Shedding light on active species in Fe, Ni and Cu catalysis
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Chapter 5

Photocatalytic oxidation of alkanes and alkenes with non-Heme Fe$^{IV}=O$ and Fe$^{III}$-OR complexes

The photochemistry of non-heme ($S = 1$) Fe$^{IV}=O$ and Fe$^{III}$-OR species in the solid state and in solution are explored for the first time. Enhancement of the reactivity of the complexes towards substrate oxidation was observed upon irradiation at 355 nm, which is ascribed to transient population of a $S = 2$ state.

5.1 Introduction

High valent Fe$^{IV}$=O intermediates formed upon activation of molecular oxygen by many non-heme enzymes, such as TauD, naphthalene dioxygenases, CytC3 and SyrB2, are proposed to be the active species involved in substrate oxidations.1 These intermediates are found to carry out challenging oxidation reactions, such as C-H bond activation,2 C=C bond epoxidation3 and oxygen transfer to hetero atoms.4 These Fe$^{IV}$=O intermediates are generally present in a high spin state (S = 2).5,1a,1b

In contrast to natural systems, the synthesis and isolation of analogous intermediates is difficult due to their reactivity. With notable exceptions, most of the reported Fe$^{IV}$=O intermediates are low spin (S = 1) in character.6 Generation of low spin (S = 1) non-heme Fe$^{IV}$=O species has been carried out chemically with oxidants such as MCPBA, CAN and PhIO etc. These intermediates can also be generated electrochemically in acetonitrile and in DCM with added water.7 Recently, Nam and Fukuzumi reported the photochemical generation of [(N4Py)Fe$^{IV}$(O)]$^{2+}$ from the corresponding [(N4Py)Fe$^{II}$(CH$_3$CN)]$^{2+}$ complex in the presence of [Ru(bpy)$_3$]$^{2+}$ as photosensitizer and [Co$^{III}$(NH$_3$)$_5$Cl]$^{2+}$ as terminal oxidant.8 Recent efforts to synthesize and isolate high spin Fe$^{IV}$=O species were reported by Borovic, Que and Bakac and co-workers.9 However, the reactivity of those complexes are not as pronounced as in biological systems and synthetic low spin Fe$^{IV}$=O species.10 The low reactivity of the biomimetic high spin Fe$^{IV}$=O species has been attributed to steric effects of the ligands used, which block the approach of the substrate towards the oxo moiety.10 The reactivity of low spin (S = 1) Fe$^{IV}$=O species was found to be enhanced in the presence of Sc$^{3+}$ ions11 and also by the addition of perchloric acid.4a,12 It was proposed, based on DFT calculations, that even for synthetic Fe$^{IV}$=O complexes that have a S = 1 ground state, reaction with substrates via a quintet transition state occurs albeit at low rates.10 It is therefore desirable to access the S = 2 state to increase reactivity towards organic substrates.

The photochemistry of [(N4Py)Fe$^{II}$(CH$_3$CN)]$^{2+}$ (4) and its analogous complex [(MeN4Py)Fe$^{II}$(CH$_3$CN)]$^{2+}$ (3) in a range of solvents is reported in chapter 3. Photo induced oxidation of Fe(II) complexes with molecular oxygen was observed with near UV and visible irradiation in water, methanol and dichloromethane.13 Notably the complexes are photochemically inactive in the presence of acetonitrile due to their high oxidation potential (1.1 V vs. SCE) and the firmly low spin character of the CH$_3$CN coordinated complexes.
Photochemical oxidation with Fe$^{IV}=O$ & Fe$^{III}$-OR complexes

In this chapter an investigation of the photochemical properties of the Fe$^{IV}=O$, Fe$^{III}$-OMe and Fe$^{III}$(OH) complexes in acetonitrile is described. The photochemistry of Fe$^{IV}=O$ complexes is explored for the first time in the solid state as well as in solution together with the effect of irradiation on their reactivity towards alkane hydroxylation and alkene epoxidation. In contrast to Fe(II) complexes, Fe$^{IV}=O$ complexes undergo photochemical reduction upon irradiation at 355 nm in acetonitrile. This process is faster in the presence of substrates such as ethyl benzene, benzyl alcohol, cyclooctene and indane etc., which undergo oxidation concomitantly. The enhanced reactivity of the Fe$^{IV}=O$ complexes towards substrate oxidation when under irradiation is attributed to the transient population of an S = 2 state.

![Figure 1 Structures of complexes 1 - 6.](image)

5.2 Results and discussions

5.2.1 Synthesis

The synthesis and solution state spectroscopic characterisation of the complexes [(MeN4Py)Fe$^{IV}$(O)](PF$_6$)$_2$ (1) and [(N4Py)Fe$^{IV}$(O)](PF$_6$)$_2$ (2) is described in chapter 4. In acetonitrile, both complexes 1 and 2 have NIR absorption bands at 687 and 696 nm, respectively. In both complexes the Fe$^{IV}=O$ stretching band was observed at 843 cm$^{-1}$ in acetonitrile and the assignments were confirmed through the observed isotope shift upon labelling with $^{18}$O. Both complexes are EPR silent at 77 K and show a room temperature magnetic moments of 3.27 and 3.23 BM, respectively, by the Evans method, in agreement with an S = 1 ground state.

