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Base-controlled Mechanistic Divergence between Iron(IV)-Oxo and Iron(III)-Hydroperoxo in the H₂O₂ Activation by a Nonheme Iron(II) Complex.

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Activation of hydrogen peroxide by Fe^{II} salts (Fenton systems) leads to a myriad of oxidizing agents whose nature, Fe^{IV}O, or hydroxyl radicals and Fe^{III} species, is dictated by the reaction conditions, in particular the pH value. Using the non heme Fe^{II} complex [Fe^{II}(L₅²⁻)(CH₃CN)]²⁺ (**1**) (where L₅²⁻ is the pentadentate ligand N-methyl-N,N',N'-tris(2-pyridylmethyl)ethane-1,2-diamine)) we have observed the simultaneous formation of two reaction intermediates, [Fe^{IV}(O)(L₅²⁻)]²⁺ and [Fe^{III}(OOH)(L₅²⁻)]²⁺, in its reaction with excess hydrogen peroxide in the presence of sub-stoichiometric amounts of triethylamine. Kinetic and spectroscopic monitoring of the reaction mixture and of independently prepared [Fe^{IV}(O)(L₅²⁻)]²⁺ in the presence of the different constituents of the reaction mixture allows drawing a mechanistic scheme. These two reactive species are formed simultaneously following two independent and competitive pathways. [Fe^{IV}(O)(L₅²⁻)]²⁺ is obtained *via* heterolytic O-O cleavage of the oxidant assisted by the base in a peroxidase-like mechanism whereas [Fe^{III}(OOH)(L₅²⁻)]²⁺ is generated upon homolytic O-O cleavage of hydrogen peroxide. The relative contribution of these two pathways can be tuned by adjusting the amount of base used.

Introduction

Activation of hydrogen peroxide by Fe^{II} species leads to oxidizing media. In the Fenton reaction (*i.e.* in which Fe^{II} salts are implemented) the long-term debate regarding the nature of the actual oxidant, iron(IV)-oxo or hydroxyl radicals, has been rendered obsolete due to recent evidences that the generation of either active species could be controlled by the pH in a similar reaction medium.¹ More generally, the mechanisms of Fenton-like processes are extremely complex and are highly dependent on the reagents and reaction conditions.² As elaborated declensions of Fenton systems, bioinspired Fe^{II} complexes are widely developed to activate hydrogen peroxide to perform small molecule oxidation reactions, stabilize reaction intermediates in order to provide information on their reactivity, and hence lead to a better understanding of the mechanism in oxygenase enzymes.³⁻⁵ In the case of nonheme Fe^{II} complexes bearing pentaazadentate ligands, it has been established for two decades that their reaction with an excess of hydrogen peroxide accumulates Fe^{III}(OOH) species in a steady state.^{6,7} In practice, this reaction requires 2 equiv. H₂O₂ and occurs in two steps (Scheme 1, A). First, the one electron oxidation of Fe^{II} related to the

homolytic cleavage of hydrogen peroxide results in the formation of Fe^{III}(OH) or Fe^{III}(OMe), the reaction being most often performed in MeOH. Then, substitution of the alkoxide by the oxidant yields the Fe^{III}(OOH) intermediate and the release of methanol.⁸⁻¹¹ In contrast, very rare examples have been reported where the reaction of an Fe^{II} complex with hydrogen peroxide yields Fe^{IV}(O).¹²⁻¹⁴ In these cases, mechanistic investigations indicated a stoichiometric reaction between the Fe^{II} precursor and H₂O₂ entailing an heterolytic cleavage of the oxidant. Que *et al.*¹³ and our group¹⁴ have demonstrated that either the use of lutidine or an internal second coordination sphere amine, leads to the formation of the Fe^{IV}(O) intermediate by driving proton transfer from the proximal to the distal oxygen in an Fe^{II}-H₂O₂ intermediate thus promoting heterolytic O-O bond cleavage (Scheme 1, B). The comparison between all of these examples suggests that the switch from homolytic O-O cleavage of hydrogen peroxide (and formation of Fe^{III} species) to heterolytic (generation of Fe^{IV}) can be achieved under appropriate conditions, which bears similarity with Fenton systems. However, a recent report by Chen *et al.* questions this latter proposition, since they demonstrated that the Fe^{III}(OOH) and Fe^{IV}O intermediates are mechanistically related and are formed following successive reactions. In their study, the (N₅)Fe^{IV}O intermediate was generated upon homolytic cleavage of the corresponding (N₅)Fe^{III}(OOH) complex provided this latter was formed from near stoichiometric H₂O₂/Fe^{II} mixtures. Following this methodology, steady-state conditions for the formation of (N₅)Fe^{III}(OOH) were not achieved.¹⁵

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Scheme 1. General mechanism for the reaction in MeOH of H₂O₂ with (A) Fe^{II} complexes bearing pentaazadentate ligands and (B) with a pentaaza Fe^{II} complex incorporating a non coordinating base (adapted from ref. ¹⁴).

