Chapter 5

Manganese catalysed oxidation of alkenes in two phase reaction with H$_2$O$_2$

In this chapter, the activity of several Mn-tmtacn complexes in the oxidation of both hydrophilic and hydrophobic alkenes under two phase reaction conditions, is investigated. The aim is to determine whether or not oxidation can be achieved by rapid transfer of the substrate and product between two phases rather than transfer of the catalyst. Evidence is presented for the localisation of catalytic oxidation in the aqueous phase of a two phase system, with the second phase either heptane, toluene or an alkene such as styrene. These data indicate that oxidation chemistry under the two phase conditions presented is restricted to the aqueous layer and that the use of a phase transfer catalyst in these systems is not beneficial.

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Introduction

Contemporary industrial catalytic processes ranging from bulk chemical synthesis, pharmaceuticals, materials and polymers employ multiphase reactions (e.g., two phase). This approach provides an industrially attractive method for generation and recovery of reaction components with concomitant environmental and cost effectiveness. The opportunity for efficient separation of product and catalyst present in multiphase reactions, while maintaining the advantages of homogenous catalysis, has led to the concept of liquid-liquid two phase catalysis, the catalyst is present in solution in one of the two phases and the substrate is essentially completely in the other liquid phase. Two-phase reactions find application in areas of chemistry as diverse as hydroformylations, carbonylations, hydrogenations, allylic substitutions, hydrodimerizations and Suzuki couplings. Several combinations have been studied intensely in recent years, including water (aqueous two phase) or supercritical CO2, ionic liquids, and fluorous two phase systems. Many reactions involve a two phase system in which the catalyst is in the aqueous phase and the substrate and product in the organic phase, such as the aqueous two phase oxidation reported by Neumann et al using a water-soluble polyoxometalate Na12[(WZn3(H2O)2][(ZnW9O34)2] for the selective oxidation of various functional groups with H2O2. The oxidation of alcohols, olefins, and sulfides, without additional organic solvents and halides, using H2O2 as oxidant with the catalyst Na2WO4 and Q1HSO4 (when Q is CH3(n-C8H17)3N) was reported by Noyori and coworkers. Recently, Bishopp and coworkers reported the epoxidation of sunflower oil with H2O2 using sodium tungstate catalyst by increasing the interfacial area through emulsification, which can overcome the mass transfer limitations observed under normal biphasic conditions, enabling recovery and recycling of the catalyst.

While water is used widely as solvent for two phase reactions, it presents several challenges. For instance, chemical modification of the catalysts is often needed to increase water solubility, which often reduces catalytic activity, and the use of a phase transfer catalyst is often required. The toxicity associated with the use of phase transfer catalysts makes a two phase reaction proceeding without their use highly preferable. A further challenge in two phase reactions is that optimizing reaction conditions, requires understanding of the various processes that take place during such a reaction and the multiple physical and well as chemical effects that changes in individual parameters can have. Although catalysis in two phase reactions has found widespread application in organic synthesis, identifying in which phase the catalysed reactions take place presents a substantial analytical challenge.

The oxidation of alkenes plays a fundamental role in the preparation of value-added intermediates in a wide range of industrial chemical processes. The oxidation of olefins to their corresponding epoxides is of particular synthetic value, from both an academic and an industrial perspective as it is provides access to highly functionalized organic compounds. The use of environmentally benign oxidants such as oxygen or hydrogen peroxide is highly desirable also. H2O2 is a low cost oxidant which does not present inherent environmental problems since water is the sole byproduct. However, oxidations with H2O2 are slow and hence catalysts, preferably based on relatively nontoxic metals, are used to achieve useful reaction rates. Among them, manganese complexes have been reported to exhibit excellent catalytic activity in several oxidative transformations.
The complexes $[\text{Mn}^{IV,IV}_2(\mu-O)_3(\text{Me}_3\text{tacn})_2](\text{PF}_6)_2$ (1), and its analogues such as $[\text{Mn}^{III,III}_2(\mu-\text{CH}_3\text{CO}_2)_2(\mu-O)(\text{Me}_3\text{tacn})_2](\text{PF}_6)_2$, were reported as catalysts for clean and efficient low-temperature bleaching as well as the epoxidation of olefins. Indeed already in 1994, Unilever reported the application of the complex $[\text{Mn}^{IV,IV}_2(\mu-O)_3(\text{tmtacn})_2]^{2+}$ in low temperature stain bleaching with 100 equiv. of $\text{H}_2\text{O}_2$ w.r.t. substrate. Subsequently, complex 1 was studied for a wide range of oxidative transformations in industry, in industrial bleaching the oxidation of phenols, alcohols, sulphides, alkanes, azo-dyes, and the epoxidation and cis-dihydroxylation of alkenes. A particularly remarkable property of this catalyst is that it can be used in both organic and aqueous solvents at both low and high pH.

