Mechanisms in iron, nickel, and manganese, catalysis with small molecule oxidants

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Chapter 2
Conflicting role of water in the activation of H₂O₂ and the formation and reactivity of Non-Heme Fe₃⁺-OOH and Fe₃⁺-O-Fe₃⁺ complexes at room temperature

Abstract
The formation of an Fe₃⁺-OOH species by reaction of the complex 1 ([([MeN3Py)FeII(CH3CN)]²⁺) with H₂O₂ at room temperature is reported and is studied by a combination of UV-vis absorption, EPR and resonance Raman spectroscopies. The formation of the Fe₃⁺-OOH species, and its subsequent conversion to relatively inert Fe₃⁺-O-Fe₃⁺ species, is shown to be highly dependent on the concentration of water, with excess water favoring the formation of the latter species, which is studied by UV-vis absorption spectrophotometry also. The presence of acetic acid increases the rate and extent of oxidation of 1 to its iron(III) state and inhibits the wasteful decomposition of H₂O₂ but does not affect significantly the spectroscopic properties of the Fe₃⁺-OOH species formed.

2.1 Introduction

Synthetic non-heme iron complexes that activate \( \text{H}_2\text{O}_2 \) are of increasing interest as models for non-heme mononuclear iron dependent oxygenases\(^1\) and in the catalytic oxidation of C-H bonds.\(^2\),\(^3\),\(^4\) The development of synthetic catalytic systems presents many opportunities in both achieving selective and efficient oxidations under ambient conditions and in allowing access to reactive species that provide insight into the mechanism by which non-heme iron dependent enzymes achieve a wide range of oxidative transformations, e.g., the oxidation of arenes by Rieske oxygenases.\(^5\) The oxidation of alkenes to epoxides and 1,2-diols is of synthetic as well as biomimetic interest\(^6\) and in recent years several non-heme complexes have been shown to be particularly useful in this regard.\(^7\) In particular, iron complexes that present two solvent accessible sites, as is found for example in napthalene dioxygenase, which ligates Fe(II) with two histidines and a bidentate aspartic acid,\(^8\) are of particular interest in that they can use H\(_2\)O\(_2\) as terminal oxidant,\(^9\),\(^10\) and because of the ‘water assisted’ mechanism by which putative iron(V)=O species are proposed to be formed from \((\text{HO})\text{Fe}^{\text{III}}\cdot\text{OOH}\)\(^11\) and \((\text{AcO})\text{Fe}^{\text{III}}\cdot\text{OOH}\)\(^12\) intermediates.

**Figure 1** Ligands and corresponding Fe(II) complexes discussed in the text.

Notable examples include complexes bearing tetradaentate (N4) ligands such as \([\text{TPA}]\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})_2\)\(^{2+}\) and \([\text{TMC}]\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})_2\)\(^{2+}\) (where TPA is tris(2-pyridylmethyl)amine and TMC is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) reported by Que and coworkers,\(^13\) and \([\text{MeN3Py}]\text{Fe}^{\text{II}}(\text{CH}_3\text{CN})_2\cdot\text{(ClO}_4)_2\)\(^{2+}\) (1) (Figure 1, where MeN3Py is 1,1-di(pyridin-2-yl)-N-methyl-N-(pyridin-2-ylmethyl)methanamine) reported by Feringa and coworkers, which were shown to be active in alkene dihydroxylation, as well as epoxidation.\(^14\) With notable exceptions, the involvement of Fe\(^{\text{III}}\)-OOH intermediates has been inferred only in the case of iron(II) complexes of N4 donor ligands,\(^14\) in contrast to their related N5 donor ligands and bleomycin,\(^9\),\(^15\) for which such intermediates have been characterized thoroughly. The observation of N4-Fe\(^{\text{III}}\)-OOH species under ambient conditions is rare.\(^16\) Nevertheless, it is generally considered that, even if formed, Fe\(^{\text{III}}\)-OOH species do not engage directly in oxygenation of substrates and C-H abstraction, but are instead precursors to reactive high valent Fe\(^{\text{IV}}\)=O and Fe\(^{\text{V}}\)=O species.\(^17\) Hence, identifying and determining the intrinsic reactivity of Fe\(^{\text{III}}\)-OOH species is important from a fundamental perspective.
In this contribution, we show that an Fe\textsuperscript{III}-OOH species is generated upon reaction of \textbf{1} with H\textsubscript{2}O\textsubscript{2}. Under appropriate conditions, we found that this species is sufficiently stable to be studied at room temperature by a combination of UV-vis absorption, EPR and Raman spectroscopies. Furthermore, we demonstrate that the formation of this Fe\textsuperscript{III}-OOH species, and its subsequent conversion to a relatively inert Fe\textsuperscript{III}-O-Fe\textsuperscript{III} species, is highly dependent on the concentration of water. In particular, the reaction of the iron(II) complex \textbf{1} with H\textsubscript{2}O\textsubscript{2} in acetonitrile requires that a thermodynamically unfavorable ligand exchange with water takes place initially. Hence, the concentration of water determines the rate and extent of oxidation of \textbf{1} to an Fe\textsuperscript{III}-OH species and thereby rate of the formation of the Fe\textsuperscript{III}-OOH species. Importantly, however, the water content also affects the rate of formation of inert Fe\textsuperscript{III}-O-Fe\textsuperscript{III} complexes from Fe\textsuperscript{III}-OH species. Hence, accelerating the rate of initial oxidation of \textbf{1} by increasing the concentration of water must be balanced with the increase in the rate of the subsequent formation of Fe\textsuperscript{III}-OOH species, which act as thermodynamic sinks.\textsuperscript{15,18} Furthermore, we show that the presence of acetic acid, which has been shown in many cases to enhance the efficiency of N4-donor ligand based catalysts,\textsuperscript{19} increases the rate and extent of oxidation of \textbf{1} to its iron(III) state, in large part by inhibiting the wasteful decomposition of H\textsubscript{2}O\textsubscript{2}. Importantly, however, acetic acid does not affect significantly the spectroscopic properties of the Fe\textsuperscript{III}-OOH species formed. Finally we show that the formation and loss of the Fe\textsuperscript{III}-OOH species is not significantly affected by the presence of alkenes, indicating that it is a resting state in the catalytic cycle. A summary of the processes studied is shown in Scheme 1.

\textbf{Scheme 1} Aquation of complex \textbf{1} and subsequent oxidation by H\textsubscript{2}O\textsubscript{2} yields Fe\textsuperscript{III}-OH, which undergoes ligand exchange to form an Fe\textsuperscript{III}-OOH species in competition with a thermodynamically stable Fe\textsuperscript{III}-O-Fe\textsuperscript{III} complexes.