In this paper we show that, under appropriate conditions, *i. e.* using sub-stoichiometric triethylamine, the mechanism of the reaction between a $(N_5)Fe^{II}$ precursor ($[Fe^{II}(L_5^2)(CH_3CN)]^{2+}$, $L_5^2 = N$ -methyl- N,N',N' -tris(2-pyridylmethyl)ethane-1,2-diamine) and H₂O₂ can be divergent. In our study, $(N_5)Fe^{IV}O$ and $(N_5)Fe^{III}(OOH)$ intermediates are generated in the same medium but *via* parallel reactions, thus making these species mechanistically independent. This report broadens the palette of reactions between Fe^{II} complexes and hydrogen peroxide.

Figure 1. Structure of the molecular cation of $[Fe^{II}(L_5^2)(CH_3CN)](PF_6)_2$ **1**(PF₆)₂. Bond distances (Å) Fe-N1 1.960(2); Fe-N2 1.990(2); Fe-N3 1.965(2); Fe-N4 1.997(2); Fe-N5 2.042(2); Fe-N6 1.933(2). All the hydrogen atoms and anions are omitted for clarity. Thermal ellipsoids are shown at the 30% level.

Results and discussion

The high yield generation of LS ($S=1/2$) Fe^{III}(OOH) from $(L_5^2)Fe^{II}$ -type precursors requires the use of excess hydrogen peroxide

and is generally performed in MeOH.^{16–20} In this solvent, a Fe^{III}(OH) in equilibrium with a Fe^{III}(OMe) complex (denoted Fe^{III}(OR) (R = Me, H) hereafter) is formed in the first step. The second step, leading to the Fe^{III}(OOH) intermediate, exhibits an associative character suggesting a seven-coordinated Fe^{III} in the transition state following coordination of an H₂O₂ molecule to the nascent Fe^{III}(OR).⁸ Finally, internal proton transfer from H₂O₂ to the RO[−] ligand and subsequent release of ROH yields the Fe^{III}(OOH) (Scheme 1, A). This mechanism corresponds to steady-state conditions for the Fe^{III}(OOH) intermediate since its formation is faster than its degradation. Additionally, it

Figure 2. Time resolved UV-Vis spectra of **1** (2 mM) before (black) and after addition of 50 equiv. H₂O₂ in CH₃OH at 20°C. The colored spectra were recorded 13 ms (red trace), 403 ms, 806 ms, 2 s, 4 s, 6 s, 8 s, 10 s, 12 s, 15 s and 20 s, respectively (purple traces), after mixing the reactants. The inset shows that the 730-nm feature of the Fe^{IV}O is not detected under these conditions.

provides a rationale for why MeOH is a solvent of choice for this reaction.

As an illustrative example, the reaction between $[\text{Fe}^{\text{II}}(\text{L}_5^2)(\text{CH}_3\text{CN})]^{2+}$ (**1**) (Figure 1) with 50 equiv. H_2O_2 in MeOH was monitored by UV-visible absorption under stopped flow conditions (Figure 2). The $[\text{Fe}^{\text{III}}(\text{OR})(\text{L}_5^2)]^{2+}$ species, which does not exhibit any characteristic feature in the visible,^{21–24} was obtained immediately (see red trace in Figure 2) as testified by the appearance of a characteristic low spin rhombic signal with g values 2.32, 2.14 and 1.93 in X-band EPR (Supporting Information, Figure S1 A). The latter complex was then converted to $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ in a ca. 60 % yield, based on its characteristic LMCT band at 537 nm ($1000 \text{ M}^{-1}\text{cm}^{-1}$)¹⁷ following first order kinetics in both Fe and H_2O_2 and the appearance of its characteristic axial X band EPR spectrum (Supporting Information, Figures S1 B and S2 A).