Although over the last several decades, mechanistic research in manganese catalysed oxidation catalysis towards application in organic solvents has received considerable attention, extension of these mechanistic insights to understanding the behaviour of these catalysts in multi-phase media is limited. A central question in the application of these complexes in such processes is in which phase the catalysed reaction takes place.

In this chapter, the activity of several manganese catalysts in the oxidation of alkenes under two phase organic/aqueous reaction conditions, is investigated. The oxidation of styrene sulfonate (SS) and styrene (S) is compared and contrasted. Styrene is a hydrophobic alkene and styrene oxide is an important fine chemical intermediate for producing fragrances, drugs, sweeteners, epoxy resins, etc. Therefore, environmental friendly catalytic methods for the epoxidation of styrene with environmentally benign oxidants are of interest. Several heterogeneous catalysts including titanium silicate molecular sieves, TS-1, Ti-SiO$_2$, TS-2, and γ-Al$_2$O$_3$ have been reported. Homogeneous catalytic epoxidation of styrene can take place under mild conditions and good selectivity is achieved with porphyrins, or “soluble metal oxides” such as methyltrioxorhenium (MeReO$_3$ or MTO) and the Venturello-Ishii catalytic system. However, a common issue is the difficulty encountered in catalyst recycling. In 2000, Yadav et. al reported the epoxidation of styrene to styrene oxide using a classical phase-transfer catalysis methodology by applying a combination of aqueous $\text{H}_2\text{O}_2$, heteropoly acids and phase-transfer catalyst in a two phase system Ishii-Venturello system. Gao et. al reported the epoxidation of styrene catalysed by a reaction-controlled phase transfer catalyst $[(\text{C}_{18}\text{H}_{37})(30\%) + \text{C}_{16}\text{H}_{33}(70\%)\text{N(CH}_3)_3\text{][PW}_3\text{O}_{16}]$ with $\text{H}_2\text{O}_2$ in a two phase system. The catalyst used in that system undergoes dissolution-precipitation during the reaction, allowing the catalyst to be recovered for reuse.

In this chapter, the central question is whether oxidation can be achieved by rapid transfer of the substrate and product between two phases rather than transfer of the catalyst. Hence, establishing in which phase the catalysed reaction actually takes place, i.e. whether phase transfer of either catalyst, substrate and/or oxidant is important and if so which species go transfer between the phases. In the present study, this is addressed by studying the activity of Mn-tmtacn complexes in the oxidation of both hydrophilic and hydrophobic alkenes under two phase conditions. Several approaches are taken to identify in which phase the catalysed reaction takes place. The oxidation of two substrates with $\text{H}_2\text{O}_2$ catalysed by manganese complexes was examined (Figure 1) i.e. the water soluble styrene sulfonate (SS) which was shown to be oxidized effectively.
with the several Mn-tmtacn catalysts in aqueous solutions (see chapter 2) and styrene (S) as a hydrophobic alkene in a two phase system.\cite{24,44}

\[
\begin{align*}
\text{(I)} & \quad \text{[S]} \xrightarrow{\text{H}_2\text{O}_2(5 \text{ eq})} \xrightarrow{\text{Catalyst, biphasic mixture, r.t.}} \text{(O)} \\
\text{(II)} & \quad \text{[S]} \xrightarrow{\text{H}_2\text{O}_2(5 \text{ eq})} \xrightarrow{\text{Catalyst, biphasic mixture, r.t.}} \text{(SS)}
\end{align*}
\]

**Figure 1** Model reactions examined; the oxidation of styrene (S) and styrene-p-sulfonate (SS).

The relative insensitivity of Raman spectroscopy to water and the strength of the Raman scattering of the C=C stretching modes of alkenes in the range 1600–1700 cm\(^{-1}\) makes it a key tool to monitor reaction progress in aqueous/non-aqueous two phase systems, as shown schematically in Scheme 1.

**Scheme 1** Approach taken in present study and example of in line monitoring of an aqueous phase by Raman spectroscopy

**Results**

The PF\(_6^–\) salt of 1 was used as a hydrophilic catalyst and the BARF\(^–\) salt of 1 as a hydrophobic catalyst (Figure 2). Complex 2 was synthesized from 1 and heptyloxy benzoic acid, as an lipophilic catalyst due to the long alkyl chain present in the carboxylato bridging ligand.
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Figure 2 Structure of complexes 1-3 and the ligand Me₃tacn

Partitioning of catalysts

The partitioning of [Mn₂^{IV,IV}(μ-O)₃(Me₃tacn)]₂(PF₆)₂ (1), [Mn₂^{III,III}(μ-O)(μ-4-heptyloxybenzoato)]₂(Me₃tacn)]₂(PF₆)₂ (2), styrene and H₂O₂ between aqueous and organic layers was determined by UV/vis absorption, ¹H NMR and Raman spectroscopy.