5.2.2 Solid state characterisation of 1 and 2

The Fe$^{IV}=O$ stretching band was observed in the solid state by Raman spectroscopy
at 840 cm\(^{-1}\) for 1 and at 834 cm\(^{-1}\) for 2. The solid state analysis of 1 and 2 was extended to Mössbauer spectroscopy and SQUID experiments.

5.2.2.1 Magnetic Susceptibility (SQUID experiments)

Temperature dependent magnetic susceptibility studies were carried out in the solid state for 1 and 2 (Figure 2).

![SQUID plots](image)

**Figure 2** (SQUID) Magnetic susceptibility plots for 1 and 2 in the solid state; (a) \(M\) vs. applied magnetic field at 300 K and temperature (K) dependent plots against (b) \(1/\chi_M\), (c) \(\chi_M T\) and (d) \(\mu\) at 1000 Oe applied field.

A magnetic moment of 2.666 BM for 1 and 2.502 BM for 2 was observed at 300 K with an applied field of 1000 Oe. These values are slightly lower compared to the magnetic moment calculated with a spin only formula for systems with two unpaired electrons (2.83 BM). Nevertheless, these data show that both complexes have an \(S = 1\) ground state in the solid state.\(^{16}\) From Figure 2d it can be seen that for both complexes the magnetic moment (\(\mu\) BM) is nearly constant over the temperature range 300-35 K, but decreases sharply below 35 K. A similar trend was also observed for the plots \(\chi_M T\) (mol\(^{-1}\) K cm\(^3\)) vs. temperature (K) (Figure 2c). The Curie (C) and Curie-Weiss (\(\theta\)) constants are 0.9233 and -9.233 for 1 and 0.8095 and -8.107 for 2 (Figure 2b). A linear relation between mass susceptibility (\(\chi_g\)) and
Photocatalytic oxidation with Fe^{IV}=O & Fe^{III}-OR complexes

applied magnetic field was observed (Figure 2a).

5.2.2.2 $^{57}$Fe Mössbauer spectroscopy
The Mössbauer spectra of complexes 1 and 2 in the solid state at 4 K can be fitted with two doublets. This is in contrast to the reported Mössbauer spectrum of [(N4Py)Fe^{IV}(O)]^{2+} in solution at 4 K, which showed only one doublet with an isomer shift ($\delta$) of -0.04 mm/s and quadrupole splitting ($\Delta$E_Q) of 0.93 mm/s. The contribution of each doublet, isomer shift and quadrupole splitting data of complexes 1 and 2 are given in table 1. The near zero isomer shifts of both doublets in complexes 1 and 2 exclude the complexes being in the Fe(II) state and are characteristic of the Fe(III) and Fe(IV) oxidation state. The doublets may indicate the presence of two distinct Fe(IV) species in the solid state, albeit such a conclusion needs further evidence to support of it.

| Table 1. Mössbauer spectral data for 1 and 2 in the solid state at 4 K. | 1 | 2 |
|---|---|---|---|---|
| Isomer shift ($\delta$ mm/s) | Doublet 1 | Doublet 2 | Doublet 1 | Doublet 2 |
| -0.0252 (25) | -0.0230 (25) | -0.0319 (94) | -0.0055 (84) |
| Quadrupole splitting ($\Delta$E_Q mm/s) | 0.757 (15) | 1.059 (18) | 0.692 (36) | 1.095 (42) |
| Site population | 46.8 (71) | 53.2 (74) | 39.0 (12) | 61.0 (14) |
5.2.3 Photochemistry of 1 and 2 in the solid state

The photochemical activity of 1 and 2 in the solid state was examined with irradiation at $\lambda_{\text{exc}}$ 473 nm and simultaneous monitoring with Raman spectroscopy (Figure 4). Irradiation (at $\lambda_{\text{exc}}$ 473 nm) of solid suspensions (dispersed in KCl) of 2 resulted in a decrease in the intensity of the band assigned to the Fe$^{IV}$=O stretch at 832 cm$^{-1}$, with a concomitant increase in the bands associated with [(N4Py)Fe$^{III}$](X)$^{n+}$ and [(N4Py)Fe$^{II}$](X)$^{n+}$ complexes (Figure 5). For comparison the Raman spectra of [(N4Py)Fe$^{II}$](CH$_3$CN)$^{2+}$ (4) and [(N4Py)Fe$^{III}$](OMe)$^{2+}$ suspended in KCl are shown in Figure 5. The bands that increase over time match closely with those of [(N4Py)Fe$^{II}$](CH$_3$CN)$^{2+}$ (4) and also with [(N4Py)Fe$^{III}$](OMe)$^{2+}$ (5).
Photocatalytic oxidation with Fe$^{IV}=O$ & Fe$^{III}$-OR complexes

Figure 4 Changes in the Raman spectrum of 2 dispersed in KCl at $\lambda_{exc}$ 473 nm. The band at 832 cm$^{-1}$ is assigned to an Fe$^{IV}=O$ stretching mode.