In the presence of NEt_3 (0.7 equiv. vs Fe) but otherwise identical conditions, the formation of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ was also observed but was preceded by the very fast formation and disappearance of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$, as attested by its 730 nm absorption band (Figure 3, green traces and Supporting Information, Figure S3). Its maximum accumulation was observed between ca. 60 – 100 ms and it almost vanished after 195 ms. The $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ LMCT then developed in a slower process. These two spectral evolutions proceed without any isosbestic point. Since NEt_3 did not induce any spectral modification on the UV-visible absorption spectrum of the Fe^{II} precursor (Supporting Information, Figure S4), it can be inferred that it does not coordinate to the metal center. Further kinetic analysis for the formation of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ showed that the reaction was first order in Fe and hydrogen peroxide (Supporting Information, Figure S2 B).

Eyring analysis of the temperature dependence of this reaction under pseudo first order conditions afforded an activation enthalpy $\Delta H^\ddagger$ of $3.9 \text{ kcal.mol}^{-1}$ and an activation entropy $\Delta S^\ddagger$ of $-37.3 \text{ cal.mol}^{-1}\text{K}^{-1}$ for the formation of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ (Supporting Information, Figure S5, left). These values compare well with those reported for the formation of $[\text{Fe}^{\text{IV}}\text{O}(\text{NH}^{\text{Bn}}\text{-tpen})]^{2+}$ that was shown to occur by heterolytic O–O cleavage of its $\text{Fe}^{\text{II}}\text{-H}_2\text{O}_2$ precursor thanks to the assistance of the non-coordinating dialkylamine group of the ligand ($\Delta H^\ddagger = 3.75 \text{ kcal.mol}^{-1}$ and $\Delta S^\ddagger = -43.3 \text{ cal.mol}^{-1}\text{K}^{-1}$).¹⁴ Hence, we propose that NEt_3 promotes the heterolytic cleavage of hydrogen peroxide by shuttling the proton from the proximal to the distal oxygen atom, thus playing the role of the distal His residue in a peroxidase-like mechanism.²⁵ Similar conclusions were drawn for the formation of $[\text{Fe}^{\text{IV}}\text{O}(\text{TMC})]^{2+}$ upon reaction of H_2O_2 with $\text{Fe}^{\text{II}}(\text{TMC})$ in the presence of 2,6-lutidine.^{13,26}

Regarding the formation of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$, the activation parameters obtained under the same conditions were $\Delta H^\ddagger = 5.6 \text{ kcal.mol}^{-1}$ and $\Delta S^\ddagger = -43.3 \text{ cal.mol}^{-1}\text{K}^{-1}$ (Supporting Information, Figure S5, middle). Interestingly, the same activation parameters were determined in the absence of NEt_3 (Supporting Information, Figure S5, right), indicating that the formation of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ is not dependent on the base.

Figure 3. Time resolved UV-Vis spectra of **1** (2 mM) before (black) and after addition of 50 equiv. H_2O_2 in the presence of 0.7 equiv. NEt_3 in CH_3OH at 20°C . The green traces were recorded 13 ms, 65 ms (bold trace), 91 ms, 117 ms and 195 ms, respectively, after mixing the reactants. The purple traces were obtained after 403 ms, 806 ms, 2 s, 4 s, 6 s, 8 s, 10 s, 12 s, 15 s, 20 s and 30 s.

The effect of NEt_3 on the reaction between **1** and H_2O_2 was then examined. In the absence of base, no $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ was formed as shown by the absence of the characteristic band at 730 nm (Figure 2 inset and Figure 4, left, pink trace) and the amount of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ was maximal as observed by the increased absorption at 537 nm (Figure 4, right, pink trace). Increasing the quantity of NEt_3 from 0 up to 1 equiv. vs Fe promoted the formation of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ to progressively reach a transient accumulation of > 20% (Figure 4, left, green trace). In contrast, the yield of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ formed decreased down to < 15% in the presence of increasing amounts of base (Figure 4, right).

Thus, the more $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ is formed at the start of the reaction, the less $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ is observed. This observation suggests that, under our reaction conditions, $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ and $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ are not successive species along the same reaction pathway, which contrasts with the study reported by Chen *et al.*¹⁵ Conversely, our results suggest that the formation of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ and $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ intermediates is done in parallel and follows different reaction pathways. Additionally, this indicates that the fast degradation process of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ yields a species which is unproductive

Figure 4. Visible absorption time traces for $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ at 730 nm (left) and $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ at 537 nm (right) for the reaction of **1** (2 mM) with 50 equiv. H_2O_2 in the presence of various equiv. NEt_3 (indicated by x) in CH_3OH at 20°C . The yields of formation for the two intermediates are evaluated on the basis of their extinction coefficients ($\epsilon([\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}) = 300 \text{ M}^{-1}\text{cm}^{-1}$; $\epsilon([\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}) = 1000 \text{ M}^{-1}\text{cm}^{-1}$).

for the formation of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ in the slow process since the amount of this latter species is diminished in the presence of NET_3 .