The partitioning of 1 between aqueous and organic phases was monitored by UV/Vis absorption spectroscopy (Figure 3), with two absorption bands observed at λ_max 392 and 487 nm in the aqueous phase, and no absorption in the organic phase, confirming that 1 is essentially present only in the aqueous phase and is excluded from the organic phase. Partitioning of complex 2 between water and heptane or toluene, monitored by UV/Vis absorption spectroscopy, shows the characteristic absorption bands of the {Mn₂^{III,III}(μ-carboxylato)₂(μ-O)} motif at λ_max 488, 525 and a broad band at 740 nm in the organic phase, while no absorption related to the complex was observed in the aqueous phase (Figure 3).

Figure 3 (left) UV/vis absorption spectra of 1 (1 mM) in water (black) and heptane (red). (right) UV/Vis absorption spectrum of 2 (1mM) in toluene (blue), water (red). (Mixtures are stirred overnight.)

Partitioning of H₂O₂ (0.5 M in 15 ml water) was determined by Raman spectroscopy (Figure 4) after equilibration with toluene (15 ml). The difference in the intensity of O-O νₛ of H₂O₂ at 870 cm⁻¹ normalized to the H₂O band at 1620 cm⁻¹, shows some
partitioning between the aqueous layer and the organic layer, with the major part, ~85%, remained in the aqueous phase. In addition some partitioning of toluene into the aqueous layer is apparent.

Figure 4 Partitioning of H₂O₂ (0.5 M) in two phase system containing water (15 ml) and toluene (15 ml). Raman spectrum of aqueous phase (orange) before and (blue) after equilibration with toluene.

Distribution of styrene in aqueous phase

The solubility and partitioning of various mole ratios of styrene and styrene oxide into water was determined by ¹H NMR spectroscopy after equilibration for ca. 0.5 h (Table 1). The bar chart shows, in all cases, that formation of diol, due to the slow hydrolysis of styrene oxide, occurs also. In addition, the concentration of styrene decreases as expected in the aqueous phase as the mole fraction of styrene in the organic phase decreases (Figure 5).

Table 1. Quantity (in grams) of the substances contained in each vial and distribution of styrene, styrene oxide and 1-phenyl-1,2-ethanediol in D₂O determined by ¹H NMR spectroscopy. The methyl signal of potassium acetate (6.63 mM) was used as internal reference.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Styrene (g)</th>
<th>Styrene oxide (g)</th>
<th>Potassium acetate (6.63 mM) in D₂O</th>
<th>Compound transferred in aqueous phase</th>
<th>Styrene (mM)</th>
<th>Styrene oxide (mM)</th>
<th>1-Phenyl-1,2-ethanediol (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entry 1</td>
<td>0.000</td>
<td>1.000</td>
<td>1 mL</td>
<td>Entry 1</td>
<td>0</td>
<td>17</td>
<td>5.26</td>
</tr>
<tr>
<td>Entry 2</td>
<td>0.501</td>
<td>0.504</td>
<td>1 mL</td>
<td>Entry 2</td>
<td>1.2</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>Entry 3</td>
<td>0.693</td>
<td>0.314</td>
<td>1 mL</td>
<td>Entry 3</td>
<td>1.8</td>
<td>5.9</td>
<td>2.17</td>
</tr>
<tr>
<td>Entry 4</td>
<td>1.000</td>
<td>0.000</td>
<td>1 mL</td>
<td>Entry 4</td>
<td>2.25</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
A series of mixtures with a constant amount of styrene and variation of styrene oxide were equilibrated with D₂O containing potassium acetate as internal reference (Table 2). Partitioning of organics into the aqueous phase was determined by °H NMR spectroscopy. With increasing amounts of styrene oxide in the organic phase, the amount of styrene distributed into the aqueous phase decreased and styrene oxide was transformed to the diol in D₂O (Table 2). The partition-coefficient of styrene was the same (K = 0.29 (± 0.03) ×10⁻³) in all cases. Hence, even where styrene is present in greater or equal mole fraction compared to styrene oxide in the organic layer, in the aqueous phase styrene oxide is present to a greater extent. This difference is pronounced with a 1:1 ratio of styrene and styrene oxide in the organic layer but after equilibration the proportion of styrene in the aqueous layer is less than that of styrene oxide in addition to presence of diol in this layer. These data indicate that as consumption of styrene and formation of the product, which has a higher solubility in the aqueous phase proceeds, a decrease in partitioning of styrene into the aqueous phase will be observed.