\textbf{2.2 Results}

The synthesis and X-ray structural characterization of [(MeN3Py)Fe\textsuperscript{II}(CH\textsubscript{3}CN)\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} (\textbf{1}) was reported earlier.\textsuperscript{14} The Raman spectra of \textbf{1} in the solid state and in acetonitrile (Figure 2) indicate that the molecular structure of \textbf{1} in the solid state is retained in solution. The \textsuperscript{1}H NMR spectrum of \textbf{1} in CD\textsubscript{3}CN shows signals in the range 0 - 15 ppm as expected for a low spin iron(II) complex, with increased broadening and shift to lower
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fields when compared with the spectra of related low spin N4 iron(II) complexes, such as \([\text{TPA}]\text{Fe}^{II}(\text{CH}_3\text{CN})_2]\text{(ClO}_4\text{)}_2\)\(^{20}\). The broadening is ascribed to slow exchange, on the NMR time scale, between the CH\(_3\)CN ligands with adventitious H\(_2\)O to form the high spin complex \([\text{(MeN}_3\text{Py})\text{Fe}^{II}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]^{2+}\). The rate of exchange was increased by addition of D\(_2\)O (1 M), which resulted in further broadening of the signals and shifting to lower field (20 - 120 ppm)\(^{21}\). These data indicate that the reversible exchange of acetonitrile ligands for D\(_2\)O is rapid on the \(^1\)H NMR timescale, however, the equilibrium lies towards the acetonitrile bound complex, as confirmed by UV-vis absorption spectroscopy and cyclic voltammetry.

![Raman spectra](image)

**Figure 2** Raman spectra of 1 in solid (red) and in CH\(_3\)CN (black). Spectra were recorded at \(\lambda_{\text{exc}} 785\) nm. * Artifact from solvent subtraction.

1 shows two electronic absorption bands in the visible region (359 and 429 nm), which are assigned to metal to ligand charge transfer (MLCT) transitions (vide infra), and a pyridyl centered \(\pi\rightarrow\pi^*\) transition between 200 and 300 nm (by comparison with the absorption spectrum of the unbound ligand)\(^{22}\).

![UV-vis absorption spectra](image)
![Cyclic voltammetry](image)

**Figure 3** (left) UV-vis absorption spectra of 1 (0.25 mM) in water (blue line), in acetonitrile (black line), and in acetonitrile with increasing amounts of water (0.5 M to 8.25 M, (red lines) and 13.75 M, (green line)). Spectra are corrected for dilution. # instrumental artifact. (right) Cyclic voltammetry of 1 (0.25 mM) in acetonitrile (0.1 M TBAPF\(_6\)) with H\(_2\)O; 0.00 M (black), 1.25 M (red), 2.5 M (green) and 3.75 M (blue).
A blue shift and broadening of the visible absorption bands as well as a substantial decrease in molar absorptivity (ca. 70%) is observed in water compared to acetonitrile (Figure 3). There is a substantial decrease in the visible \(^1\)MLCT absorption bands only upon addition of > 1 M H\(_2\)O (Figure 3). Addition of H\(_2\)O (13.75 M) results in a blue shift in the pyridyl centered π→π* transitions and a broadening and decrease in the visible absorption bands, resulting in a spectrum (Figure 3, green line) similar to that observed in water alone (Figure 3, blue line). The two spectra are not exactly the same but it should be noted that the absorption spectrum of complexes such as 1 show a pronounced pH dependence\(^{22}\) and hence it can be concluded that with >8 M H\(_2\)O both acetonitrile ligands are exchanged with H\(_2\)O. Indeed, addition of acetonitrile (2 - 25 vol%) to an aqueous solution of 1, did not affect the UV-vis absorption spectrum obtained in water.\(^{14,21,22}\) The \(^1\)H NMR spectrum of 1 in acetonitrile is affected to a greater extent by the addition of water than the UV-vis absorption spectrum indicating that the exchange of acetonitrile and aqua ligands is rapid. The effect of water on both the UV-vis absorption and \(^1\)H NMR spectra are consistent with exchange of the acetonitrile ligands with water to form high spin Fe(II) complexes (i.e. where one and then both of the acetonitrile ligands are exchanged).\(^{23}\) The ligand field strength of the aqua ligands is much less than that of acetonitrile and hence the concomitant switch to a high spin (presumably quintet) state results in a decrease in molar absorptivity of the MLCT bands (\(^1\)MLCT vs \(^3\)MLCT).

1 undergoes reversible oxidation (Fe\(^{III}\)/Fe\(^{II}\)(CH\(_3\)CN)\(_2\) redox couple) at 1.14 V vs. SCE. Addition of water (1.25 M) renders the oxidation chemically irreversible (due to rapid ligand exchange (CH\(_3\)CN/H\(_2\)O) in the Fe\(^{III}\) state) and shifts the peak potential (E\(_{p,a}\)) to 1.0 V vs. SCE (due to electrostatic stabilization).\(^{22,24}\) On the return cycle towards negative potentials a new reversible redox wave is observed at 0.65 V vs. SCE, assigned, tentatively, to the Fe\(^{III}\)/Fe\(^{II}\)(OH\(_2\))(CH\(_3\)CN) redox couple, in addition to reduction waves at 0.35 and 0.15 V vs. SCE (Figure 3 right) assigned to fully aquated species and \(\mu\)-oxido bridged dinuclear complex (vide infra). Further addition of water (up to 3.75 M) resulted in a complete loss of the redox wave at 1.0 V and the appearance of a new redox wave at E\(_{p,a}\) 0.4 V due to the formation of the aquated complexes LFe\(^{III}\)(CH\(_3\)CN)(H\(_2\)O) and eventually LFe\(^{III}\)(H\(_2\)O)\(_2\), and on the reverse scan only the reduction at 0.3 V is observed indicating rapid ligand exchange and deprotonation of the aqua ligands in the more acidic iron(III) state, with respect to the electrochemical timescale (Figure 3, right).

In water (pH 6.5), 1 shows a reversible redox wave at ca. 0.40 V vs. SCE ascribed to an Fe\(^{III}\)/Fe\(^{II}\)(OH\(_2\)) redox couple and a reduction wave at 0.28 V vs. SCE.\(^{22}\) Addition of acetonitrile (to 1.25 M) results in only a minor decrease (15%) in peak current of Fe\(^{III}\)/Fe\(^{II}\)(OH\(_2\)) redox wave. Consistent with the UV-vis absorption spectral data,\(^{21}\) the redox wave at ca. 1.0 V did not appear upon addition of acetonitrile.

Resonance Raman spectra of 1 in acetonitrile were recorded at \(\lambda_{\text{exc}}\) 355 and 457 nm (i.e. in resonance with the absorption bands at 359 and 429 nm, Figures S5 and S6, respectively). The bands at 1613, 1571, 1555, 1296, 1282, 1157, and 656 cm\(^{-1}\) are assigned to pyridyl based vibrational modes in comparison with the Raman spectrum of [Fe(bpy)]\(_3\)^{2+} (1608, 1565, 1492, 1322, 1278, 1175, 1026 cm\(^{-1}\))\(^{25}\) and are consistent with assignment of both absorption bands as \(^3\)MLCT bands. The modes at 1297, 1223, 1201 cm\(^{-1}\) are assigned to the modes of the alkyl amine backbone of the ligands by
comparison with [(N4Py)Fe\(^{II}\)(CH\(_3\)CN)]\(^{2+}\). Addition of water (1.25 M) results in a decrease in the intensity of the Raman bands of the complex (Figures S5 and Figure 4), which is consistent with the decrease in absorption observed at both wavelengths (Figure 3).