To account for the fast degradation of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$, control experiments were performed to independently evaluate the effect of MeOH, hydrogen peroxide or NET_3 on its decay. For these controls, $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ was preliminarily prepared by reaction of **1** with PhIO in acetonitrile since $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ displays a much longer lifetime in this solvent (Supporting Information, Experimental section and Figure S3).

In the presence of MeOH, the decay of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ was significantly accelerated with respect to its regular decay in acetonitrile (Supporting Information, Figure S6). This is in line with the reaction between $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ and MeOH to yield formaldehyde¹⁵ whereas MeCN is a solvent difficult to oxidize.²⁷

The addition of 0.5 equiv. H_2O_2 vs $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ in MeCN was enough to fully consume this latter in a fast reaction (Figure S7 B). This observation is fully consistent with the oxidation of hydrogen peroxide by $\text{Fe}^{\text{IV}}\text{O}$ following an $\text{Fe}^{\text{IV}}\text{O} : \text{H}_2\text{O}_2$ 2:1 reaction:^{15,28}

Accordingly, 0.25 equiv. H_2O_2 reacted with only half of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ in a fast process before the remaining $\text{Fe}^{\text{IV}}\text{O}$ decays following a slower reaction (Figure S7 A). As described in Scheme 1, the metal complex arising from this reaction, $[\text{Fe}^{\text{III}}(\text{OH})(\text{L}_5^2)]^{2+}$, is a precursor of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$. Consistently, in the presence of 50 equiv. H_2O_2 vs $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$, the fast decay of this latter is followed by the accumulation of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ with a 65 % conversion (Figure S8). This conversion is similar to the one observed when the reaction of $[\text{Fe}^{\text{II}}(\text{L}_5^2)(\text{CH}_3\text{CN})]^{2+}$ (**1**) with 50 equiv. H_2O_2 is carried out in MeOH (Figure 2). In contrast, reaction of **1** with 50 equiv. H_2O_2 in MeCN only yields ca. 20 % $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ (data not shown), which can be explained by an unfavorable formation of $[\text{Fe}^{\text{III}}(\text{OH})(\text{L}_5^2)]^{2+}$ with respect to $[\text{Fe}^{\text{III}}(\text{L}_5^2)(\text{CH}_3\text{CN})]^{3+}$ in acetonitrile.

Finally, the effect of triethylamine on the fate of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ was investigated. Addition of 0.7 equiv. NET_3 vs $\text{Fe}^{\text{IV}}\text{O}$ in MeCN led to the bleach of the 730 nm signal and formation of a red chromophore with an absorption at ca. 510 nm (Figure S9). Such a feature is characteristic of $(\mu\text{-oxo})\text{diiron(III)}$ complexes regardless of the nature of other bridging units.^{29–32} EPR monitoring of this sample after complete disappearance of the $\text{Fe}^{\text{IV}}\text{O}$ reveals the formation of $[\text{Fe}^{\text{III}}(\text{OR})(\text{L}_5^2)]^{2+}$ (Figure S9 E, red trace). Double integration of this signal indicates that it accounts for 30–35% of the initial $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ complex indicating that this sample is mainly constituted of EPR silent species, in agreement with the formation of $(\mu\text{-oxo})\text{diiron(III)}$ complexes. Addition of 50 equiv. H_2O_2 to this red species yielded a moderate increase of the absorption intensity between 500 and 600 nm without the appearance of a well-defined band, followed by its decay (Figure S9 B and D). EPR indicates that this increase in intensity is related to the formation of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$. Considering the extinction coefficient of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ at 525 nm ($1000 \text{ M}^{-1}\text{cm}^{-1}$) this

absorption increase corresponds to ca. 6% conversion vs the initial $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$. While the reaction of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ with 50 equiv. H_2O_2 leads to the accumulation of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ with the same conversion as **1** reacted with 50 equiv. H_2O_2 in MeOH (ca. 60%), only a very small amount of this $\text{Fe}^{\text{III}}(\text{OOH})$ intermediate is formed when H_2O_2 is added on the red species, i.e. after decay of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ in the presence of NET_3 .