Table 2 Quantity of the substances contained in each vial and distribution of styrene, styrene oxide and 1-phenyl-1,2-ethanediol in D₂O measured by °H NMR spectroscopy. The CH₃ signal of potassium acetate (6.63 mM) was used as internal reference signal.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Styrene (g)</th>
<th>Styrene oxide (g)</th>
<th>Stoene in aqueous phase</th>
<th>Styrene oxide in aqueous phase</th>
<th>Styrene diol in aqueous phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entry 1</td>
<td>0.500 g (4.8 mmol)</td>
<td>0 g (0 mmol)</td>
<td>2.330 mM</td>
<td>0 mM</td>
<td>0 mM</td>
</tr>
<tr>
<td>Entry 2</td>
<td>0.500 g</td>
<td>0.250 g (2.0 mmol)</td>
<td>1.742mM</td>
<td>7.49 mM</td>
<td>2.57 mM</td>
</tr>
<tr>
<td>Entry 3</td>
<td>0.500 g</td>
<td>0.500 g (4.1mmol)</td>
<td>1.305 mM</td>
<td>11.50 mM</td>
<td>4.07 mM</td>
</tr>
<tr>
<td>Entry 4</td>
<td>0.500 g</td>
<td>1.000 g (8.3 mmol)</td>
<td>1.005 mM</td>
<td>14.28 mM</td>
<td>7.14 mM</td>
</tr>
</tbody>
</table>
Oxidation of alkenes catalysed by complex 1

Raman spectra of styrene sulfonate and its epoxide product (OSS) and those of styrene (S) are shown in (Figure 6). The spectra were followed in the ranges 1200–1300 cm\(^{-1}\) and 1600–1650 cm\(^{-1}\) and to a lesser extent the range between 600 and 900 cm\(^{-1}\), as the Raman scattering from carbonates or organic solvent has minimum contribution in these regions. The bands in the range 1600–1650 cm\(^{-1}\) are characteristic of C=C stretching vibrations of vinyl and aryl groups, where are useful in monitoring reaction progress.

Initially, the epoxidation of styrene sulfonate was carried out using complex 1 under monophasic condition containing in aqueous NaHCO\(_3\) (0.1 M) or water at pH = 8. The Raman spectra were recorded at the start and end of the reaction.\(^1\) The loss of the alkene stretching bands at 1600-1630 cm\(^{-1}\) indicated full conversion of styrene sulfonate at pH 8 in bicarbonate buffer and 20% conversion at pH 8 in water. The epoxide product was isolated and characterized by \(^1\)H NMR spectroscopy (Figures 7, 8 and 9).\(^44\)

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\(^1\) The workup procedure is described in chapter 2.
Figure 8 On-line reaction monitoring ($\lambda_{\text{exc}}$ 785 nm) oxidation of styrene sulfonate (0.1 M) with a single addition of $\text{H}_2\text{O}_2$ (0.5 M) and 1 (0.1 mM) in aqueous NaHCO$_3$ (0.1 M) at pH = 8.

Figure 9 $^1$H NMR spectra of sodium 4-styrene sulfonate (I), sodium 4-styrene oxide sulfonate (II) and sodium 4-styrene glycol sulfonate (III) in D$_2$O.

The oxidation of styrene sulfonate with 1 and $\text{H}_2\text{O}_2$ resulted in almost full conversion of the alkene to the epoxide product in aqueous NaHCO$_3$/heptane and 20% conversion in water/heptane, i.e. as observed under single phase (water or aqueous NaHCO$_3$) conditions (Figure 10).
Figure 10 Raman spectra of the aqueous phase of the reaction mixture with styrene sulfonate (0.1 M) in left) aqueous NaHCO₃ (0.1 M) /heptane and right) water/heptane with 1 (0.1 mM) at pH 8, t=0 (blue), t=20 h (red)

Oxidation of styrene under two phase reaction conditions was studied with 1, i.e. with styrene in heptane together with water or aqueous NaHCO₃. In both cases, conversion of styrene was not observed. Furthermore, although complete decomposition of H₂O₂ was observed in the presence of aqueous NaHCO₃, with water H₂O₂ was not consumed (Figure 11).

Figure 11 (left) Raman spectra of the organic phase of in the reaction of styrene (0.1 M) in heptane mixed with water (green) or aqueous NaHCO₃ (0.1 M) (blue) with 1 (0.1 mM) at pH 8 after 20 h. (right) Raman spectra of aqueous phase, blue (aqueous NaHCO₃ (0.1 M)), green (water) after 20 h.