![Raman spectra](image)

**Figure 4** Resonance Raman spectra of 1 in acetonitrile (0.25 mM, black) and with water (1.25 M, red). Spectra were recorded at \(\lambda_{\text{exc}}\) 457 nm. * artefact due to imperfect solvent subtraction.

### 2.2.1 Reaction of 1 with H\(_2\)O\(_2\) in acetonitrile

Addition of 1 equiv. of H\(_2\)O\(_2\) to 1 in acetonitrile resulted in only a 10% decrease in absorbance at 429 nm and 359 nm (over 200 s) and a concomitant increase in absorbance at 310 nm. No change in absorbance was observed at longer wavelengths (Figure 5a). In contrast, addition of 1 equiv. of H\(_2\)O\(_2\) to 1 in acetonitrile with water (1.25 M), results in a faster (ca. 10 fold) and greater extent of decrease in absorbance (by ca. 80%) in the visible region with a concomitant increase in absorbance at 310 nm with maintenance of an isosbestic point at 340 nm (Figure 5b).

![Absorption spectra](image)

**Figure 5** UV-vis absorption spectra of 1 (0.25 mM, black line) in acetonitrile (a) (4, 25, 50, 100, 150, and 200 s) after addition of 1 equiv. of H\(_2\)O\(_2\) and (b) after addition of H\(_2\)O (1.25 M, red line) followed by 1 equiv. of H\(_2\)O\(_2\) (2, 25, 50, 100, 150, and 200 s).
Addition of 1 equiv. of H$_2$O$_2$ had relatively little effect on the Fe$^{II}$/Fe$^{II}$(CH$_3$CN) redox couple (Figure 6a), with only a minor decrease in $I_{p,a}$ (corresponding to the decrease observed in visible absorption). Addition of 10 equiv. of H$_2$O$_2$ results in a 50% decrease in $I_{p,a}$, however, new redox waves were not observed and the reversibility of the Fe$^{III}$/Fe$^{II}$(CH$_3$CN) redox couple was maintained (Figure 6). Addition of water (0.5 M) renders the Fe$^{III}$/Fe$^{II}$(CH$_3$CN) redox couple of 1 irreversible, although $I_{p,a}$ remains relatively unchanged, and $E_{p,a}$ shifts to a slightly less positive potential (vide supra). In addition, on the return cycle, new reduction waves at 0.63, 0.36 and 0.14 V vs. SCE are observed, which are consistent with exchange of CH$_3$CN for H$_2$O being favored in the Fe$^{III}$ oxidation state. Subsequent addition of 1 equiv. of H$_2$O$_2$ resulted in a ca. 60% decrease in the $I_{p,a}$ of the Fe$^{III}$/Fe$^{II}$(CH$_3$CN) redox couple (Figure 6b) in agreement with changes observed by UV-vis spectroscopy (Figure 5b). Notably, the additional redox waves at lower potential disappeared upon addition of H$_2$O$_2$ also; replaced by a reduction wave at 0.2 V (vide infra).

**Figure 6** Cyclic voltammetry of 1 in acetonitrile (0.5 mM, 0.1 M TBAPF$_6$) (a) before (black) and after addition of 1 equiv. H$_2$O$_2$ (red), and (b) before (black) and after addition of H$_2$O (0.5 M, red) and subsequent addition of 1 equiv. H$_2$O$_2$ (blue).

**Figure 7** UV/vis absorption at 278 K of 1 (0.25 mM) (a) in acetonitrile and (b) in acetonitrile with water (1.25 M, black) before (black) and 4 s (red) and 100 s (blue) after addition of 1 equiv. of H$_2$O$_2$.

At 278 K the addition of 1 equiv. of H$_2$O$_2$ does not affect the absorption spectrum of 1 and prior addition of excess water (1.25 M) results in only a 20% decrease in visible absorbance (Figure 7). At higher concentration (0.5 mM with 1 equiv. of H$_2$O$_2$) a minor decrease in absorbance at 429 nm was observed. However, in contrast to that observed
at 293 K, a concomitant increase (followed by a slower decrease) in absorbance at $\lambda_{\text{max}}$ 551 nm\textsuperscript{26} (to Abs 0.012) is observed at 278 K over 100 s (Figure 8a). In contrast, as at 293 K, with a large excess of water present (5.5 M), addition of 1 equiv. of H$_2$O$_2$ at 278 K to 1 (0.5 mM) results in a rapid and complete loss in absorbance is observed at a 429 nm and no increase in absorbance is observed at 551 nm (Figure 8b). The sensitivity of the system to the concentration of water is remarkable and emphasizes the delicate balance between the rates of the various processes which occur upon addition of H$_2$O$_2$ to

![Figure 8](image.png)

**Figure 8** UV-vis absorption at 278 K of 1 (0.5 mM) (a) in acetonitrile and (b) in acetonitrile with water (5.5 M, black) before (black) and 2 s (red) and 100 s (blue) after addition of 1 equiv. of H$_2$O$_2$.

Hence, although addition of several hundred equiv. of water does not result in significant aquation of 1, the rate of CH$_3$CN/H$_2$O ligand exchange is sufficiently rapid to allow for oxidation to the iron(III) state by H$_2$O$_2$ to proceed at a relatively fast overall rate. Notably, the observation of an absorption (at 278 K) at 551 nm indicates the formation of a reactive intermediate.

### 2.2.2 Reaction of 1 with excess H$_2$O$_2$

Addition of 25 equiv. of H$_2$O$_2$ to 1 (0.25 mM) in acetonitrile at 293 K results in a more rapid decrease in the visible absorption than observed with 1 equiv. of H$_2$O$_2$. Furthermore, the transient absorption at 551 nm is observed at 293 K, and reaches a maximum (Abs 0.09) within 25 s and subsequently decreases over 300 s, with a concomitant increase in absorbance at 310 nm (Figure 9a and b, with 100 equiv. a maximum of 0.15 is reached within 10 s).\textsuperscript{27}

Addition of 100 equiv. of H$_2$O$_2$ to 1 in acetonitrile at 278 K, resulted in similar changes but with a decrease in the rate of the reaction and an increase in the maximum absorbance (0.14) at 551 nm reached (Figure 9c and d). Again the absorbance at 551 nm decreased (< 300 s) concomitant with an increase in absorbance at 310 nm. Further additions of H$_2$O$_2$ resulted in an increase, although much less than initially, in absorbance at 551 nm (vide infra, Figure 14). In all cases, although complete conversion of 1 to an iron(III) oxidation state was not reached, all of the H$_2$O$_2$ had been consumed by the end of the reaction (vide infra). Changes to the Raman spectra ($\lambda_{\text{exc}}$ 355nm) are consistent with UV-vis absorption spectroscopic data.\textsuperscript{21}
Mechanism of Fe(II)MeN3Py complex in acetonitrile

Figure 9 UV-vis absorption of 1 (0.25 mM) in acetonitrile at 293 K (a) upon addition of 25 equiv. of H$_2$O$_2$ ((b) corresponding time dependence of absorbance at 310 nm (blue), 429 nm (black), and 561 nm (red)), and (c) upon addition of 100 equiv of H$_2$O$_2$ ((d) corresponding time dependence of absorbance at 310 nm (blue), 429 nm (black), and 561 nm (red)).