Figure 5 Comparison of the Raman spectra of 2 and its photoproduct with that of [(N4Py)Fe$^{II}$(CH$_3$CN)]$^{2+}$ (4) and [(N4Py)Fe$^{III}$(OMe)]$^{2+}$ (5) dispersed in KCl at $\lambda_{exc}$ 473 nm. The band at 832 cm$^{-1}$ is assigned to an Fe$^{IV}=O$ stretching mode.
Indeed an weighted sum spectrum of 4 and 5 matched closely with that of the photoprodut of 2 and, hence, the photoprodut is ascribed as a mixture of Fe(II) or Fe(III) complexes. It should be noted that in the solid state the conversion, although resulting in very intense spectral features, is likely to be very low in fact since the bands of the Fe(II) and Fe(III) complexes formed are resonantly enhanced.

**Figure 6** Solid state Raman spectra dispersed in KCl at $\lambda_{exc}$ 473 nm of photoprodut of 2 and of a simulated weighted sum spectrum of \( \{4 + 5\} \).

Similarly, irradiation of 1 in the solid state resulted in a decrease in intensity of the band at 840 cm\(^{-1}\) (Fe\(^{IV}\)=O stretch), accompanied by a concomitant increase in bands...
Photocatalytic oxidation with $Fe^{IV}=O$ & $Fe^{III}$-OR complexes related to the corresponding Fe(II) and Fe(III) species (Figure 7). For comparison the Raman spectra of $[(MeN4Py)Fe^{II}(CH3CN)]^{2+}$ (3) and $[(MeN4Py)Fe^{II}(Cl)]^{+}$ suspended in KCl are shown in Figure 8.

![Figure 8](image_url) Changes in the Raman spectrum of 1 dispersed in KCl at $\lambda_{exc}$ 473 nm. For the purpose of comparison the Raman spectra of 3 and $[(MeN4Py)Fe^{II}(Cl)](Cl)$ are shown. The band at 840 cm$^{-1}$ is assigned to an $Fe^{IV}=O$ stretching mode.

5.2.4 Photochemistry of 1 and 2 in solution

In chapter 3 the photo-induced oxidation of the complexes 3 and 4 with oxygen as terminal oxidant is described in various solvents (i.e. MeOH, DCM and H2O). Importantly neither complex exhibited photochemically induced oxidation in acetonitrile, which was ascribed to the highly positive oxidation potentials (1.1 V vs. SCE) of the complexes when CH3CN is coordinated to the Fe(II) center. In contrast to 3 and 4, complexes 1 and 2 show wavelength dependent photochemistry in acetonitrile. Although complexes 1 and 2 undergo slow conversion to 3 and 4 (ca. 7 days at room temperature) respectively, they are relatively stable over 6 h (Figure 9). Irradiation (at $\lambda_{exc}$ 355 nm) of solutions of 1 and 2 in acetonitrile, however, results in a rapid decrease in their NIR absorption bands over time at 687 nm for 1 and 696 nm for 2. Absorption bands typical of 3 and 4 were observed to grow in concomitantly at 459 and 454 nm, respectively (Figure 9). A similar
effect was observed at a $\lambda_{\text{exc}}$ of 400 nm. However, neither irradiation at $\lambda_{\text{exc}}$ 449 nm nor 691 nm induced changes in the UV/Vis absorption spectra (data not shown).

Figure 9 Changes in the UV/Vis absorption spectra of (a) 1 (0.5 mM), (b) 2 (0.5 mM) in acetonitrile upon irradiation (at $\lambda_{\text{exc}}$ 355 nm). Time dependence of the absorbance at (c) 687 nm for 1 (squares) and 696 nm for 2 (circles) and (d) 459 nm for 1 (squares) and 454 nm for 2 (circles) in the dark and under irradiation.

5.2.5 Photo catalysis
Fe$^{IV}$=O complexes (e.g., 2) have been shown to be capable of hydroxylating C-H bonds in alkanes, epoxidation of alkenes and oxygenation of thioanisole and PPh$_3$. The photo-induced reduction of 1 and 2 in acetonitrile prompted examination of the activity of these complexes towards C-H bond hydroxylation, alkene epoxidation and hetero atom oxygenation when under irradiation. Except for PPh$_3$, product analysis was not carried out for the substrates employed in the present study. However, it was shown already that Fe$^{IV}$=O complexes are able to oxidise the substrates employed in this study.$^{2,3,4}$

5.2.5.1 Photochemical catalysis with substrates with strong C-H bonds
In this section the effect of irradiation at $\lambda_{\text{exc}}$ 355 nm on the rate of consumption of the Fe$^{IV}$=O complex and rate of recovery of the Fe$^{II}$(CH$_3$CN) in the presence of
Photocatalytic oxidation with Fe$^{IV}=O$ & Fe$^{III}$-OR complexes

substrates such as ethylbenzene and cyclooctene is explored. The changes were monitored by UV/Vis absorption and EPR spectroscopy.