Disproportionation of H₂O₂ in the presence of styrene sulfonate and aqueous NaHCO₃ was examined, through monitoring of the O-O νₛ band of H₂O₂ at 870 cm⁻¹, in the presence and absence of the sequestrant DTPA (diethylene triamine pentaacetic acid, Figure 12). The presence of the sequestrant, which complexes trace metal ions present in commercial bicarbonate, prevents the decomposition of H₂O₂, confirming that traces of metal impurities present in bicarbonate are responsible for the H₂O₂ disproportionation.
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Figure 12 Raman spectra of a mixture of styrene sulfonate and H$_2$O$_2$ in aqueous NaHCO$_3$ (0.1 M) (left) without and (right) with the sequestrant (DTPA). t=0 (blue), t= 20 h (red).

Oxidation of alkenes catalysed by 2

The oxidation of styrene sulfonate and styrene as hydrophilic and lipophilic model substrates, respectively, was examined using 2 as an organic phase soluble catalyst.

Complex 2 dissolves readily in toluene. Addition of the aqueous layer at pH 8 caused the colour of the toluene layer to change from pink to pale yellow, with the aqueous phase changing from colourless to pale yellow also, which remained unchanged thereafter, indicating that the catalyst is not stable in toluene in the presence of the aqueous phase. Oxidation of styrene sulfonate was monitored overnight, with ca. 80% conversion (Figure 13).

Figure 13 Oxidation of styrene sulfonate with 2 and H$_2$O$_2$ under two phase conditions monitored by Raman spectroscopy. (a) aqueous NaHCO$_3$ (0.1 M)/ toluene, (b) water/ toluene.

A control reaction was performed by using Mn$^{2+}$ salt as catalyst under the same conditions. Consistent with the report of Burgess and coworkers,$^{46}$ in aqueous bicarbonate solution, Mn$^{2+}$ provides full conversion of the styrene sulfonate to the corresponding epoxide, however, conversion was not observed in the absence of carbonate. Hence, it can be excluded that Mn$^{2+}$ formed by the decomposition of 2 in water under two phase conditions is not responsible for the catalytic activity observed (Figure 14).
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Figure 14 Oxidation of SS by H$_2$O$_2$ with Mn$^{2+}$ under two phase conditions. (a) in aqueous NaHCO$_3$/toluene, (b) in water/toluene, (c) in aqueous NaHCO$_3$/heptane, (d) in water/heptane.

Again styrene did not undergo conversion in toluene/water or aqueous NaHCO$_3$ mixtures with 2 and H$_2$O$_2$. Notably the colour of the organic layer, which was pink due to the presence of 2 changed to pale yellow upon addition of aqueous NaHCO$_3$ or water at pH 8. Although heptane or toluene does not interfere with the catalytic activity of 1 in the oxidation of styrene sulfonate, they inhibit the oxidation of styrene.

Figure 15 Raman spectra of the reaction mixture of neat styrene mixed with aqueous NaHCO$_3$ (0.1 M) (red) or water (green) with 2 at pH 8 after 20 h, t=0 (blue).
When neat styrene was used as an organic phase, the lipophilic catalyst 2 dissolved in the styrene layer and aqueous layer (water or aqueous NaHCO₃) at pH 8. After addition of H₂O₂ the reactions were monitored by in-line Raman spectroscopy. With aqueous NaHCO₃, higher conversion (~45%), was observed compared to with water, (~10%) (Figure 15). The inhibition of catalytic activity in toluene or heptane is probably due to the limited partitioning of styrene into the aqueous layer in those cases.

The change in colour of complex 2 under biphasic conditions indicates that it is not stable. When in contact with an aqueous layer dissociation of the carboxylato ligands from the complex result in the transfer of the remaining complex to the aqueous phase (Figure 16).

![Figure 16 UV Raman (λ_{exc} 244 nm) spectra of 2 in heptane mixed (a) with water at pH 8, (b) aqueous NaHCO₃ at pH 8, (c) of heptyloxybenzoic acid in heptane and (d) water layer and (e) aqueous bicarbonate layer equilibrated with heptane.](image)

**Oxidation of alkenes catalysed by 1BARF**

The catalyst 1BARF (BARF: tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate) was dissolved in styrene with an aqueous layer containing H₂O₂ (added over 5 h) and with an aqueous NaHCO₃ solution with the ratio of (1:1 v/v the organic/aqueous phase). The ¹H NMR spectra of neat styrene, after the reaction with 1 (I) and with 3 (II) are shown in Figure 17. The differences are apparent as the alkene is converted to the epoxide in the case of using 1 (~13%) and negligible conversion is observed by using 3 under the same conditions. The signals of the aromatic hydrogens at around 7.4 ppm are as expected. The signals of the vinyl hydrogens give rise to three signals between 5 and 7 ppm. For the epoxide these signals are shifted upfield to 2.5 – 4 ppm.
Control experiments with a Mn$^{2+}$ salt showed only ~ 1% conversion of styrene and conversion was not obtained without addition of 1, 2 or Mn$^{2+}$ (Figure 18). Increasing the concentration of bicarbonate results in increased conversion of styrene in the case of 1 (Figure 19).
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![Figure 18](image1.png)

