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Selective Formation of an Fe^{IV}O or an Fe^{III}OOH Intermediate From Fe^{II}-H₂O₂ : Controlled Heterolytic vs Homolytic O-O Bond Cleavage by the Second Coordination Sphere

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Abstract: Direct formation of Fe^{IV}-oxo species from nonheme Fe^{II} complexes and H₂O₂ is highly attractive for the development of selective oxidation reactions. Nonetheless, when using this oxidant, most of the Fe^{II} species known to date undergo a single electron oxidation generating Fe^{III} and hydroxyl radicals prone to engaging in uncontrolled radical chemistry. Here, we demonstrate that the devised incorporation of a dialkylamine group into the second coordination sphere of an Fe^{II} complex allows to switch the reactivity from the usual formation of Fe^{III} species towards the selective generation of an Fe^{IV}-oxo intermediate. We characterized the Fe^{IV}-oxo complex by UV-visible absorption and Mössbauer spectroscopy. Variable temperature kinetic analyses point towards a mechanism where the heterolytic cleavage of the O-O bond is triggered by a proton transfer from the proximal to the distal oxygen atom in the Fe^{II}-H₂O₂ complex with the assistance of the pendant amine. Density functional theory studies reveal that this heterolytic cleavage is actually initiated by a homolytic O-O bond cleavage immediately followed by a proton-coupled electron transfer that leads to the formation of the Fe^{IV}-oxo species and release of water through a concerted mechanism.

More than a century ago, Fenton discovered that the reaction of an Fe^{II} species with H₂O₂ led to the efficient oxidation of organic substrates in acidic aqueous media.^[1] Ever since that discovery, debate continues on whether the active species of such systems is an OH radical^[2-4] or an Fe^{IV}-oxo species^[5] resulting from either the homolytic or heterolytic cleavage of the O-O bond in its Fe-peroxide precursor. Beyond this historical controversy, understanding the key steps in the reactivity of Fe^{II} species with H₂O₂ is of great interest for the development of synthetic

oxidation catalysts. Indeed, the production of high-valent Fe-oxo species capable of performing *a priori* selective 2-electron oxidation reactions, instead of hydroxyl radicals that would engage in uncontrolled oxidations has been a long term goal.^[6] Recent works suggest that changing the experimental conditions such as the pH may drive the reaction to a pathway or another.^[7,8] Additionally, understanding the reaction between Fe^{II} and H₂O₂ is relevant to the comprehension of O₂ activation at the Fe^{II} centers of Fe enzymes^[9] such as tetrahydropterin-dependent monooxygenases,^[10] or isopenicillin N synthase.^[11] It has been suggested that during the O₂ activation process by these enzymes, an Fe^{IV}-oxo species is formed *via* the heterolytic O-O cleavage of an Fe^{II}OOH(H) intermediate. However, this reaction proved to be difficult to reproduce with synthetic catalysts and most of the Fe^{IV}-oxo species known to date have been obtained from the reaction of Fe^{II} complexes with oxygen donors such as iodosylbenzene (PhIO) or *m*-chloroperbenzoic acid (*m*CPBA).^[12,13] The use of H₂O₂ with Fe^{II} complexes usually leads to the formation of the corresponding Fe^{III} complexes under stoichiometric conditions and yields Fe^{III}OOH intermediates with excess H₂O₂.^[14-17] Only a few examples of nonheme Fe^{II} complexes have shown the direct formation of an Fe^{IV}-oxo species from their reaction with H₂O₂,^[18,19] or from the evolution of a putative Fe^{II}OOH(R) intermediate.^[20] Que *et al.* reported the nearly quantitative formation of [Fe^{IV}O(TMC)]²⁺ from [Fe^{II}(TMC)]²⁺ and H₂O₂ in the presence of 2,6-lutidine.^[18] DFT calculations showed that lutidine acted as a general base that promoted the proton transfer from the proximal to the distal O atom, thus facilitating the heterolytic O-O cleavage.^[21] The role played by lutidine was similar to that played by the distal His residue in horseradish peroxidase (HRP),^[22] with the exception that it was added as a cofactor in solution and was not part of the catalyst scaffold. Thus, we reasoned that designing a ligand containing a non-coordinating base in the vicinity of the Fe^{II} ion would drastically influence its reactivity *versus* H₂O₂. Herein, we demonstrate that the incorporation of a secondary amine as a second coordination sphere group in the [Fe^{II}(Bn-tpen)]²⁺ complex **2**^{II} to give the new [Fe^{II}(^{NH}Bn-tpen)]²⁺ **1**^{II} (Fig. 1) allows the direct formation of the [Fe^{IV}O(^{NH}Bn-tpen)]²⁺ species **1**^{IV-O} from the stoichiometric reaction between **1**^{II} and H₂O₂. Interestingly, the reactivity of **1**^{II} turns into the conventional reactivity of the original complex **2**^{II} when the amine group is protonated, *i.e.* formation of an Fe^{III} species.^[23] Experimental and theoretical investigations of **1**^{IV-O} formation converge towards a heterolytic O-O cleavage of the initial Fe^{II}-H₂O₂ complex promoted by a proton transfer assisted by the neighbouring amine. To the best of our knowledge, this is the

