease in pH was observed during the reaction. These data show that in contrast to Mn²⁺(SO₄), which is inactive in water at all pHs, 1 shows activity at pH 8 and pH 9 especially with lower catalyst loading (Figure 11).

![Figure 11](image)

**Figure 11** Oxidation of SS (0.1 M) with 1 (left, 0.1 mM and right, 10 and 1 μM) in water. Conversion of SS is shown in blue, consumption of H₂O₂ (0.5 M) in red. Changes in pH over reaction are shown in green.

Monitoring the oxidation of SS, at pH 8 shows that the consumption of H₂O₂ is faster than the conversion of substrate over 5 h, and hence H₂O₂ is decomposed at a faster rate than oxidation. The pH of the reaction mixture decreases gradually over the 5 h also (Figure 12).

![Figure 12](image)

**Figure 12** Consumption of SS (blue) and H₂O₂ (red) and change in pH (green) with 1 in water at pH 8.
Reactivity of 1 in aqueous bicarbonate

Conversion of SS is observed between pH 6-8 with 1, however, at pH 9 only decomposition of H$_2$O$_2$ is observed. Again the conversion of the substrate coincided with an increase in pH from 6 and 7 to pH 8. No change in the pH was observed with an initial pH of 8 and 9. Monitoring the conversion of substrate, consumption of H$_2$O$_2$ and change in pH over time reveals a lag phase which stands in each case until the pH reaches ca. pH 8. The conversion of SS and H$_2$O$_2$ proceeds at a faster rate above pH 7. At pH 7 the lag phase is reduced compared to pH 6 and at pH 8 the lag phase is essentially absent. Between an initial pH of 6-8, the conversion of SS is concomitant with depletion of H$_2$O$_2$ (Figure 13)

![Graph showing reaction conversion and pH changes](image)

**Figure 13** Oxidation of SS (0.1 M) with H$_2$O$_2$ (0.5 M) catalysed by 1 (0.1 mM) in NaHCO$_3$(aq) (0.1 M), (a) SS (blue) and H$_2$O$_2$ conversion (red) and pH change (green), and reaction progress at pH (b) 6 (c) 7 and (d) 8.

Comparison of the reaction rate with 1 and Mn$^{II}$(SO$_4$)

The rate of oxidation of SS in NaHCO$_3$(aq) between pH 6 and 8 with 1 and Mn$^{II}$ was compared. In all cases, the rate of oxidation with Mn$^{II}$(SO$_4$) was higher compared to that with 1. However, this behaviour is only observed when the concentration of bicarbonate was 0.1 M, i.e. 1:1 with respect to SS. At lower bicarbonate concentrations (e.g., 0.01 M), Mn$^{II}$(SO$_4$) showed no reactivity in regarding to SS conversion and only decomposition of H$_2$O$_2$ was observed. The oxidation of SS in the presence of 1 and sequester DTPA was followed by Raman spectroscopy. With Mn$^{II}$(SO$_4$), conversion was not observed in the presence of DTPA, while with 1, activity is still observed albeit with
Effect of additives and pH on the reactivity of Manganese catalysts

reduced conversion. The observation of conversion of SS with 1 in the presence of DTPA, therefore confirms that Mn$^{II}$ salts that could be formed by decomposition of 1 is not responsible for the oxidation of SS observed (Figure 14).

![Figure 14](image)

**Figure 14** Oxidation of SS (0.1 M) with H$_2$O$_2$ (0.5 M) and 1 (0.1 mM) in NaHCO$_3$(aq) (0.1 M), initial spectrum (blue), and after the reaction with DTPA (0.4 mM, red) and without DTPA (green).

These data indicate that activity with Mn$^{II}$(SO$_4$) is only observed with sufficiently high concentrations of bicarbonate while with 1 exhibits catalytic activity in water at pH 8 and 9, as well as in NaHCO$_3$(aq). These observations are consistent with reports by Eldik and coworkers, in which the formation of a Mn$^{II}$-peroxycarbonate complex was proposed in the presence of H$_2$O$_2$ in a NaHCO$_3$(aq).

![Figure 15](image)

**Figure 15** Conversion of SS with 1 (blue) and with Mn$^{II}$ (red) in NaHCO$_3$(aq) (0.1) at pH 6, 7 and 8.

Reactions were carried out with and without 1 in water and aqueous bicarbonate at pH 9. Raman spectroscopy showed that in water, decomposition of H$_2$O$_2$ occurs only in presence of 1, however in bicarbonate solution, decomposition was observed both with and without 1 which means that in addition to catalyst, other species are present in bicarbonate which can decompose H$_2$O$_2$. Addition of sequestrant (DTPA) suppresses the decomposition of H$_2$O$_2$ in bicarbonate solution at pH 9.