![Graphs showing changes in absorbance over time for reactions with substrates 1 and 2 under irradiation and in the dark.](image)

**Figure 10** Reaction between 1 and 2 (0.5 mM in acetonitrile) with ethylbenzene (EB, 50 equiv) in the dark (circles) and under irradiation (squares) (at $\lambda_{exc}$ 355 nm). Changes in absorption (a) at 687 nm for 1, (b) at 696 nm for 2, (c) at 459 nm for 1 and (d) at 454 nm for 2 over time.

Photo-induced acceleration of the rate of reaction of Fe$^{IV}=O$ was observed with substrates bearing relatively strong C-H bonds such as ethyl benzene (benzylic C-H bond strength is 87 kcal/mol). In the absence of irradiation both complexes show low activity towards oxidation of ethyl benzene (Figure 10). For 2, irradiation at $\lambda_{exc}$ 355 nm in the presence of ethyl benzene (EB) resulted in the absorption band at 696 nm diminishing accompanied by an increase in absorption related to the Fe$^{II}$-CH$_3$CN complex at 454 nm (*vide infra*). By contrast only a small increase in the rate of consumption of 1 was observed upon irradiation in the presence of EB. It should be noted that the loss of the characteristic absorption of Fe$^{IV}=O$ is not concomitant with the recovery of the Fe(II)-CH$_3$CN complex manifested in an increase in absorption at 454 nm.

EPR spectral analysis of the reaction mixture reveals the formation of an Fe(III) species during the reaction. A low spin Fe(III) species ($g = 2.36, 2.13$ and
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1.94) is dominant for 1, whereas both high \((g = 4.34)\) and low spin Fe(III) species were observed for 2 (Figure 11).\(^{18}\)

![Graph showing UV/Vis absorption spectrum and EPR spectra](image)

**Figure 11** (a) Changes in the UV/Vis absorption spectrum of 2 (0.5 mM in acetonitrile) upon addition of ethylbenzene (EB, 50 equiv) in the dark and (b) EPR spectra obtained on a frozen sample (77 K) prepared 25 min after addition of EB to acetonitrile solutions of 1 and 2.

In the dark, reaction of 1 and 2 with cyclooctene is slow. When irradiated in the presence of cyclooctene (CO), complex 2 reacts faster compared to 1 (Figure 12). In this case the absorption band at 696 nm decreased concomitantly with an increase in the absorption band at 454 nm. As with the ethyl benzene (*vide supra*) a low spin Fe(III) species was observed for 1 (with values \(g = 2.36, 2.13\) and 1.94), and both low and high spin Fe(III) species \((g = 4.34)\) were evident for 2 (Figure 12) during the reaction.\(^{18}\)
Photocatalytic oxidation with $\text{Fe}^{IV}=\text{O}$ & $\text{Fe}^{III}$-OR complexes

Figure 12 Reaction between 1 and 2 (0.5 mM in acetonitrile) with cyclooctene (CO, 50 equiv) in the dark (circles) and under irradiation (squares) (at $\lambda_{\text{exc}}$ 355 nm). Changes in absorption over time (a) at 687 nm for 1 and at 696 nm for 2, (b) at 459 nm for 1 and at 454 nm for 2, and (c) EPR spectra obtained from a frozen sample (77 K) prepared 25 min after addition of CO to acetonitrile solutions of 1 and 2.

5.2.5.2 Oxidation of benzyl alcohol with 1 and 2

Reaction of 1 or 2 with 50 equiv of benzyl alcohol in the dark and under irradiation ($\lambda_{\text{exc}}$ 355 nm) led to the oxidation of benzyl alcohol. The time dependence of changes to the UV/Vis absorption spectra (Figure 13) show that with irradiation, addition of benzyl alcohol to 1 led to a decrease in absorbance at 687 nm, accompanied by an increase in absorbance at 459 nm assigned to the Fe(II) complex (3). The rate of consumption of the $\text{Fe}^{IV}=\text{O}$ species is only slightly higher when under irradiation for 1 (Figure 13a). Similarly for 2, both in the dark and under
irradiation the absorbance at 696 nm decreased with a concomitant increase in the absorbance at 454 nm assigned to the Fe(II) complex (4). In contrast to 1, complex 2 reacts with benzyl alcohol at the same rate in the dark as under irradiation (Figure 13b). Hence, in terms of loss of absorbance of the FeIV=O species (1 and 2) it can be said that irradiation has little noticeable additional effect over the already fast thermal reaction.