In contrast addition of 25 or 100 equiv. of H$_2$O$_2$ to 1 in acetonitrile with water (1.25 M) present led to the rapid decrease in visible absorbance with a direct concomitant increase in absorbance at ca. 310 nm and without a significant increase in absorbance at 551 nm (Figure 10).

Figure 10 UV-vis absorption of 1 (0.25 mM) in acetonitrile (black line) and after addition of water (red line, 1.25 M) at 293 K followed by addition of 25 equiv. of H$_2$O$_2$ (after 2 s (blue), 5 s (orange), 25 s (cyan), and 175 s (grey)) and (b) corresponding time dependence of absorbance at 310 nm (blue), 429 nm (black) and 561 nm (red).
2.2.3 Effect of alkenes on the formation and disappearance of Fe$^{III}$-OOH

The oxidation of alkenes by 1 with H$_2$O$_2$ was reported earlier. The addition of cyclooctene (0.875 M) to 1 (0.875 mM) has no effect on the latter’s absorption spectrum and only a minor effect on the changes to the absorption spectrum of 1 that occur upon addition of H$_2$O$_2$. Under the conditions used in the catalyzed oxidation of alkenes, i.e. periodic addition of H$_2$O$_2$ (100 equiv. w.r.t. 1 in total) over one hour, the incremental loss of absorbance of 1 and the repeated appearance and subsequent disappearance of the Fe(III)-OOH species is observed (Figure 11), together with the formation of the epoxide and cis-diol products (Figure 12).

**Figure 11** Time dependence of the absorbance at 429 and 561 nm following batch wise addition (ca. 7 equiv. each) of a total of 100 equiv. of H$_2$O$_2$ to 1 (0.875 mM) in acetonitrile (left) without and (right) with cyclooctene (0.875 M).

**Figure 12** $^1$H NMR spectra of the product mixtures of oxidation of cyclooctene to epoxide and diol products by 1 with H$_2$O$_2$. (a) Cyclooctene oxide (12.3 equiv., 4.7 mg) and cis-1,2-cyclooctane diol (22 equiv., 8.3 mg) were added to 3 ml of CD$_3$CN with cyclooctene (0.875 M, 1000 equiv.) followed by 14 μl of H$_2$O was added. An aliquot of the mixture was passed over anhydrous MgSO$_4$ and its $^1$H NMR spectrum was recorded (note that the spectra before and after passing over MgSO$_4$ was the same). (b) Cyclooctene (0.875 M, 1000 equiv.) was added to 1 (0.875 mM, 1 equiv.) in CD$_3$CN followed by addition of 50 eq. H$_2$O$_2$ over 1 h with stirring and monitoring by UV/Vis absorption spectroscopy. After 1 h, an aliquot of the solution was passed over anhydrous MgSO$_4$ and its $^1$H NMR was recorded.
Notably the loss of absorbance at 429 nm (i.e. of 1) occurs concomitant with the increase in the absorption band at 551 nm, while the recovery of absorbance at 429 nm occurs concomitant with the decrease in absorption band at 551 nm. This latter increase in absorption at 429 nm is ascribed to formation of Fe$^{III}$-OH and Fe$^{III}$-O-Fe$^{III}$ species and not recovery of 1. Notably, although initially the rate of decrease in the absorbance due to the Fe$^{III}$-OOH species is marginally faster in the presence of cyclooctene, after several additions of H$_2$O$_2$, the differences in the rates of all processes are marginal and hence it can be concluded that the Fe$^{III}$-OOH does not react with the alkene itself but instead decomposes to a secondary species, e.g., an Fe$^{IV}$=O species, spontaneously.

### 2.2.4 Resonance Raman, EPR and $^1$H NMR spectroscopy of 1 with H$_2$O$_2$

The intermediate species formed, which absorbs at 551 nm, was studied by Raman spectroscopy at $\lambda_{\text{exc}}$ 532 nm.$^{29}$ The Raman spectrum recorded upon addition of 100 equiv. H$_2$O$_2$ to 1 in acetonitrile shows bands at 801, 643 and 623 cm$^{-1}$ (Figure 13 left).$^{30}$ The band at 801 cm$^{-1}$ was assigned, tentatively, to an O-O stretch and the band at 623 cm$^{-1}$ to the Fe-O stretch of a [(Me-N$_3$Py)Fe$^{III}$(X)(OOH)]$^{2+}$ species (where X = solvent), by comparison with related complexes such as [(TPA)Fe$^{III}$(OOH)]$^{2+}$ and [(N4Py)Fe$^{III}$(OOH)]$^{2+}$. The band at 643 cm$^{-1}$ is assigned tentatively to a Fe-N stretch by analogy with the Raman spectra of related Fe$^{III}$-OCl species.$^{34}$ The Raman band at 869 cm$^{-1}$ ($v_\text{(O-O)}$ of H$_2$O$_2$) decreases concomitantly albeit slightly faster than the bands at 801 cm$^{-1}$ and 623 cm$^{-1}$. Addition of further equivalents of H$_2$O$_2$ do not lead to the reappearance of the bands at 623, 643 and 801 cm$^{-1}$ but the consumption of H$_2$O$_2$ is manifest in the decrease in the Raman band ($v_\text{(O-O)}$ of H$_2$O$_2$) at 869 cm$^{-1}$ (Figure 14, left).

As observed by UV-vis absorbance spectroscopy (vide supra), in the presence of water, the Fe$^{III}$-OOH species is not observed, however, the consumption of H$_2$O$_2$ over several additions is observed by Raman spectroscopy (Figure 13, right).

**Figure 13** Resonance Raman spectra at $\lambda_{\text{exc}}$ 532 nm of (left) (a) 1 in acetonitrile (1 mM), and (b) 5 s, (c) 14 s, (d) 87 s and (e) 140 s after addition of 100 equiv. of H$_2$O$_2$. (right) (a) 1 (1 mM) in acetonitrile with 0.55 M water, (b) 5 s, (c) 26 s and (d) 64 s after addition of 100 equiv. of H$_2$O$_2$, and (e) $2^{\text{nd}}$ addition of 100 equiv. of H$_2$O$_2$ at 223 s, and (f) 315 s. *Spectra are normalized to solvent band at 750 cm$^{-1}$.  

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Figure 14 (left) Resonance Raman spectra at \( \lambda_{\text{exc}} \) 532 nm of (a) 1 in acetonitrile (1 mM), (b) 5 s and (c) 133 s after addition of 100 equiv. of \( \text{H}_2\text{O}_2 \), (d) 2\textsuperscript{nd} addition of 100 equiv. of \( \text{H}_2\text{O}_2 \) at 167 s, and after (e) 508 s, (f) 3\textsuperscript{rd} addition of 100 equiv. of \( \text{H}_2\text{O}_2 \) 533s, and (g) 972 s.* Spectra are normalized to solvent band at 750 cm\(^{-1}\). (right) UV-vis absorption spectrum of 1 (1 mM) in acetonitrile (black) upon addition of first (red), second (green), and third (blue) 100 equiv. of \( \text{H}_2\text{O}_2 \), and after 30 min (cyan) with corresponding time dependence of absorbance at 429 nm (black) and 561 nm (red).