Comparison of the observed rates of these control experiments allows gathering additional mechanistic information. The decay of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ in the presence of 0.7 equiv. NET_3 appears to be a rather slow process which requires minutes to proceed ($k_{\text{obs}} = 0.24 \text{ min}^{-1}$, Figure S9 C). Similarly, the decay of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ in a MeCN/MeOH 1:1 mixture proceeds with a similar rate constant of 0.21 min^{-1} which is much faster than in neat MeCN (Figure S6). According to Chen *et al.*,¹⁵ the reaction of a $(\text{N}_5)\text{Fe}^{\text{IV}}\text{O}$ species with MeOH leads to the formation of formaldehyde. In contrast, the reaction of hydrogen peroxide with $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ is comparatively very fast (Figures S7 and S8), as already reported.¹⁵ In the presence of 50 equiv. H_2O_2 , the decay of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ is achieved within a few seconds. Hence, this reaction must be the principal pathway for its degradation and therefore, the oxidation of MeOH or NET_3 must be very marginal when the reaction between **1** and H_2O_2 is conducted in MeOH in the presence of NET_3 .

From there, the decay of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ upon reaction with H_2O_2 yields its $\text{Fe}^{\text{III}}(\text{OH})$ analog. While this latter species should lead to $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ in the presence of 50 equiv. H_2O_2 , the presence of NET_3 inhibits this reaction and promotes the formation of EPR silent species, i. e. $(\mu\text{-oxo})\text{diiron(III)}$ complexes. In support to this proposition, comparison of the EPR spectra of **1** + 1 equiv. H_2O_2 in the presence or absence of 0.7 NET_3 shows that $[\text{Fe}^{\text{III}}(\text{OR})(\text{L}_5^2)]^{2+}$ ($\text{R}=\text{H}, \text{Me}$) is the unique species observed and indicates a lower amount of this complex due to the presence of the base (Supporting Information, Figure S10). Accordingly, for samples obtained from **1** + 50 equiv. H_2O_2 with or without NET_3 monitored in time by EPR, the presence of base always induces a lower amount of LS Fe^{III} species ($[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ and $[\text{Fe}^{\text{III}}(\text{OR})(\text{L}_5^2)]^{2+}$). Moreover, the signature of $[\text{Fe}^{\text{III}}(\text{OR})(\text{L}_5^2)]^{2+}$ progressively disappears indicating the formation of diamagnetic species (Supporting Information, Figure S11).

On the basis of these observations, a global mechanism to account for the reaction of **1** with hydrogen peroxide in MeOH in the presence or absence of NET_3 can be proposed (Scheme 2). In the absence of base, the $\text{Fe}^{\text{III}}(\text{OOH})$ is formed under steady-state conditions from the $\text{Fe}^{\text{III}}(\text{OR})$ ($\text{R}=\text{H}, \text{Me}$) complex. This latter species is obtained following the very fast one electron oxidation of the Fe^{II} precursor (Scheme 1 A and Scheme 2, lower pathway, blue arrow). In the presence of NET_3 , the stoichiometric reaction between the Fe^{II} precursor and H_2O_2 yields $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ following a peroxidase-like mechanism as already proposed for parent systems (Scheme 1 B).^{13,14} In this step, the base acts as an acid/base catalyst and is regenerated at the end (Scheme 2, upper pathway, green arrow). This reaction is very fast and kinetically competitive

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Scheme 2. Reactions between the Fe^{II} precursor **1** and hydrogen peroxide in MeOH in the presence or absence of NEt_3 . The $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ and $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ intermediates are formed following competitive base-dependent (top pathway, green) and base-independent (bottom pathway, blue) mechanisms, respectively. The stoichiometry for the disproportionation of H_2O_2 is formal. The formation of $(\mu\text{-oxo})$ diiron(III) complexes is promoted by the base. A diversity of structures can be envisioned with $\text{L} = \text{solvent, water, OH}^-$, which have not been determined precisely.

with the first step of the lower branch (compare red trace in Figure 2 with green traces in Figure 3).

Hence, both of these pathways are expected to proceed simultaneously when NEt_3 is present. Once generated, $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ reacts readily with hydrogen peroxide to release $[\text{Fe}^{\text{III}}(\text{OH})(\text{L}_5^2)]^{2+}$. Under these conditions, *i.e.* in the presence of the base, the pH is sufficiently high to promote the condensation of the $\text{Fe}^{\text{III}}(\text{OH})$ species into $\mu\text{-oxo}$ dinuclear complexes. These latter are a thermodynamic sink and do not react further. In the absence of NEt_3 (Scheme 2, lower pathway), residual protons coming from the intrinsic acidity of aqueous hydrogen peroxide (pH *ca.* 4–5 for 35% aqueous H_2O_2) hamper the dimerization of the $\text{Fe}^{\text{III}}(\text{OH})$ complexes which allows their reaction with another equivalent of H_2O_2 and the subsequent formation of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$.