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first example of a nonheme Fe system where such a transformation is performed *via* an intra-molecular reaction. The ^{NH}Bn-tpen ligand was designed in such a way that the secondary amine fragment could not bind the metal through a stable 5- or 6-membered metallocycle. The X-ray structure of [Fe^{II}(^{NH}Bn-tpen)(OH₂)²⁺ (**1^{II}**) is displayed in Fig. 1. It shows that the first coordination sphere of Fe^{II} is constituted of the typical N₅ environment provided by Bn-tpen and related ligands^[23-25] and confirms that the secondary amine (N6) is not coordinated to the metal center. The coordination sphere is completed by a water ligand, which is H-bonded to the secondary amine N-atom of the neighboring complex in the crystal (S.I., Fig. S1). The mean Fe-N bond distance is 2.21 Å, which is typical of a high spin (S=2) Fe^{II}. Further characterizations indicate that the structure of **1^{II}** is preserved in solution (S.I. Fig. S2 and S3).

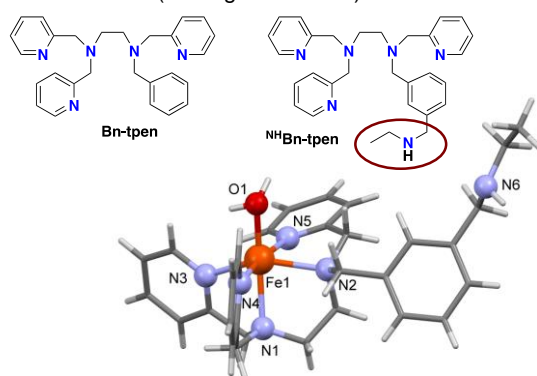


Figure 1. Structure of the ^{NH}Bn-tpen and Bn-tpen ligands and X-ray structure of the molecular cation, **1^{II}**. Anions and disordered atoms were omitted for clarity. Bond distances (Å): Fe-N1 2.24, Fe-N2 2.24, Fe-N3 2.15, Fe-N4 2.18, Fe-N5 2.23, Fe-O1 1.92.

The reaction of **1^{II}** (1 mM) with 2.5 equiv. H₂O₂ in MeOH at 25°C monitored by stopped flow absorbance spectroscopy leads to the formation of a new species with an absorbance of 0.18 at 740 nm and a shoulder at 900 nm (Fig. 2, green trace). Under these conditions, the maximum accumulation of this species occurred after 3 s but decayed afterwards (S.I., Fig. S4). Addition of PhIO (25 equiv. vs Fe) as oxidant instead of H₂O₂ yielded the same intermediate (S.I., Fig. S5). Its spectroscopic signature is very similar to that observed for the [Fe^{IV}O(Bn-tpen)]²⁺ species, **2^{IV}-O** (λ_{max} = 739 nm with a shoulder at 900 nm, ε = 400 M⁻¹ cm⁻¹ in acetonitrile).^[26] Hence, the intermediate observed in Fig. 2 can be assigned as [Fe^{IV}O(^{NH}Bn-tpen)]²⁺ **1^{IV}-O**. The observation of an isosbestic point at 495 nm and the absence of any other intermediate in the course of the formation of **1^{IV}-O** suggests its direct formation from **1^{II}** and H₂O₂.