The X-band EPR spectrum (at 77 K) of 1 in acetonitrile after addition of 1 equiv. of \( \text{H}_2\text{O}_2 \) in the absence and presence of water showed only a weak signal at \( g = 4.3 \), characteristic for high spin iron(III) species. In contrast, the EPR spectrum obtained upon flash freezing (at 77 K) of 1 in acetonitrile with 100 equiv. \( \text{H}_2\text{O}_2 \) upon reaching a maximum absorbance at 551 nm (Figure 14), shows relatively strong signals at \( g = 2.24, 2.16, 1.96 \) (Figure 15) assigned\(^{16,35}\) to a \([\text{MeN3PyFe}^{\text{III}}(X)(\text{OOH})]^2+\) species (where \( X = \text{solvent} \)), which are close to those of bleomycin Fe\(^{\text{III}}\)-OOH (\( g = 1.95, 2.17 \) and 2.26).\(^{36}\) Over time (60 s at 293 K) the signals at \( g = 2.24, 2.16 \) and 1.96, together with a weaker signal at ca. \( g \approx 4 \) (vide infra), disappeared with only a weak signal \( g = 4.3 \) remaining. When water (1.25 M) was added prior to addition of 100 equiv. of \( \text{H}_2\text{O}_2 \), only the weak signal at \( g = 4.3 \) was observed at any time.

Figure 15 X band EPR spectra at 77 K of 1 in acetonitrile (1 mM) (a) before, and (b) 15 s, (c) 40 s, (d) 120 s, and (e) 240 s after addition of 100 equiv. \( \text{H}_2\text{O}_2 \).
Addition of 10 equiv. H$_2$O$_2$ to 1 in CD$_3$CN with H$_2$O (1 M) results in a shift of signals in the $^1$H NMR spectrum up-field which are consistent with the formation of an antiferromagnetically coupled dimer (Figure 16), by comparison with the spectra of analogous dimers. 11a,18,19

**Figure 16** $^1$H NMR (400 MHz) spectra of 1 (a) 1 mM, and (b) spectra 10 mM in CD$_3$CN after addition of water (1 M, blue), and further subsequent addition of 18 and 25 equiv. H$_2$O$_2$ (brown), respectively.

### 2.2.5 UV-vis absorption spectroelectrochemistry

The electrochemical oxidation and subsequent reduction of 1 under thin layer conditions enables simultaneous recording of UV-vis absorption spectroscopy during cyclic voltammetry and the trapping of oxidation products at the electrode (Figure 17). 1 undergoes oxidation at 1.14 V in acetonitrile (vide supra), which is manifested in a decrease in the absorption bands at 359 nm and 429 nm and a minor increase in absorption at 310 nm (Figure 17).

**Figure 17** (a) UV-vis absorption spectra of 1 (1 mM) in acetonitrile before (black) and after electrochemical oxidation at >1.2 V (blue) and after subsequent reduction at 1.10 V (red). The spectrum obtained with 1 (1 mM) in acetonitrile with water (0.36 M) at > 1.2 V is shown in green; the initial spectrum and spectrum recorded at 0.1 V were equivalent to the black and blue spectra, respectively. (b) Corresponding thin layer cyclic voltammograms {(i) – in CH$_3$CN and (ii) – in CH$_3$CN with 0.36 M H$_2$O (offset by 30 µA for clarity)}; with points at which spectra were recorded indicated by arrows, 0.1 M TBAPF$_6$, at 100 mV s$^{-1}$. 41
The changes were largely reversed upon reduction at ca. 1.1 V, although a full recovery of initial spectrum was observed only at 0.2 V, which together with the absence of isosbestic points and the difference in $I_{p,a}$ and $I_{p,c}$ indicate partial chemical irreversibility, i.e. partial ligand exchange with adventitious water present in the electrolyte. Addition of water (0.36 M) to 1 (1 mM) in acetonitrile resulted in a minor decrease in visible absorbance (vide supra). Oxidation at 1.17 V was, in this case, completely irreversible, with a complete loss of absorbance at 429 nm and a concomitant increase in absorbance at 310 nm. Notably, reduction and recovery of the original spectrum was only observed at < 0.26 V under thin layer conditions (Figure 17), however, a clear isosbestic point was maintained at 343 nm once reduction commenced. These data indicate that the irreversibility is due to exchange of solvent (i.e. H$_2$O vs CH$_3$CN ligands) in the iron(III) oxidation state and confirm that this exchange is rapid. Furthermore, it is apparent that although the presence of water has relatively little effect on 1 in the iron(II) state, in the iron(III) state its presence results in rapid ligand exchange and the formation of a stable dinuclear Fe$^{III}$-(μ-O)-Fe$^{III}$ complex, which is reduced only at 0.2 V.

In summary, it is evident that in the absence of water a mixture of [[(MeN3Py)Fe$^{III}$](CH$_3$CN)$_2$]$^{3+}$, [[(MeN3Py)Fe$^{III}$](CH$_3$CN)(OH)]$^{2+}$ and [(MeN3Py)Fe$^{III}$](OH)$_2$]$^{+}$ are formed upon oxidation of 1 in acetonitrile, which show absorbance in the visible region. In the presence of water, rapid formation of an Fe$^{III}$-(μ-O)-Fe$^{III}$ species occurs with characteristic absorption bands at 310 and 360 nm and reduction at ca. 0.2 V vs. SCE.

### 2.2.6 Effect of acetic acid on the formation and decay of [[(MeN3Py)Fe$^{III}$](X)(OOH)]$^{2+}$

Addition of acetic acid (0.1 M) to 1 in acetonitrile does not affect its absorption spectrum or the extent of formation of the Fe$^{III}$-OOH species upon addition of 100 equiv. of H$_2$O$_2$ (Figure 18a). However, acetic acid does affect the rate of formation and subsequent disappearance of the Fe$^{III}$-OOH species. Full conversion of 1 occurred within several seconds of addition of H$_2$O$_2$ with an increase in absorbance at 551 nm (i.e. Fe$^{III}$-OOH) (Figure 18b). This absorption band decreased subsequently and more rapidly than without acetic acid and concomitant with an increase in absorbance at 310 nm.

![Figure 18](image-url) (a) UV-vis absorption of 1 (0.25 mM) in acetonitrile (black) and with acetic acid (100 equiv., red), immediately after addition of 100 equiv. of H$_2$O$_2$ (blue), after 200 s (green) and after 1527 s (pink). (b) Time dependence of the absorbance at 331 (blue), 429 (black), and 561 nm (red).
Notably, additional absorption bands that are characteristic of a \([\{LFe^{III}\}_2(\mu-O)(\mu-CH_3CO_2)\}]^{3+}\) complex were observed between 400 and 550 nm.\(^{35,40}\) The formation of this latter species is apparent even prior to reaching a maximum in absorbance at 551 nm. Furthermore, closer inspection of the time dependence of the absorbance at 429 nm shows the appearance and disappearance of an additional intermediate also, assigned tentatively as \([\{MeN3Py\}Fe^{III}(OH)(OH_2)\}]^{2+}\).