Finally, the formation of both $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ and $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ occurs simultaneously from the same **1** / H_2O_2 / NEt_3 reaction mixture following the pathways initiated by the two competitive steps indicated by the blue and green arrows in Scheme 2. In the absence of NEt_3 , only the lower pathway is possible and $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ is predominantly accumulated. The addition of increasing equivalents of base leads to a progressive shift from the lower to the upper pathway and to the formation of increasing amounts of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$. Then, $[\text{Fe}^{\text{III}}(\text{OH})(\text{L}_5^2)]^{2+}$ obtained either from a

pathway or another can react with excess H_2O_2 to generate the $\text{Fe}^{\text{III}}(\text{OOH})$ intermediate or can yield $(\mu\text{-oxo})$ diiron(III) complexes *via* condensation. Similar to the first step of each pathway, there is a progressive shift from the generation of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ to the formation of dinuclear complexes with increasing amounts of NEt_3 . This mechanism is in agreement with the experimental observations, in particular with the yields of formation observed between $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ and $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ as a function of the amount of NEt_3 .

Conclusions

The reactivity of a non heme Fe^{II} complex, $[\text{Fe}^{\text{II}}(\text{L}_5^2)(\text{MeCN})]^{2+}$, with excess hydrogen peroxide in the presence of sub-stoichiometric amounts of triethylamine, was inspected. Two reaction products, $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ and $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$, were observed in the reaction medium. These two species are formed *via* competitive mechanistic pathways following second order reactions (first order in both Fe^{II} precursor and H_2O_2). $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ is formed in a very fast reaction in which NEt_3 promotes the heterolytic O–O bond cleavage of an $\text{Fe}^{\text{II}}\text{-H}_2\text{O}_2$ in a peroxidase-like mechanism, corresponding to a net Fe^{II} to Fe^{IV} two electron oxidation. In contrast, $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ is obtained in a much slower process, independent on the presence of the base, which is caused by

the homolytic cleavage of H_2O_2 and a single electron, Fe^{II} to Fe^{III} , oxidation. $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ also degrades readily by oxidizing hydrogen peroxide to yield $[\text{Fe}^{\text{III}}(\text{OH})(\text{L}_5^2)]^{2+}$. Under basic conditions, this latter complex undergoes condensation reactions leading to oxo bridged dinuclear complexes which are a thermodynamic sink. Decreasing the amount of NEt_3 progressively disfavors the Fe^{II} to $\text{Fe}^{\text{IV}}\text{O}$ pathway and the formation of $(\mu\text{-oxo})\text{diiron(III)}$ complexes while favoring the formation of $\text{Fe}^{\text{III}}(\text{OOH})$ via the hydrogen peroxide homolytic cleavage pathway.

This study bears resemblance with Fenton systems for which the heterolytic or homolytic activation of hydrogen peroxide and subsequent generation of $\text{Fe}^{\text{IV}}\text{O}$ or $(\text{Fe}^{\text{III}} + \text{OH}^*)$ oxidizing intermediates, respectively, can be achieved by the control of experimental parameters such as the pH.

Conflicts of interest

There are no conflicts of interest to declare.

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*Supporting Information for***Base-controlled Mechanistic Divergence between Iron(IV)-Oxo and Iron(III)-Hydroperoxo in the H₂O₂ Activation by a Nonheme Iron(II) Complex.**

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Experimental Section.

All moisture and oxygen sensitive compounds were prepared using standard high vacuum line, Schlenk and cannula techniques. All reagents were purchased from Aldrich or Acros and used as received unless noted otherwise. Acetonitrile solvent was purified by distillation, under argon, over CaH_2 .

$[\text{Fe}^{\text{II}}(\text{L}_5^2)](\text{MeCN})(\text{PF}_6)_2$ (**1**) was prepared by reacting $[\text{Fe}^{\text{II}}\text{Cl}(\text{L}_5^2)](\text{PF}_6)$ ¹ (635 mg, 1.09 mmol) with 1.1 equiv. AgPF_6 in MeCN at RT. The initial yellow solution became red and turbid upon AgCl precipitation. The mixture was stirred for 2 hours, concentrated by evaporation of the solvent under low pressure and placed at -20°C overnight. The white precipitate was then filtrated off and the resulting solution was placed at -20°C overnight. Finally, the remaining solid was removed by using a syringe with a $0.45\ \mu\text{m}$ teflon filter. Addition of Et_2O yielded $[\text{Fe}^{\text{II}}(\text{L}_5^2)(\text{MeCN})(\text{PF}_6)_2$ as a red solid (500 mg, 86%). Single crystals were obtained by layering an acetonitrile solution of the complex with Et_2O .