**Effect of additives on the catalytic oxidation of chrysin with 1**

As mentioned in the introduction, a major application of 1 is in bleaching catalysis. Initially, 1 was applied in tea stain bleaching with H$_2$O$_2$ and later on various substrate such as wood pulp and raw cotton. A key challenge in the application of transition metal catalysts is that the presence of iron or manganese ions, particularly in alkaline solutions, can cause the formation of iron oxides or manganese dioxide, which may
decompose H$_2$O$_2$ into dioxygen and water, decreasing the efficiency of the reaction and can generate hydroxyl radicals that damage natural fibres.\textsuperscript{13} Furthermore, these oxides can form brown stains themselves. Hence, to prevent of formation of these species, sequestrants are used to bind and solubilise metal cations.

Chrysin was chosen as a model substrate for reactions carried out under conditions used for bleaching.\textsuperscript{20} The UV/vis absorption spectrum of chrysin is comprised of two resolved absorption bands. A transition in the (near) visible region at 359 nm is attributed to the B ring and a high energy transition at 273 nm is attributed to the A ring (Figure 1 and Figure 16).\textsuperscript{25} As shown in chapters 3 and 4, the oxidation of chrysin catalysed by manganese complexes under bleaching conditions can be monitored readily by UV/vis absorption spectroscopy.

![UV/vis absorption spectrum of chrysin [40 µM] at pH 11.4 in NaHCO$_3$(aq) (0.1 M).](image1)

**Figure 16** UV/vis absorption spectrum of chrysin [40 µM] at pH 11.4 in NaHCO$_3$(aq) (0.1 M). The oxidation of chrysin with manganese complexes and Mn$^{II}$ was studied in the presence of acetate, borate and bicarbonate as well as in water only, with H$_2$O$_2$ was as terminal oxidant.

Control experiments were carried out in the absence of catalyst or H$_2$O$_2$. When either catalyst or H$_2$O$_2$ was absent, oxidation of chrysin was not observed. The reactivity of manganese based catalysts were compared to the catalytic activity of Mn$^{II}$ ions in bicarbonate solution. In all cases the dinuclear catalysts showed faster oxidation of chrysin than with Mn$^{II}$ ions (Figure 17).

![Dependence of the conversion and rate of oxidation of chrysin in various buffers, at pH 10 (blue), 11 (red). Chrysin [40 µM], 1 [1 µM], H$_2$O$_2$ [5 eq], and additive [10 mM], at 23 °C.](image2)

**Figure 17** Dependence of the conversion and rate of oxidation of chrysin in various buffers, at pH 10 (blue), 11 (red). Chrysin [40 µM], 1 [1 µM], H$_2$O$_2$ [5 eq], and additive [10 mM], at 23 °C.

In all cases, except in borate buffer, higher catalytic activity was observed at pH 11 than at pH 10. These data are consistent with previous data which reported higher reactivity of 1 at higher pH in the bleaching of stains.\textsuperscript{14} Inhibition of the activity of 1 was observed
in borate buffer at pH 11 and in acetate at both pH 10 and 11. Indeed the highest reaction rates were obtained in water alone. The data obtained here are consistent with data discussed in chapter 3 in the analysis of the complex Mn$_2$III,IV dtne at high pH and the effect of various additives on its behaviour.\textsuperscript{20} The bleaching of chrysins at pH 10 only takes place to some extent in the presence of water or borate with a slow rate, while no activity was observed at pH 11 with borate and acetate. In the presence of bicarbonate the oxidation of chrysins was slower compared to water.

**Discussion**

It is apparent that the effect of additives, such as commonly used buffering agents, can be markedly different depending not only on the catalyst used but also the oxidation state of the catalyst e.g., 1 vs 2. Carbonate, however, stands out as a special case in comparison to acetate, citrate and borate in that the formation of peroxycarbonates appears to be facile and leads to distinct reactivity.

In several cases a lag-time was observed, which could be ascribed to catalyst activation, as in the case of the conversion of 1 to 2 in acetonitrile (see chapter 1)\textsuperscript{15} or decomposition of the complexes to simple Mn$^{ll}$ salts. However, monitoring of the pH during the reaction provides a simpler rationalisation of the lag-time. In aqueous solutions above pH 6, the lag period can be ascribed to a strong pH dependence of the reaction, especially for 1, with in every case the end of the lag period corresponding to a change to a pH between 7.5 and 8.5. The formation of simple Mn(II) salts is possible also, however, it should be noted that Mn$^{ll}$(SO$_4$)$_2$ does not show activity except in the presence of carbonate at high concentrations, whereas 1 shows activity only at pH 8 and at pH $> 9$ with lower concentration of catalyst. In bicarbonate, both catalyst 1 and 2 show activity between pH 7 and 9, with rapid decomposition of H$_2$O$_2$ observed with 1 at pH 9 or higher.