Figure 13 Reaction of 1 and 2 (0.5 mM in acetonitrile) with benzyl alcohol (BA, 50 equiv) in the dark (circles) and under irradiation (squares) (at $\lambda_{\text{exc}}$ 355 nm). Changes in absorption over time (a) at 687 nm for 1 and (b) at 696 nm for 2.

EPR spectral analysis of the reaction mixture reveals the formation of an Fe(III) intermediate during the reaction. Low spin Fe(III) species ($g = 2.30, 2.13$ and $1.96$) were observed with both 1 and 2 (Figure 14). Interestingly, the observed ‘g’ values in the present case do not match those of the corresponding complexes $[(\text{MeN}4\text{Py})\text{Fe}^{\text{III}}(\text{OH})]^{2+}$ and $[(\text{N}4\text{Py})\text{Fe}^{\text{III}}(\text{OH})]^{2+}$ ($g = 2.41, 2.15$ and $1.92$), but match with those of $[(\text{N}4\text{Py})\text{Fe}^{\text{III}}(\text{OMe})]^{2+}$ ($g = 2.29, 2.12$ and $1.96$). Hence the Fe(III) species is likely to be an FeIII-OR ($R = \text{PhCH}_2^-$) species, which is also photochemically active (vide infra). Overall, therefore, it can be concluded that the FeIV=O species react rapidly with benzyl alcohol to form an Fe(III) species (vide infra) together with formation of some of the corresponding Fe(II) complexes (3 or 4). Irradiation at 355 nm does not have a substantial effect on this already rapid process (Figure 13).
Photocatalytic oxidation with \( \text{Fe}^{\text{IV}}=\text{O} \) & \( \text{Fe}^{\text{III}}\)-OR complexes

![EPR spectra](image)

**Figure 14** EPR spectra obtained from frozen samples (77 K) prepared 10 min after addition of benzyl alcohol to acetonitrile solutions of 1 and 2.

Interestingly, for both complexes the appearance of the absorbance band related to the corresponding Fe(II) complexes was observed to be concomitant with the loss of \( \text{Fe}^{\text{IV}}=\text{O} \) band when under irradiation. But this is not the case in the absence of irradiation, *i.e.* the increase in absorption at 459 and 454 nm did not occur at the same rate and stopped completely after full consumption of the \( \text{Fe}^{\text{IV}}=\text{O} \) complexes (*i.e.* loss of absorption at 687 nm and 696 nm, respectively, for 1 and 2) (Figure 15). These data indicate that an intermediate step occurs in the reaction which is under photochemical control also.

![Reaction curves](image)

**Figure 15** Reaction of 1 and 2 (0.5 mM in acetonitrile) with benzyl alcohol (50 equiv) in the dark (circles) and under irradiation (squares) (at \( \lambda_{\text{exc}} \) 355 nm). Changes in absorption over time (a) at 459 nm for 1 and (b) at 454 nm for 2.

### 5.2.5.3 Photocatalysis with substrates with weak C-H bonds

As with benzyl alcohol, irradiation does not show an effect on the rate of decrease in the absorbance of the \( \text{Fe}^{\text{IV}}=\text{O} \) species when substrates with weak C-H bonds are employed, primarily due to the already rapid thermal reaction. However, in the second step, *i.e.* \( \text{Fe}^{\text{III}} \) to \( \text{Fe}^{\text{II}} \), irradiation is again important. For fluorene (C-H bond energy of 79.5 kcal/mol), reactions with 1 or 2 in the dark and under
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Irradiation ($\lambda_{\text{exc}}$ 355 nm) led to its hydroxylation (Figure 16). In the case of 2, a decrease in the band at 696 nm is observed to proceed at the same rate as an increase in absorbance at 459 nm and irradiation has no effect on the process. In contrast although complex 1 reacts with fluorene at the same rate both in the dark and under irradiation, the recovery of the band at 459 nm is much faster under irradiation. EPR spectral analysis of the nonirradiated reaction mixture reveals the formation of a low spin Fe(III) intermediate ($g = 2.30, 2.13$ and 1.96) for 1, and both high ($g = 4.34$ and 6.74) and low spin Fe(III) species for 2 (Figure 17a). At the end of the reaction, formation of an Fe$^{II}$-CH$_3$CN (*i.e.* 3 and 4) species was confirmed by Raman spectroscopy (Figure 17b).

**Figure 16** Reaction of 1 and 2 (0.5 mM in acetonitrile) with fluorene (FL, 50 equiv) in the dark (circles) and under irradiation (squares) (at $\lambda_{\text{exc}}$ 355 nm). Changes in absorption over time (a) at 687 nm for 1, (b) at 696 nm for 2, (c) at 459 nm for 1 and (d) at 454 nm for 2.
Figure 17 (a) EPR spectra obtained from a frozen sample (77 K) prepared immediately after addition of fluorene (FL) to acetonitrile solutions of 1 and 2 and (b) resonance Raman spectra of reaction mixture at the end of the reaction and comparison with the 3 in acetonitrile at $\lambda_{\text{exc}}$ 473 nm. Several additional bands present in the spectrum originate from fluorene.