$[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ was obtained following the procedure reported by Thibon et al.² Reaction of $[\text{Fe}^{\text{II}}(\text{MeCN})(\text{L}_5^2)]^{2+}$ (1.6 mM) with excess solid PhIO in MeCN at RT was stirred until decoloration of the intense red orange color of the Fe^{II} precursor. The residual PhIO was then removed by filtration to leave a clear green solution.

UV-visible absorption spectrophotometry was performed with a Varian Cary 60 spectrophotometer equipped with a Hellma immersion probe (1 cm optical path length) and fiber-optic cable. Low temperature was maintained using a Thermo Haake CT90L cryostat.

Stopped Flow absorption spectrophotometry was performed at 20°C on a BioLogic SFM-4000 coupled to a J&M Tidas diode array spectrometer. Final concentration in Fe was 2 mM.

X-band EPR X-band EPR spectra were recorded at 90 K on a Bruker ELEXSYS 500 spectrometer equipped with a Bruker ER 4116DM X band resonator, an Oxford Instrument continuous flow ESR 900 cryostat, and an Oxford ITC 503 temperature control system.

X-ray diffraction data for $[\text{Fe}^{\text{II}}(\text{L}_5^2)](\text{MeCN})(\text{PF}_6)_2$ (**1**) were collected by using a Bruker AXS Kappa ApexII Diffractometer with $0.71073\ \text{\AA}$ Mo-K α radiation. Crystal was mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. For compound **1**, the temperature of the crystal was maintained at the selected value by means of a 700 series Cryostream cooling device to within an accuracy of $\pm 1\text{K}$. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97³ and refined against F^2 by full-matrix least-squares techniques using SHELXL-2018⁴ with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.⁵ The crystal data collection and refinement parameters are given in Table S1.

CCDC 1944504 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/Community/Requestastructure>.

Table S1. Crystallographic data and structure refinement details.

Compound	[Fe ^{II} (L ₅ ²)(CH ₃ CN)](PF ₆) ₂ (1(PF ₆) ₂)
CCDC	1944504
Empirical Formula	C ₂₃ H ₂₈ Fe N ₆ , 2(F ₆ P)
<i>M_r</i>	734.30
Crystal size, mm ³	0.21 x 0.10 x 0.09
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	16.4343(4)
<i>b</i> , Å	20.4024(5)
<i>c</i> , Å	17.2272(5)
<i>α</i> , °	90
<i>β</i> , °	17.2272(5)
<i>γ</i> , °	90
Cell volume, Å ³	5773.6(3)
<i>Z</i> ; <i>Z'</i>	8 ; 2
<i>T</i> , K	100(1)
Radiation type ; wavelength Å	Mo-Kα ; 0.71073
<i>F</i> ₀₀₀	2976
<i>μ</i> , mm ⁻¹	0.738
<i>θ</i> range, °	1.547 - 30.594
Reflection collected	104 511
Reflections unique	17 680
<i>R</i> _{int}	0.0680
GOF	1.024
Refl. obs. (<i>I</i> > 2σ(<i>I</i>))	12 203
Parameters	840
w <i>R</i> ₂ (all data)	0.1032
<i>R</i> value (<i>I</i> > 2σ(<i>I</i>))	0.0419
Largest diff. peak and hole (e ⁻ ·Å ⁻³)	0.688 ; -0.532

Figure S1. (A) X-band EPR at 90 K of $[\text{Fe}^{\text{III}}(\text{OR})(\text{L}_5^2)]^{2+}$ ($\text{R} = \text{H}, \text{Me}$) obtained from $[\text{Fe}^{\text{II}}(\text{L}_5^2)(\text{MeCN})]^{2+}$ (**1**, 2 mM) and 1 equiv. H_2O_2 in CH_3OH at 20°C . (B) X-band EPR at 90 K of the sample obtained from $[\text{Fe}^{\text{II}}(\text{L}_5^2)(\text{MeCN})]^{2+}$ (**1**, 2 mM) and 50 equiv. H_2O_2 in CH_3OH at 20°C . The characteristic resonances of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ are indicated by purple labels, those related to $[\text{Fe}^{\text{III}}(\text{OR})(\text{L}_5^2)]^{2+}$ are indicated by black labels. Microwave frequency 9.6 GHz, microwave power 1 mW, modulation amplitude 8 G, gain 50 dB.