**Figure 18** $^1$H NMR spectrum of styrene after reaction without 1 in D$_2$O.

![Figure 19](image2.png)

**Figure 19** $^1$H NMR spectra in CDCl$_3$ of styrene after reaction with H$_2$O$_2$ and 1 (2 mM) in aqueous NaHCO$_3$ (0.6 M).

The oxidation of styrene only reached ca. 15 % conversion. In presence of the sequestrant DTPA, ~7% conversion of the styrene was obtained in aqueous NaHCO$_3$ (0.3 M) with 1. That H$_2$O$_2$ remained in aqueous phase was confirmed by Raman spectroscopy. Styrene sulfonate was added to the two phase mixture, subsequently, and ca. 70% conversion of styrene sulfonate was observed, which shows that 1 is still active even after oxidation of styrene has ceased (Figure 20). Hence, the limited conversion and loss of activity with respect to the oxidation of styrene is due neither to deactivation of the catalyst nor decomposition of H$_2$O$_2$. 

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Figure 20 Raman spectra ($\lambda_{\text{exc}}$ 785 nm) of the reaction of styrene sulfonate (0.3 M) in aqueous NaHCO$_3$ (0.3 M) with 1 (2 mM) at pH 8, following the oxidation of styrene under two phase condition obtained overnight. Regions of most interest are noted.

Figure 21 $^1$H NMR spectra of styrene after reaction (I) with complex 1 and (II) with Mn$^{2+}$ in the presence of DTPA in D$_2$O.
The stability and activity of 1 in the conversion of styrene and styrene sulfonate under these conditions is confirmed by comparison with the same reaction in presence of Mn$^{2+}$ and DTPA. Conversion of neither styrene nor styrene sulfonate was observed and $> \sim 90\%$ of H$_2$O$_2$ was present in the aqueous phase at the end of the reaction (Figure 21). Furthermore, these data show that sufficient catalyst (1) and H$_2$O$_2$ are present with styrene / aqueous NaHCO$_3$ to continue the oxidation of styrene. The loss of activity correlates with the distribution of styrene into the aqueous phase, as it shown above as the consumption of styrene and the formation of products (styrene oxide and subsequently formation of diol), which are more soluble in aqueous phase than styrene, the partitioning of styrene into the aqueous phase decreases and hence the rate of conversion of styrene decreases also (Table 1, Figure 5).

**Oxidation of substrates under homogenous conditions**

As it appears that the oxidation of styrene takes place exclusively in the aqueous phase, the rate of conversion of styrene was determined in water under single phase conditions (i.e. with water saturated with styrene).

![Figure 22](image)

**Figure 22** Oxidation of styrene under two phase condition. Water saturated with styrene (3 mM), H$_2$O$_2$ (5 eq or 166 eq w.r.t substrate)

The experiment was performed in D$_2$O/NaHCO$_3$ (0.1 M) to limit overlap of the C=C stretching band with the bending mode of H$_2$O. Full conversion was obtained for styrene (Figure 23). The reaction was carried out with higher concentrations of H$_2$O$_2$ (33 times more) to simulate the reaction under biphasic conditions. The reaction showed full conversion of styrene over a shorter period. These data revealed that even at a higher concentration of oxidant, the catalyst remains active, albeit that disproportionation of H$_2$O$_2$ was observed also, manifested in the increased Raman signal of oxygen at 1550 cm$^{-1}$.

![Figure 23](image)

**Figure 23** Consumption of styrene versus time (min) with 1, a) 15 mM, b) 500 mM of H$_2$O$_2$ added as a single addition, monitored with Raman spectroscopy ($\lambda_{exc}$ 532 nm) in D$_2$O (blue dots), by integration of the band at 1634 cm$^{-1}$.
Figure 24 Oxidation of saturated styrene (3 mM) with 500 mM of H₂O₂ added at once and 1, monitored with Raman spectroscopy (λ_exc 532 nm) in D₂O (blue dots), by integration of the peak at 1634 cm⁻¹.