The presence of acetic acid (0.1 M) has no effect on the resonance Raman spectrum at \(\lambda_{exc} 532\) nm of the Fe\(^{III}\)-OOH species formed immediately upon reaction of \(\mathbf{1}\) with \(H_2O_2\), i.e. the resonantly enhanced bands are observed at 801, 643 and 622 cm\(^{-1}\) (Figure 19, left). In contrast to that observed in the absence of acetic acid, however, the Raman band at 869 cm\(^{-1}\) (\(v_{O-O}\) of \(H_2O_2\)) persists for a considerable time after the disappearance of the bands at 801, 643 and 622 cm\(^{-1}\). Similarly, X-band EPR spectroscopy shows the appearance and disappearance of signals characteristic of a low spin Fe\(^{III}\)-OOH species (\(g = 2.19, 2.14, 1.96\)) concomitant with the absorption band at 551 nm. In addition a weaker signal (\(g = 8.36, 5.52, 4.32\)) characteristic of a high spin iron(III) complex is present and persists over the entire period with a maximum in intensity reached concomitant with the disappearance of the 551 nm absorption. It should be noted that, although much weaker, these signals are also discernable in the EPR spectra obtained without acetic acid (Figure 15). The appearance and disappearance of this latter EPR signal tracks the increase and decrease in absorbance at ca. 429 nm.

**Figure 19** (left) Resonance Raman spectra at \(\lambda_{exc} 532\) nm (a) before, (b) 25 s, (c) 40 s, (d) 65 s, and (e) 265 s after addition of 100 equiv. of \(H_2O_2\) and (right) X-band EPR spectra (at 77 K) of flash frozen samples obtained (a) 20, (b) 44, and (c) 202 s after addition of 100 equiv. of \(H_2O_2\) to \(\mathbf{1}\) (1 mM) in acetonitrile with 0.1 M acetic acid. *Raman spectra are normalized to the solvent band at 750 cm\(^{-1}\).

### 2.3 Discussion

The role of ligand exchange on the rate of formation of Fe\(^{III}\)-OOH species was studied through a combination of UV-vis absorption, resonance Raman, \(^1\)H NMR, and EPR spectroscopy and electrochemistry. It is evident that although the formation of Fe\(^{III}\)-OOH species requires the presence of water to enable oxidation of \(\mathbf{1}\) to its iron(III) state, the
stability of these species and the rate of formation of Fe\(^{III}\)-O-Fe\(^{III}\) dimers (a thermodynamic sink) is also dependent on the concentration of water. The sensitivity of the system to even minor changes in water content is perhaps to be expected considering the highly non-linear dependence of the activity of water on concentration.\(^{41}\)

In acetonitrile, \(1\) shows two absorption bands in the visible region assigned to \(^3\)MLCT transitions. Addition of excess of water results in a decrease in absorbance and a hypsochromic shift in the visible absorption bands, ultimately leading to a spectrum that is similar to that observed in water. In contrast to N5-ligand based complexes such as \([\text{N4Py}]\text{Fe}^{II}\text{(CH}_3\text{CN})\text{]}^{2+}\), for which addition of even 1 vol% acetonitrile to an aqueous solution results in a full recovery of the absorption spectrum seen in acetonitrile, in the case of \(1\) in water addition of up to 25 vol% has little effect on the spectrum.\(^{22}\) This difference indicates that the barrier to exchange of both of the \(\text{CH}_3\text{CN}\) ligands of \(1\) to form \([\text{MeN3Py}]\text{Fe}^{II}\text{(OH}_2\text{)}\text{(CH}_3\text{CN})\text{]}^{2+}\) and \([\text{MeN3Py}]\text{Fe}^{II}\text{(OH}_2\text{)}_2\text{]}^{2+}\) is low compared with the corresponding N5-ligand based complexes (Scheme 2). The exchange of the \(\text{CH}_3\text{CN}\) ligands for \(\text{H}_2\text{O}\) in \(1\) results in both a decrease in oxidation potential and allows for ligand exchange with \(\text{H}_2\text{O}_2\), both of which facilitate the initial oxidation from the iron(II) to the iron(III) state (vide infra).

**Scheme 2** Redox state dependent ligand exchange of \(\text{CH}_3\text{CN}\) ligands of \(1\) with water. [It should be noted that the assignment of the ligands as aqua or hydroxido is arbitrary and is not confirmed in the present case.]

Upon electrochemical oxidation of \(1\), to the iron(III) state, exchange of the \(\text{CH}_3\text{CN}\) ligands with water becomes energetically highly favorable. Importantly, however, in the presence of excess water, oxidation and ligand exchange is followed rapidly by the formation of oxido bridged dimers, which are reduced to the iron(II) state only at low potentials. Indeed the effect of water in facilitating the formation of oxido bridged iron(III) dimers is manifested clearly in the differences observed by spectroelectrochemistry in the absence and presence of water. The effect of water on the spectroelectrochemical behavior is essentially the same as observed upon chemical oxidation with \(\text{H}_2\text{O}_2\).
Addition of 1 equiv. of H$_2$O$_2$ to 1 in CH$_3$CN results in only ca. 10% conversion to the iron(III) oxidation state. In contrast, with > 0.1 M water, almost complete conversion of 1 to an EPR silent complex is observed. Although with ca. 0.1 M H$_2$O only partial (i.e. < 10-15%) conversion of 1 to [(MeN3Py)Fe$^{II}$(OH)$_2$(CH$_3$CN)]$^{2+}$ is observed, $^1$H NMR spectroscopy and cyclic voltammetry confirm that the rate of exchange of the CH$_3$CN ligands with water is high. Hence it is reasonable to conclude that formation of [(MeN3Py)Fe$^{II}$(CH$_3$CN)(OOH)]$^+$ or [(MeN3Py)Fe$^{II}$(OH)$_2$(OOH)]$^+$ can occur also followed by rapid heterolytic cleavage of the iron(II)-peroxy O-O bond to form [(MeN3Py)Fe$^{IV}$(OH)$_2$(O)]$^{2+}$ and subsequent reaction with [(MeN3Py)Fe$^{II}$(OH)$_2$(CH$_3$CN)]$^{2+}$ to form two equiv. of [(MeN3Py)Fe$^{III}$(OH)$_2$(OH)]$^{2+}$. This latter complex either undergoes further reaction with H$_2$O$_2$ or undergoes dimerization to form EPR silent (at 77 K) complexes, e.g., [(MeN3Py)Fe$^{III}$(OH)$_2$]$_2$(O)$^{4+}$ (Scheme 3). Notably, however, in the absence of water, the Fe(III) complexes formed react more rapidly with H$_2$O$_2$ (to decompose it) than does 1. This difference in reactivity, together with the instability of both the iron(II) and iron(III) peroxy species and Fe(IV) oxido species formed, results in only the initial complex 1 and the final Fe$^{III}$-O-Fe$^{III}$ dimer being observed at significant concentrations.