The consumption of the Fe$^{IV}=O$ species proceeds at the same rate as the appearance of the Fe(II) complex in the reaction between 1 and 2 with indane (IN) under irradiation but not in the dark (Figure 18). Again, the rate of consumption of Fe$^{IV}=O$ is the same for both complexes, but the appearance of the bands related to Fe(II) complexes is not concomitant. Moreover, generation of the Fe(II)-CH$_3$CN complex is faster for 1 than 2, which is in contrast to where fluorene was used as substrate. Again, a low spin Fe(III) species ($g = 2.36, 2.13$ and $1.93$) is observed for 1, whereas both high ($g = 4.34$) and low spin Fe(III) species ($g = 2.36, 2.13$ and $1.93$) were observed for 2 (Figure 18).
Figure 18 Reaction of 1 and 2 (0.5 mM in acetonitrile) with indane (IN, 50 equiv) in the dark (circles) and under irradiation (squares) (at $\lambda_{exc}$ 355 nm). Changes in absorption over time (a) at 687 nm for 1 and at 696 nm for 2, (b) at 459 nm for 1 and at 454 nm for 2 and (e) EPR spectra obtained on a frozen sample (77 K) prepared immediately after addition of indane to 1 and 2.

5.2.5.4 Oxygen atom transfer reactions

Addition of thioanisole or triphenylphosphine (PPh$_3$) resulted in an immediate disappearance of the NIR absorption bands of 1 and 2, accompanied by an increase in absorbance of the corresponding Fe(II) complexes.$^{19}$ Oxygen atom transfer reactions are too fast (0-6 s) in the case of PPh$_3$ to allow a significant effect of irradiation on the reaction rate to be observed. There was no evidence for the formation of Fe(III) intermediates by UV/Vis absorption and EPR spectroscopy (Figure 19). Moreover an isosbestic point at 570 nm was observed in the reaction
Photocatalytic oxidation with Fe$^{IV}=$O & Fe$^{III}$-OR complexes

between 2 and thioanisole or triphenylphosphine and in contrast to C-H oxidation catalysed by 1 and 2, an intermediate step is not observed in the oxo transfer reactions to the thioanisole and PPh$_3$. Formation of the OPPh$_3$ was confirmed by $^{31}$P NMR spectroscopy (data not shown).

Figure 19 Changes in the UV/Vis absorption spectrum of 2 in acetonitrile (a) after addition of 50 equiv of thioanisole and (b) 50 equiv of triphenylphosphine. Inset: EPR spectrum obtained on the frozen sample (77 K) prepared shortly after addition of thioanisole to 2.

5.2.6 Photochemistry of 5 and 6 in acetonitrile

It was apparent from the data reported above that an Fe(III) species formed is also photochemically active. The photochemical properties of two Fe(III) complexes 5 and 6 were studied in acetonitrile to elucidate the origin of the photochemistry. Under irradiation at 355 nm, complex 5, which has an Fe$^{III}$-OMe moiety, shows a rapid increase in absorption at 378 and 454 nm, which is characteristic of the Fe$^{II}$-CH$_3$CN complex 4. The corresponding thermal reaction (i.e. in the dark) was much slower (Figure 20).

Figure 20 (a) Changes in the UV/Vis absorption spectrum of 5 (0.5 mM) in acetonitrile, initial (solid line), after 80 min irradiation with $\lambda_{exc}$ 355 nm (dotted line) and after 80 min in the dark (dashed line) and (b) time dependence of the absorbance at 454 nm in the dark (circles) and under irradiation (squares).
In sharp contrast, complex 6, which bears an Fe$^{III}$-OH unit, does show a much less pronounced effect of irradiation on its absorption spectrum with only a slow increase in absorption at 378 and 454 nm observed compared to 5 (Figure 21). Nevertheless, a significant increase in absorbance at 378 and 454 nm was observed in the case of 6 under irradiation, compared to a sample kept in dark.

![Figure 21](image_url)

**Figure 21** Changes in the UV/Vis absorption spectrum of 6 (0.5 mM) in acetonitrile, initial (solid line), after 2 h irradiation with $\lambda_{exc}$ 355 nm (dashed line) and after 2 h in the dark (dotted line).

Irradiation, of an equimolar mixture of 5 and 6 in acetonitrile, shows similar changes as observed for 5 alone. Interestingly, the absorption of the Fe$^{II}$-CH$_3$CN species ($\lambda_{max}$ at 454 nm) observed in this case originates from complex 5 (which bears a methoxy unit) and not from 6 based on the absorption maxima. In conclusion species similar to 5, which bears a methoxido ligand, are most likely responsible for the observed photochemical activity (Figure 22).