Figure S2. Plot of the observed rate constant as a function of the concentration of hydrogen peroxide for the formation of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ (generated from **1**, 2 mM, and H_2O_2) (A) and for the formation of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ (generated from **1**, 2 mM, and H_2O_2 in the presence of 0.7 NEt_3) (B).

Figure S3. Visible absorption (left) and experimental and theoretical ESI-MS features (right) of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ obtained from $[\text{Fe}^{\text{II}}(\text{L}_5^2)(\text{MeCN})]^{2+}$ (**1**) and PhIO in CH_3CN . The top left panel overlays the visible absorption spectrum of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ obtained from **1** and PhIO (blue trace) with the one obtained from the reaction of **1** with 50 H_2O_2 and 0.7 NEt_3 (green trace) corresponding to the bold green trace in Figure 3 of the main text.

Figure S4. UV-visible absorption spectrum of $[\text{Fe}^{\text{II}}(\text{L}_5^2)(\text{MeCN})]^{2+}$ (**1**) in CH_3OH in the absence (blue) or in the presence (green) of 0.7 eq. NEt_3 .

Figure S5. Eyring plots for the formation of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ (left) and $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ (middle) in the reaction of **1** (2 mM) with 50 equiv. H_2O_2 in the presence of 0.7 equiv. NEt_3 in CH_3OH . (Right) Eyring plot for the formation of $[\text{Fe}^{\text{III}}(\text{OOH})(\text{L}_5^2)]^{2+}$ in the reaction of **1** (2 mM) with 50 equiv. H_2O_2 in CH_3OH in the absence of NEt_3 .

Figure S6. UV-visible (A) and time trace at 730 nm (B) of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ (1.5 mM) in MeCN/MeOH (1/1 v/v) at 20°C; and (C) time trace at 730 nm of a similar sample in neat MeCN .

Figure S7. Evolution of the UV-visible spectrum of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ (1.6 mM in MeCN) at 20°C in the presence of 0.25 equiv. H_2O_2 (A) or 0.5 H_2O_2 (B), and time traces at 730 nm over 65 minutes (C), or focusing on the first 10 minutes (D). Red and blue dots correspond to the reaction mixtures containing 0.25 or 0.5 equiv. H_2O_2 .

Figure S8. Evolution of the UV-visible spectrum of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ (1.5 mM in MeCN) at 20°C in the presence of 50 equiv. H_2O_2 (A) and time traces at 730 (green line) and 525 nm (purple line) (B).

Figure S9. (A) Evolution of the UV-visible spectrum of $[\text{Fe}^{\text{IV}}\text{O}(\text{L}_5^2)]^{2+}$ (1.6 mM in MeCN) at room temperature in the presence of 0.7 NEt_3 (green) and evolution towards the red species (red). (B) Effect of the addition of 50 equiv. H_2O_2 on the red species monitored by UV-visible. (C) Time traces at 730 nm and 525 nm for the spectral evolution displayed in panel A. (D) Time traces at 730 nm and 525 nm upon addition of 50 equiv. H_2O_2 . (E) EPR spectra for the samples taken before and after addition of H_2O_2 as indicated in panel D.

Figure S10. X-band EPR at 90 K of **1** (2 mM) with 1 equiv. H_2O_2 in the presence (green trace) or absence (blue trace) of 0.7 equiv. NEt_3 in CH_3OH at 20°C . Microwave power 1 mW, modulation amplitude 8 G, gain 50 dB. The intensity of these spectra have been normalized and can be directly compared.

Figure S11. X-band EPR spectra monitored in time for the reaction of **1** (2 mM) with 50 equiv. H_2O_2 in the presence (green trace) or absence (blue trace) of 0.7 equiv. NEt_3 in CH_3OH at 20°C . $T = 90\text{ K}$, microwave power 1 mW, modulation amplitude 8 G, gain 50 dB. The intensity of these spectra have been normalized and can be directly compared.

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An Fe^{II} complex reacts with excess H_2O_2 in the presence of sub-stoichiometric NEt_3 to give $\text{Fe}^{\text{IV}}(\text{O})$ and $\text{Fe}^{\text{III}}(\text{OOH})$ reactive species following a base-dependent and a base-independent pathway, respectively.