**Scheme 3** Reaction of H$_2$O$_2$ with 1 in acetonitrile in the presence and absence of water.

It should be noted that addition of excess H$_2$O$_2$ (25-100 equiv.), results in the simultaneous addition of a similar excess of H$_2$O (45-180 equiv.). In this case the oxidation of 1 to the iron(III) state is rapid, aided by ligand exchange (CH$_3$CN with H$_2$O) in
and is accompanied by the appearance of a visible absorption band that is characteristic of an \( \text{Fe}^{\text{III}}\cdot\text{OOH} \) species, which was confirmed by both resonance Raman and EPR spectroscopy. The decay of \( \text{Fe}^{\text{III}}\cdot\text{OOH} \) species formed is accelerated by the presence of water and with > 0.1 M \( \text{H}_2\text{O} \), the steady state concentration of the \( \text{Fe}^{\text{III}}\cdot\text{OOH} \) species is too low to be observed despite both the rapid oxidation of \( \text{I} \) and the consumption of the excess \( \text{H}_2\text{O}_2 \). Indeed the UV-vis absorption and \(^1\text{H}\) NMR spectra after oxidation (either electrochemical or with \( \text{H}_2\text{O}_2 \)) together with the absence of a significant EPR signal indicates that essentially complete conversion to an \( \text{Fe}^{\text{II}}\cdot\text{O}^\cdot\text{Fe}^{\text{III}} \) dimer occurs. ESI-MS data\(^{21}\) indicates the formation of various dinuclear \( \text{Fe}^{\text{III}} \) complexes, albeit a definitive correlation between MS data and data obtained by other techniques is hampered by the conditions of the ESI-MS measurements. Notably, the addition of acetic acid,\(^{42}\) although not reacting directly with \( \text{I} \), allows full oxidation to the iron(III) state with fewer equivalents of \( \text{H}_2\text{O}_2 \), by suppressing the decomposition of \( \text{H}_2\text{O}_2 \).

Furthermore, although acetato bridged \( \text{Fe}^{\text{III}}\cdot\text{O}^\cdot\text{Fe}^{\text{III}} \) dimers form in the presence of acetic acid,\(^{19}\) there is no evidence that an acetate bound \( \text{Fe}^{\text{III}}\cdot\text{OOH} \) species is formed. The effect of acetic acid in enhancing the efficiency of non-heme iron complexes in the oxidation of organic substrates has been noted frequently in earlier studies.\(^{19}\) In the present study the suppression of \( \text{H}_2\text{O}_2 \) decomposition by addition of acetic acid observed raises the possibility that in related systems that this effect contributes substantially to the enhancement in catalytic efficiency observed.

### 2.4 Conclusions

In conclusion, the electrochemical and spectroscopic analysis demonstrates that the two \( \text{CH}_3\text{CN} \) ligands of \( \text{I} \) undergo rapid ligand exchange with water, albeit with the equilibrium lying on the side of coordination of the \( \text{CH}_3\text{CN} \) ligands. Nevertheless the decrease in redox potential when \( \text{CH}_3\text{CN} \) is exchanged for water (or \( \text{H}_2\text{O}_2 \)) allows for rapid oxidation of \( \text{I} \) to the iron(III) state presumably via an \( \text{Fe}^{\text{IV}}\cdot\text{O} \) intermediate generated by heterolysis of the O-O bond in an \( \text{Fe}^{\text{II}}\cdot\text{OOH} \) species. The exchange of water with \( \text{CH}_3\text{CN} \) is the rate determining step in the reaction of \( \text{I} \) with \( \text{H}_2\text{O}_2 \) in \( \text{CH}_3\text{CN} \) and competes with the decomposition of \( \text{H}_2\text{O}_2 \) by the iron(III) complexes formed.

The formation of detectable amounts of an \( \text{Fe}^{\text{III}}\cdot\text{OOH} \) complex of an N4 ligand at room temperature depends critically on the concentration of water. As mentioned above the first role played by water is to accelerate the exchange of \( \text{CH}_3\text{CN} \) ligands with \( \text{H}_2\text{O}_2 \). If this process is too slow then the competing decomposition of \( \text{H}_2\text{O}_2 \) will preclude reaching a significant steady state concentration of the \( \text{Fe}^{\text{III}}\cdot\text{OOH} \) species. Hence water is needed to form the \( \text{Fe}^{\text{III}}\cdot\text{OOH} \) species. However, a second effect of water is to accelerate the formation of \( \text{Fe}^{\text{III}}\cdot\text{O}^\cdot\text{Fe}^{\text{III}} \) dimers, which act as thermodynamic sinks preventing a build-up of a significant concentration of the \( \text{Fe}^{\text{III}}\cdot\text{OOH} \) species. This balance between assisting and inhibiting the formation of an \( \text{Fe}^{\text{III}}\cdot\text{OOH} \) species is of importance in catalysis where addition of oxidant (i.e. \( \text{H}_2\text{O}_2 \)) is normally concomitant with addition of water. Furthermore, the lack of reactivity of the \( \text{Fe}^{\text{III}}\cdot\text{OOH} \) species with cyclohexene indicates that it is a resting state on the way to formation of the kinetically competent oxidant, presumably an iron(IV)=O species.

Finally, the effect of acetic acid on the formation and stability of the \( \text{Fe}^{\text{III}}\cdot\text{OOH} \) species is limited to the rates of the processes involved and there is no spectroscopic evidence for the formation of a distinct acetato bound peroxy species. Importantly, the presence of
acetic acid reduces the rate of decomposition of $H_2O_2$ substantially and results in the formation of acetato bridged dinuclear iron(III) complexes. It is likely that these latter effects will be important in improving the outcome of catalytic oxidations with 1 and $H_2O_2$. Future studies will focus on the formation of such species in other solvents and on the studying the effect of formation of the dinuclear complexes on the rate of substrate oxidation.

2.5 Experimental details

MeN3Py and 1 were prepared and isolated as previously reported.9,21 Commercially available chemicals were used without further purification unless stated otherwise. Solvents for electrochemical and spectroscopic measurements were UVASOL (Merck) grade or better. $H_2O_2$ was obtained from Sigma (50 wt%).

Caution. The drying or concentration of solutions that potentially contain $H_2O_2$ should be avoided. Prior to drying or concentrating, the presence of $H_2O_2$ should be tested for using peroxide test strips followed by neutralization on solid NaHSO₃ or another suitable reducing agent. When working with $H_2O_2$, suitable protective safeguards should be in place at all times due to the risk of explosion.43

$[[\text{MeN3Py}]Fe^{II}(CH_3CN)_2](\text{ClO}_4)_2$ (1). A solution of Fe(ClO₄)₂.6H₂O (170.2 mg, 0.46 mmol) in CH₃CN (1.5 ml) was added to a solution of MeN3Py (129 mg, 0.44 mmol) in methanol (1.5 ml). The dark red solution was placed in an ethyl acetate bath, and after three days dark red crystals were isolated (212 mg, 71 %) and washed with ethyl acetate (3 ml). Anal. calcd for C₂₂H₂₄Cl₂FeN₆O₈: C 42.13, H 3.86, N 13.40; Found: C 41.52, H 3.85, N 13.18.