It is possible that the photoreduction proceeds through the formation of a strong oxidant i.e. an Fe$^{III}$-CH$_3$CN complex ($E_{1/2} = 1.1$ V vs. SCE)$^{19}$ through ligand exchange. This species can oxidise both Fe$^{III}$-OH or Fe$^{III}$-OR (ca. 0.85 V vs. SCE, chapter 4) to yield an Fe$^{II}$-CH$_3$CN complex and an Fe$^{IV}$=O complex. Formation of Fe$^{II}$-CH$_3$CN was confirmed by its characteristic absorption bands at 378 and 454 nm (Figure 20 and 22) and by $^1$H NMR spectroscopy. However, formation of an Fe$^{IV}$=O complex was not observed by UV/Vis absorption spectroscopy. However, it is important to remember that the Fe$^{IV}$=O species is itself photochemically active under irradiation at 355 nm and this may be the reason for the absence of Fe$^{IV}$=O absorption in the UV/Vis absorption spectrum.
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Figure 22 (a) Changes in the UV/Vis absorption spectra of a mixture of 5 (0.5 mM) and 6 (0.5 mM) in acetonitrile, initial (solid line), after 100 min irradiation with $\lambda_{\text{exc}}$ 355 nm (dashed line) and after 100 min in the dark (dotted line) and (b) time dependence of the absorbance at 454 nm in the dark (circles) and under irradiation (squares).

5.3 Summary

Complexes 1 and 2 are low spin with an S = 1 ground state in solution (confirmed by Evans method) and in the solid state confirmed by SQUID measurements and Mössbauer spectroscopy. In the solid state, irradiation at $\lambda_{\text{exc}}$ 473 nm results in partial photoreduction to Fe(III) and Fe(II) complexes. It was shown in chapter 3 that complexes 3 and 4, where acetonitrile is bound to Fe(II) centre, are photochemically inactive in acetonitrile due to their high oxidation potentials and singlet ground state. Importantly and in sharp contrast to their Fe$^{II}$-CH$_3$CN complexes, the Fe$^{IV}=O$ complexes 1 and 2 show photochemical activity in acetonitrile which lead, ultimately to reduction to the corresponding Fe$^{II}$-CH$_3$CN complex via an Fe$^{III}$-OH$_2$ intermediate. It was shown in chapter 4 that Fe$^{II}$-OH and Fe$^{IV}=O$ react rapidly to yield two molecules of Fe$^{III}$-OH. However, in acetonitrile the Fe$^{II}$-CH$_3$CN complex does not react with Fe$^{IV}=O$ species. Indeed, even with 20 vol% of water in acetonitrile, addition of 3 or 4 has no effect on the absorption spectrum of the Fe$^{IV}=O$ species. These data suggests that the observation of Fe$^{III}$-OH/OR species during the reaction between Fe$^{IV}=O$ and several substrates, with the exception of PPh$_3$ and thioanisole in dark and under irradiation, is not due to the reaction between Fe$^{II}$-OH/OR and Fe$^{IV}=O$ complexes.
Scheme 1 Reaction between Fe(II) and Fe$^{IV}=$O species for the formation of Fe(III)-OH species.$^{16}$

Overall the data suggests that there are two steps involved in the photochemically promoted reaction of 1 and 2 with substrates (Scheme 2). Except for PPh$_3$ and thioanisole, the first step is the conversion from Fe$^{IV}=$O to Fe$^{III}-$OH/OR followed by a second photochemical step in which it is probable that Fe$^{III}-$OR converts to Fe$^{III}-$CH$_3$CN (see section 5.2.4), which is a powerful enough oxidant to oxidise Fe$^{III}-$OH/OR to the Fe$^{IV}=$O state and form the Fe$^{II}-$CH$_3$CN complex also.$^{13,19}$ These data suggests that the reaction proceeds via a rebound mechanism.

Scheme 2 Steps involved in the photochemistry of 1 and 2 in acetonitrile.

When compared to 1, complex 2 is more reactive towards substrate oxidation under irradiation, e.g., ethyl benzene. This suggests a difference in reactivity of the quintet
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states or a difference in the photochemical quantum yields of 1 and 2.\textsuperscript{20} Irradiation has no significant effect on the rate of formation of the Fe(III) species, in the presence of substrates with weaker C-H bonds (e.g., indane and fluorene). However, there is a substantial effect on the recovery of the Fe^{II}-CH\textsubscript{3}CN species. The Fe(III) species generated in the reaction between PhCH\textsubscript{2}OH and Fe^{IV}=O has the same g values as 5, indicating formation of Fe^{III}-OCH\textsubscript{2}Ph. Further irradiation leads to formation of Fe^{II}-CH\textsubscript{3}CN. These data are consistent with the rebound pathway in the case of the initial oxidation step.