Since a distinct behaviour is observed in bicarbonate compared to other buffers, the second part of this study focused on investigation of the reactivity of Mn$^{ll}$ salts and 1 in water and bicarbonate between pH 6 and 9. The origin in the pH dependence of activity lies in the active species that are involved in the oxidation reactions and also changes in pH that precede the onset of reactivity. The Pourbaix diagram for manganese shows the thermodynamic stability of various manganese species as a function of pH. Between (pH -2 to 7), Mn$^{ll}$ is the dominant species in solution. At all pHs levels, MnO$_4^-$, is predominate species at high redox potentials, however, its formation was not detected in the present study. Under alkaline conditions, manganese oxide, and manganese hydroxide are stable at low redox potentials.\textsuperscript{26}

Van Eldik et al. have studied the reactivity of Mn$^{ll}$ salts under bleaching conditions.\textsuperscript{23} The formation of a complex between bicarbonate and Mn$^{ll}$ ion was studied over a range of concentrations of bicarbonate at pH 8.5. Formation of a broad band was observed by UV/Vis absorption spectroscopy at 300 nm upon the addition of HCO$_3^-$ to an aqueous Mn$^{ll}$ solution, which increased with carbonate concentration. The formation of this coloured species showed a first-order rate constant ($k_{obs}$). At higher concentrations of bicarbonate in the absence of substrate precipitation of insoluble Mn$^{ll}$CO$_3$ was observed as confirmed by elemental analysis and IR spectroscopy. The formation of a Mn(II)-HCO$_3^-$ intermediate was studied by cyclic voltammetry.\textsuperscript{23}
Richardson reported the catalysed epoxidation of alkenes with aqueous H$_2$O$_2$ at near neutral pH in the presence of bicarbonate.$^{27}$ The establishment of an equilibrium between peroxymonocarbonate and bicarbonate/H$_2$O$_2$ occurred within minutes as shown by $^{13}$C NMR spectroscopy but the rate of epoxidation was limited. However, the origin of this reactivity is clear from the effect of DTPA in the present study which confirms that the impurities such as trace metal ions in bicarbonate catalyse the reaction.

**Conclusion**

In conclusion, the present study has shown that pH and the initial state of the catalyst is as important as the additives used and importantly that carbonate and the formation of peroxycarbonate complicates the study of the reactivity of well-defined catalysts due to the activity of Mn$^{II}$ salts. In light of observations at pH > 10 noted in chapter 3, where the concentration of carbonate can increase rapidly when equilibrated with air, caution and care needs to be exercised in comparing reactivity with additives observed at below pH 10 compared to that observed above pH 10 under conditions relevant to bleaching.

**Experimental:**

**Materials**

Styrene sulfonate (SS) was obtained from Sigma-Aldrich (Steinheim, Germany). Commercially available chemicals were used without further purification unless stated otherwise. [Mn$^{IV,IV}$($\mu$-O)$_3$(tmtacn)$_2$](PF$_6$)$_2$ (1) and [Mn$^{III,III}$($\mu$-O)($\mu$-CH$_3$COO)$_2$(tmtacn)$_2$](PF$_6$)$_2$ (2) were available from earlier studies.$^{15}$

**Instrumentation**

Raman spectra were recorded using a Perkin-Elmer Raman Flex equipped with a fibre-optic probe ($\lambda_{exc}$ 785 nm) at room temperature. Raman spectra were recorded typically with 10 exposures of 8 s duration. UV/vis absorption spectra were recorded with a HP8453 spectrophotometer or a Specord600 (AnalytikJena) in 1 cm path length quartz cuvettes.

**Catalysed oxidations**

Oxidations of SS were carried out in a total volume of 3 ml of water or aqueous buffer (10$^{-3}$ M). Typical concentrations employed were 0.1 M substrate, 0.1 mM catalyst and 0.5 M H$_2$O$_2$. Time zero is taken to be the point at which the catalyst is added. The epoxide, product of SS, was isolated and characterized by $^1$H NMR spectroscopy.$^{22}$

Oxidation of chrysin (40 µM), was performed in a total volume of 2.5 mL of water or aqueous buffer (10 mM) with manganese catalyst (1 µM) and H$_2$O$_2$ (5 eq). Unless stated otherwise, all reactions were performed at ambient temperature (20-23 °C). pH was adjusted using H$_2$SO$_4$ (aq.) or NaOH (aq.).

**Analysis of Raman spectra**

Raman spectra were analysed in the spectral range 1800 to 600 cm$^{-1}$. The data analysis used the area of the bands between 1600 and 1650 cm$^{-1}$, which includes contributions
from the reactant and products only. The band at 870 cm\(^{-1}\) was used to determine H\(_2\)O\(_2\) concentrations.

References

Chapter 6


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