$^1$H NMR spectra (400 and 600 MHz) were recorded on a Varian Mercury Plus. Chemical shifts are denoted relative to the residual solvent peak ($^1$H NMR spectra CD₃CN, 1.94 ppm; D₂O, 4.79 ppm). Elemental analyses were performed with a Foss-Heraeus CHN Rapid or a EuroVector Euro EA elemental analyzer. UV-vis absorption spectra were recorded with a Specord600 (AnalytikJena) in 10 mm path length quartz cuvettes. Electrochemical measurements were carried out on a model CH1760B Electrochemical Workstation (CH Instruments). Analyte concentrations were typically 0.25 - 1 mM in acetonitrile containing 0.1 M TBA PF₆. A 3 mm diameter Teflon-shrouded glassy carbon working electrode (CH Instruments), a Pt wire auxiliary electrode, and an SCE reference electrode were employed. Unless stated otherwise all potential values are quoted with respect to the SCE. Potentials are reported ± 10 mV. Spectroelectrochemistry experiments were carried out by OTTLE cell44 (a liquid IR cell modified with Infrasil windows and a platinum mesh working and counter electrode and a Ag wire reference electrode) mounted in a Specord600 UV-vis spectrometer with potential controlled by a CH1600C potentiostat. Raman spectra were recorded at $\lambda_{exc}$ 785 nm using a Perkin Elmer Raman Station at room temperature. Raman spectra at 457 nm (50 mW at source, Cobolt Lasers) and at 532 nm (300 mW at source, Cobolt Lasers) were obtained in a 135° and a 180° backscattering arrangement, respectively. Raman scattering was collected with a 2.5 cm diameter plano-convex lens (f = 7.5 cm). The collimated Raman scattering passed through an appropriate long pass edge filter (Semrock) and was focused by a second 2.5 cm diameter plano convex lens (f = 10 cm) into a Shamrock300i spectrograph
(Andor Technology) with a 1200 L/mm grating blazed at 500 nm and acquired with an
Newton DU970N-BV or a iDus-420-BUE2 CCD camera (Andor Technology). The slit width
was set to 80 μm. Raman spectra at 355 nm (10 mW at source, Cobolt Lasers) were
acquired in a 180° backscattering arrangement. Raman scattering collected by a 2.5 cm
diameter plano-convex lens (f = 7.5 cm). The collimated Raman scattering passed
through an appropriate long pass edge filter (Semrock) and was focused by a second 2.5
cm diameter plano convex lens (f = 15 cm) into a Shamrock500i spectrograph (Andor
Technology) 2399 L/mm grating blazed at 300 nm, respectively, acquired with an iDus-
420-BU2 CCD camera (Andor Technology). The spectral slit width was set to 12 μm. Data
were recorded and processed using Solis (Andor Technology) with spectral calibration
performed using the Raman spectrum of acetonitrile/toluene 50:50 (v:v).45 Samples
were held in quartz 10 mm path length cuvettes. Multi point baseline correction was
performed for all spectra. EPR spectra (X-band, 9.46 GHz) were recorded on a Bruker
ECS106 spectrometer in liquid nitrogen (77 K). Samples for measurement which were
followed from UV-vis absorption and an aliquot of 300 μl were transferred to EPR tubes
and were frozen in liquid nitrogen immediately.

Additional Raman, UV-vis absorption, spectroelectrochemical and 1H NMR data refer to
4211–4222.

2.6 References

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The spectroelectrochemical studies were carried out under thin layer conditions in which the diffusion of products away from the electrode is prevented and a relatively high concentration of Fe(III) is maintained. Nevertheless subsequent addition of H₂O₂ leads to the formation of the same Fe(III)-OOH species as observed without cyclohexene. These reactive impurities are removed by passing the alkene over alumina immediately prior to use and in this case the same results were obtained as with cyclooctene.

The availability of 18O labelled H₂O₂ only as dilute solutions in water precludes assignment of the Raman bands of the Fe(III)-OOH species by isotopic labelling.

A shift to less positive potentials is due to electrostatic stabilization of the Fe(III) state by water. These data indicate that the molar absorptivity is greater than 560 M⁻¹ cm⁻¹. Due to the thin layer conditions E электрического поля is shifted positively compared with that for the Fe(II) state and ligand exchange with water providing a high concentration from which a Fe(III)-OOH species can be obtained as with cyclooctene.

Although the maximum of this band is at 551 nm, for analysis of the time dependence of the appearance and disappearance of this band independent of absorbance of 1, 561 nm was selected as the monitoring wavelength.

The shift to less positive potentials is due to electrostatic stabilization of the Fe(III) state. Nevertheless subsequent addition of H₂O₂ leads to the formation of the same Fe(III)-OOH species as observed without cyclohexene. These reactive impurities are removed by passing the alkene over alumina immediately prior to use and in this case the same results were obtained as with cyclooctene.

A higher concentration (1 mM) was used for resonance Raman studies at 532 nm and EPR spectroscopy to increase s/n levels. UV/Vis absorptions spectra under these conditions show essentially the same Raman bands of the Fe(III)-OOH species by isotopic labelling.
solution based voltammetry, and although two reduction waves would be expected a single wave is observed as the initial reduction to the Fe(II)-O-Fe(III) species results in formation of 1 and LFe(III)-OH, with the latter species undergoing reduction and immediate conversion to 1 as the overpotential is already several -100 mV for its reduction. The Nernst equilibrium between Fe(III)-O-Fe(III) and Fe(II)-O-Fe(III) will be reestablished concomitantly and hence only the first reduction wave is observed.


41 A long standing difficulty in the use of concentration as a proxy for activity in water/acetonitrile is the highly nonlinear dependence of the activity of water on its concentration. Indeed the activity of water rises sharply as its mole fraction is increased from 0 to 0.2 to near unit activity [French, H. T. *J. Chem. Thermodyn.*, **1987**, 19, 1155-1161]. For a detailed discussion of this issue see Blandamer, M.J.; Engberts, J. B. F. N.; Gleeson, P. T.; Reis, J. C. R. *Chem. Soc. Rev.* **2005**, 34, 440-458.


43 The source of H$_2$O$_2$ used can in some circumstances have a large effect on the results obtained due to the stabilizers present; 50% H$_2$O$_2$ supplied by Sigma-Aldrich ‘Contains propriety inorganic tin-based stabilizer’, whereas the 50% H$_2$O$_2$ PA grade and 30% medicinal grade supplied by Acros are stabilized by organic chelating agents and by Na$_2$H$_3$P$_2$O$_7$, H$_3$PO$_4$ and NH$_4$NO$_3$, respectively. In the present study the source of H$_2$O$_2$ used had no noticeable effect on the data obtained, which may be due to the limited number of equivalents of H$_2$O$_2$ used with respect to 1 and hence the concentration of stabilizer present is low compared with the catalyst.