The enhanced catalytic reactivity towards C-H activation under the irradiation is proposed here to be due to population of the S = 2 state. In enzymatic systems, such as TauD a high spin Fe^{IV}=O (S = 2) species is utilised for the substrate oxidation. By contrast, most of the synthetic Fe^{IV}=O species, which have triplet ground state are unreactive when compared with biological systems. In scheme 3, the complex \[((\text{tmg}_3\text{tren})\text{Fe}^{IV}(O))^{2+}\] has a quintet ground state, however this complex is a very weak oxidant compared to \[((\text{tmc})(\text{an})\text{Fe}^{IV}(O))^{2+}\] and \[((\text{N4Py})\text{Fe}^{IV}(O))^{2+}\] (2), which have triplet ground states. The complex \[((\text{Tp})(\text{OBz})\text{Fe}^{IV}(O))\], which has degenerate quintet and triplet states and is proposed to be a mimic for TauD shows higher reactivity than the other complexes. In the present work both complexes 1 and 2 have triplet ground states as confirmed by Evans method. Overall, when these complexes react with substrates via a quintet excited state is believed to mediate the reaction and lead to the substrate oxidation.\textsuperscript{10} In the present case therefore it could be concluded irradiation simply increases the transient population of the quintet state.

**Scheme 3** Energy profiles for the H-abstraction reactions of \[((\text{tmg}_3\text{tren})\text{Fe}^{IV}(O))^{2+}\] (left), \[((\text{tmc})(\text{an})\text{Fe}^{IV}(O))^{2+}\] and \[((\text{N4Py})\text{Fe}^{IV}(O))^{2+}\] (middle) and \[((\text{Tp})(\text{OBz})\text{Fe}^{IV}(O))\] (right) with 1,4-cyclohexadiene. RC is the reactant cluster. Reproduced from reference 10.
Chapter 5

5.4 Conclusions

In conclusion, we report the photochemically accelerated reduction of complexes 1 and 2 in the solid state as well in solution. In the solid state, irradiation causes the reduction of the Fe^{IV}=O complexes to their corresponding Fe(III) and Fe(II) complexes. In solution irradiation at $\lambda_{exc}$ 355 and 400 nm leads to the reduction of the complexes and formation of Fe(II)-CH$_3$CN complexes. The increase in the catalytic activity is ascribed to accessing of the $S = 2$ when under irradiation. Further experiments and DFT calculations are expected to confirm the origin of the photochemical reactivity.

5.5 Experimental section

The ligands 1,1-di(pyridin-2-yl)-N,N'-bis(pyridin-2-ylmethyl)methanamine (N4Py)$_2$ and 1,1-di(pyridin-2-yl)-N,N'-bis(pyridin-2-ylmethyl)ethanamine (MeN4Py)$_2$ were prepared by literature methods. The complexes [(MeN4Py)Fe$_{II}$(CH$_3$CN)](ClO$_4$)$_2$ (3) and [(N4Py)Fe$_{II}$(CH$_3$CN)](ClO$_4$)$_2$ (4) were available from earlier studies. For the complexes [(MeN4Py)Fe$_{IV}$(O)](PF$_6$)$_2$ (1) and [(N4Py)Fe$_{IV}$(O)](PF$_6$)$_2$ (2) see chapter 4. Commercially available chemicals are used without further purification.

5.5.1 Physical Methods

For details of UV/Vis absorption, Raman and resonance Raman spectroscopy see the chapter 2. For details of EPR spectroscopy see the chapter 3. All UV/Vis absorption experiments were carried out with a 400 or 420 nm long pass filter. Only the halogen lamp was employed in UV/Vis absorption spectrometer to avoid additional photochemistry. Irradiation at $\lambda_{exc}$ 355 nm employed a Zouk from Cobolt Lasers with the power 10 mW at the sample. In the case of $\lambda_{exc}$ 449 nm (35 mW at source, PowerTechnology), 400.8 (50 mW at source, PowerTechnology) and 691 nm (45 mW at source, Ondax) were employed. $^{57}$Fe Mössbauer spectra have been recorded using a conventional constant-acceleration type spectrometer equipped with a 50 mCi $^{57}$Co source and a flow-type, liquid helium cryostat. Spectra of the powder samples (ca. 30 mg) were recorded at 4 K. Least-squares fittings of the Mössbauer spectra have been carried out with the assumption of Lorentzian line shapes using the Recoil software package. The magnetisation of the samples was measured both at constant temperature (300 K) as a function of the applied field (1000 - 21000 Oe) and at a constant applied field (1000 Oe) as a function of the temperature (2 - 300 K) using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. The experimental data were corrected for the diamagnetic contribution.

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5.7 References


(16) See chapter 4 for solution state magnetic moment.

(18) Except for PhCH$_2$OH, for all other substrates the $g$ values of Fe(III) species are reported in this work are ± 0.04 uncertainty due to weaker signal intensity.


(20) Further studies (i.e. DFT calculations) are needed to evaluate these phenomena.