To further substantiate this assignment, the reaction product of **1^{II}** with H₂O₂ was studied by Mössbauer spectroscopy. Fig. 2 shows the spectra obtained when a CD₃OD solution of ⁵⁷Fe-enriched **1^{II}** was reacted with 10 equiv. D₂O₂ for ca. 5 s and frozen. The spectra of the solution recorded at either 80 K (not shown) or 4.5 K (Fig. 2A) in absence of magnetic field was dominated by a quadrupole doublet which can be simulated with a set of parameters δ = 0.015 mm/s and ΔE_Q = 0.83 mm/s. These values are very close to those reported for **2^{IV}-O** (δ = 0.01

mm/s and ΔE_Q = 0.87 mm/s)^[26] and in the usual range for Fe^{IV}O species with S = 1.^[12] This value of the spin was verified by performing an experiment under a field of 6 T applied parallel to the γ ray. The corresponding spectrum (Fig. 2B) could be nicely simulated under this assumption with an axial zero field splitting value of 21 cm⁻¹. The quadrupole doublet accounts for ca 90 % of total Fe in the sample and the remaining Fe is probably present as ferric impurities as judged from the extra lines spread on both sides of the doublet in Fig. 2A. Note that a sample obtained with 2.5 equiv. D₂O₂ vs **1^{II}** displayed identical spectroscopic characteristics.

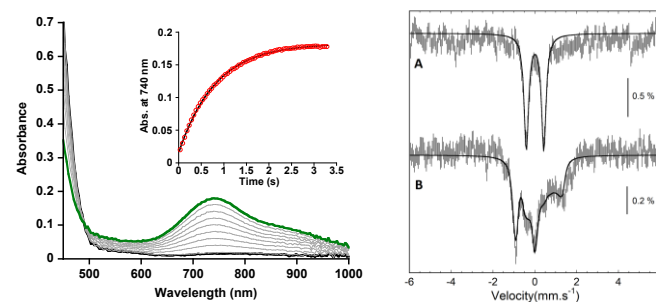


Figure 2. (Left) Time resolved UV-Vis spectra for the reaction of **1^{II}** (1 mM) with 2.5 equiv. H₂O₂ in MeOH at 25°C. Black trace, spectrum recorded 12 ms after mixing the reactants. Green trace, spectrum recorded at the maximum of the formation of **1^{IV}-O** (t = 3 s). Insert: time trace monitored at 740 nm (red circles) and first order fitting of the curve (black trace). (Right) Mössbauer spectra of **1^{IV}-O** (vertical bars) recorded at 4.5 K in absence (A) and presence (B) of a magnetic field of 6 T applied parallel to the γ ray. The black line is a spin-Hamiltonian simulation of both spectra with a unique set of parameters: δ = 0.015 mm/s, ΔE_Q = 0.83 mm/s, D = 21 cm⁻¹, E/D = 0, g_x = g_y = 2.3, and g_z = 2.0, A_{x,y,z}/g_NβN = (-18, -18, -2) T, η = 0.26.

Titration of **1^{II}** with H₂O₂ shows that the amount of **1^{IV}-O** formed was constant and maximum from 5 equiv. of added H₂O₂ up to 100 equiv. (S.I., Fig. S6). Considering that the reaction is quantitative under these conditions, an extinction coefficient of 190 M⁻¹ cm⁻¹ for the 740 nm chromophore is deduced.^[27] Additionally, the conversion in **1^{IV}-O** reached 80% and 93%, respectively, when 1 and 2.5 equiv. H₂O₂ were used. These results thus strongly suggest a 1:1 stoichiometry between **1^{II}** and H₂O₂ to yield **1^{IV}-O**. Consistently, further kinetic studies using different concentrations of H₂O₂ revealed that the reaction is first-order in both **1^{II}** and H₂O₂. At 25°C, a second-order rate constant of 0.316 L.mmol⁻¹.s⁻¹ was obtained from the plot of the pseudo first-order rate constant k_{obs} vs [H₂O₂] (S.I., Fig. S7). The temperature dependence of k_{obs} was evaluated for samples containing 1 mM **1^{II}** and 10 equiv. H₂O₂. The resulting Eyring plot afforded an activation enthalpy ΔH[‡] of 3.75 kcal.mol⁻¹ and an activation entropy ΔS[‡] of -43.3 cal.mol⁻¹.K⁻¹ (S.I., Fig. S8). These activation parameters compare well with those obtained for the formation of Fe^{IV}-oxo intermediates upon reaction of H₂O₂ with Fe^{II}(bispidine) (ΔH[‡] = 8.1 kcal.mol⁻¹, ΔS[‡] = -35.9 cal.mol⁻¹.K⁻¹)^[19] or Fe^{II}(TMC) in the presence of 2,6-lutidine (ΔH[‡] = 6.9 kcal.mol⁻¹, ΔS[‡] = -34.4 cal.mol⁻¹.K⁻¹)^[18]. For the latter complex, the formation of the Fe^{IV}-oxo was explained as a global heterolytic O-O bond cleavage assisted by the external base which resulted from a combination of partial homolytic O-O cleavage and proton-coupled electron transfer as determined by DFT calculations.^[21]