Discussion

The localisation of the catalytic oxidation of alkenes under two phase reaction conditions was examined by using a family of manganese catalysts based on the tmtacn ligand. Complexes 1, 2 and 3 have different solubility in aqueous or organic media be virtue of the ligands and counter ions. In order to locate the phase in which the conversion of alkenes to their epoxide occurred, advantage was taken of Raman spectroscopy, ¹H NMR and UV/Vis spectroscopy, enabling the monitoring of reaction progress in both the aqueous and the organic layers. Comparison of the oxidation of styrene under the various conditions showed that organic solvents reduce conversion due to a reduction in the partitioning of styrene in the aqueous phase. In contrast, the oxidation of styrene without organic solvents (i.e. the organic phase is comprised solely of the substrate) was observed with both complex 1 and 2. Although, initially 2 is present in the organic phase, the Mn²⁺,III complex 2 has lower stability compared to the Mn²⁺,IV complex 1 with regard to ligand exchange, in the presence of water dissociation of the heptyloxybenzoato ligand results in immediate protonation in the organic layer and hence the equilibrium is shifted towards the carboxylato dissociated product. This complex is no longer lipophilic and partitions into the aqueous layer where it could oxidize the alkene. Analogous behaviour was observed in the study of [Mn₂³⁺,III(μ-O)(μ-3,5-difluorobenzoato)₂(tmtacn)₂]²⁺ during the oxidation of cyclooctene in acetonitrile. The loss of activity related to the dissociation of the carboxylato group from the complex was monitored as the reaction progressed.⁴₅

Control experiments with Mn²⁺ and sequestrant allowed the degradation of complex 2 to Mn²⁺ ions to be excluded as even in the presence of DTPA, 1 and 2 remain
catalytically active, in contrast to Mn$^{2+}$ salts which are inactive. On the other hand, in the case of complex 3, which has the BARF counter anion (soluble in organic layer) conversion of styrene was not observed. Overall, these data indicate that the presence of the catalyst in the aqueous phase is a prerequisite for catalytic activity.

With the hydrophilic alkene styrene sulfonate conversion to its epoxide product was observed in many cases allowing for the catalyst deactivation to be excluded as a reason for the lack of conversion of styrene. Furthermore where styrene was present as a single phase with water full conversion was observed. The change in extent of portioning with conversion can therefore be ascribed, at least in part, to the reduction in concentration of styrene in the aqueous layer as conversion proceeds.

**Conclusions**

In the present study, evidence for the localisation of oxidation in two phase reactions where heptane, toluene or styrene is the organic phase and the other phase is aqueous were explored. In this study two strategies for the oxidation of soluble substrates in an aqueous or organic biphasic medium were taken, in order to find out where the catalytic reaction occurs. In the first approach the substrate is dissolved in, or forms itself, an organic phase. Following the reaction by Raman shows in the case of using styrene which has a negligible solubility in water as the organic phase and no extra organic solvent, conversion of styrene was observed. In the second approach the substrate and oxidant stay in the aqueous phase and the catalyst is dissolved in organic phase. Although complex 2 shows good stability and solubility in the organic layer, it is not stable upon addition of the slightly basic aqueous layer, with the dissociated heptyloxy benzoic acid remaining in the organic layer and the other part of the catalyst transferred to the aqueous phase where it showed activity. These findings show that oxidation chemistry under the two phase conditions with 1 are restricted to the aqueous layer.

Since the application of manganese catalysts based on the tmtacn ligand in bleaching processes is increasing, these findings should be taken into consideration when studying competition experiments between different hydrophilic and lipophilic dyes under simulated bleaching conditions as mass transfer of substrate between aqueous and organic phases will ultimately limit reactivity.

**Experimental Section**

**Materials.**

Reagent and solvents obtained commercially were used as received unless stated otherwise. H$_2$O$_2$ was 50% w/w in water (Acros Organics).

**Instrumentation**

UV/vis absorption spectra were recorded with a HP8453 spectrophotometer or a Specord600 (AnalytikJena) in 1 cm pathlength quartz cuvettes. Raman spectra were recorded using a Perkin-Elmer Raman Flex equipped with a fibre-optic probe ($\lambda_{exc}$ 785 nm) and Raman spectroscopy ($\lambda_{exc}$ 532 nm, 300 mW Cobolt lasers, Avantes fibre probe, Andor Shamrock 163 spectrograph, Andor iDus 420 CCD camera). Alkene and catalyst
concentrations were typically 100 mM and 0.1 mM, respectively. The pH was controlled by addition of aqueous NaOH or H$_2$SO$_4$. Spectra obtained following each phase (organic and aqueous phase) were analysed in the spectral range 1800 to 600 cm$^{-1}$, the area of the bands between 1600 and 1650 cm$^{-1}$, which includes contributions from the reactant and products only.

**Preparation of samples for distribution of catalyst in aqueous and organic phase:**

Catalyst 1 or 2 (0.015 mmol / 1mM) was added to the mixture of water (15 ml) with heptane or toluene (1/1 ratio, 15 ml), respectively, and stirred overnight. After separation of the phases in two layers, by simple decantation the layers were split in two cuvettes and examined by UV/Vis absorption spectroscopy.

**Preparation of samples for distribution of organics in aqueous phase**

The concentration of the different organic substances were determined in the early stage of the reaction (30 min of vigorous stirring) by preparing 4 vials containing different fractions of styrene and styrene oxide (Table 1). The concentration in the aqueous phase of styrene and styrene oxide were determined by $^1$H NMR spectroscopy using the aqueous (D$_2$O) phase inserted into four NMR tubes to measure quantitatively the concentration of organic species in the phase. The measurements were performed on a 400 or 500 MHz NMR spectrometer (Varian) using a known quantity of Potassium acetate (6 mM) as reference. The observed solubility of styrene in water is in good agreement with the literature values 0.031 % (ca. 3 mM) at 25 °C.\textsuperscript{48}

**Oxidation of substrates under homogenous conditions**

From a stock solution of 1 (10 mM), 10 μL was added into 3 mL of D$_2$O saturated with styrene (~3 mM) containing NaHCO$_3$ (0.1 M). The reaction was then started by addition of H$_2$O$_2$ (85 μL, 50% w/w). The progress of the reaction over time was monitored with a Raman spectroscopy.

**Catalysed oxidation of styrene and styrene sulfonate**

Oxidations of styrene sulfonate and styrene with H$_2$O$_2$ (50% w/w in water), catalysed by 1 or 2, were carried out in 50 mL round bottomed flasks containing 15 ml of aqueous phase and 15 ml organic phase. Concentrations of the reagents referred to the total volume of the biphasic system were 100 mM. First, the catalyst was dissolved in the aqueous or organic layer, then the substrate was added and hence time zero is taken to be the point at which the H$_2$O$_2$ was added. pH was adjusted prior to addition of oxidant with H$_2$SO$_4$(aq.) or NaOH(aq.) to pH 8.5. Unless stated otherwise all reactions were performed at ambient temperature (20–23°C) and were run over one night and were monitored by Raman spectroscopy at $\lambda_{exc}$ 785nm the day after. During reactions, the two layers were stirred vigorously, thus facilitating partitioning between the phases. After one night, the stirring was stopped and the phases allowed to separate. Separation of the layers was then carried out by decantation.

Oxidation of styrene and subsequently styrene sulfonate with H$_2$O$_2$ (50% w/w in water), in order to comparison catalytic activity of complex 1 or 3, were carried out in a 10 mL vial containing 2.5 ml bicarbonate solution and 2.5 ml styrene. Catalyst 1 and 3 were dissolved in the aqueous phase and organic phase, respectively. The reaction was started by addition of 2.5 ml H$_2$O$_2$ (50% w/w) over 5 h by syringe pump. The DTPA (10
mM) was used in oxidation of styrene and styrene sulfonate to compare activity of complex 1 and Mn^{4+} ion. The conversion of styrene was monitored by 2H NMR spectroscopy in CDCl_3 and conversion of styrene sulfonate in the aqueous phase was monitored by Raman spectroscopy at 785 nm.

**Synthesis of complex 2**

[Mn_{II,III}(µ-O)(µ-4-heptyloxybenzoato)_{2}(tmtacn)]_{2}[PF_6]_2. Complex 2 was prepared by modification of the general procedure reported by Hage et al. First, a solution of complex 1 (1620 mg, 2mmol) in H_2O (300 ml) and 4-heptyloxy benzoic acid (1020 mg, 4.3 mmol) in H_2O (300 ml) were mixed, followed by the addition of L-Ascorbic acid (380 mg, 2.1 mmol) in H_2O (20 ml) with rapid stirring. The colour changed to dark red and the addition of 500 ml water to this solution triggered the precipitation in the solution. The dark purple precipitation was isolated by filtration and rinsed with Et_2O. Yield 71%. Elemental analysis (calc. for Mn_{II,III}C_{20}H_{38}N_{6}O_{12}PF_{2}F_{12}): C 44.8 % (44.8 %), H 6.6 % (6.7 %), N 6.7 % (6.8 %). ESI-MS m/z 469.4 [Mn_{II,III}(µ-4-heptyloxybenzoato)_{2}(µ-O)(tmtacn)]^{2+}, 1083.6 [Mn_{II,III}(4-heptyloxybenzoato)_{2}(µ-O)_{2}(tmtacn)]^{2+}.

**References**

Chapter 5