The smaller activation enthalpy observed here suggests that, compared to an external base, the preorganization of the amine next to the metal center facilitates the formation of the Fe^{IV}-oxo intermediate.

To support the crucial role played by the dialkylamine group in the formation of **1^{IV}-O**, similar experiments were performed under acidic conditions in the presence of 2 equiv. HClO₄ vs **1^{II}**. Under these conditions and even for a small amount of added H₂O₂ (2.5 equiv. vs Fe), formation of a low spin (S=½) Fe^{III}OOH intermediate was observed with typical UV-visible ($\lambda_{\text{max}} = 539$ nm) and EPR ($g = 2.21, 2.14, 1.97$) features^[23,28,29] (Fig. 3 and Scheme 1). In the presence of protons, the reactivity of **1^{II}** switches to the conventional Fe^{II}-to-Fe^{III} reactivity exhibited by most of nonheme Fe^{II} complexes supported by pentadentate ligands.^[14,17,23,28-32] Conversely, in its neutral form, the amine interacts specifically with the Fe^{II}-H₂O₂ adduct to promote the heterolytic O-O bond cleavage to yield **1^{IV}-O**, with the function of a springboard that relays protons between the proximal and distal oxygen atoms of H₂O₂. To substantiate our hypothesis, additional experiments were carried out using D₂O₂ in CD₃OD. Under these conditions, the formation of **1^{IV}-O** was observed as well, and a large kinetic isotope effect (KIE, $k_{\text{H}}/k_{\text{D}}$) of 5.6 was measured (S.I., Fig. S9). A similar value was reported by Li *et al.* for the formation of [Fe^{IV}O(TMC)]²⁺ from the Fe^{II} complex and 2,6-lutidine as a base.^[18]

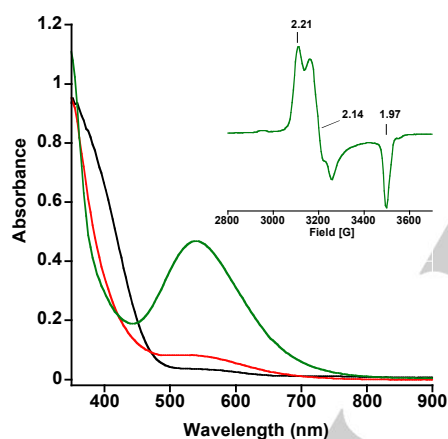
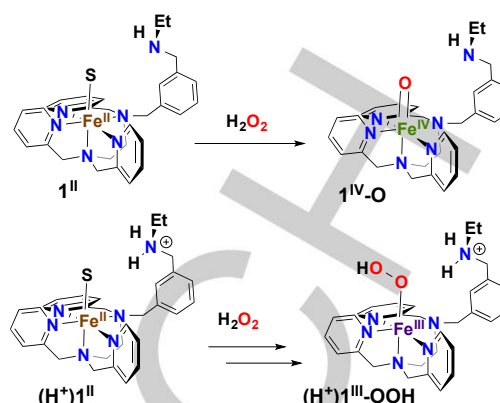


Figure 3. UV-Vis. spectra of **1^{II}** in MeOH in the presence of HClO₄ (2 equiv.) before (black trace) and after addition of H₂O₂ (2.5 equiv., red trace or 100 equiv., green trace). Insert: X-band EPR spectrum at 100 K of the sample corresponding to the green UV-Vis. spectrum (Power 0.12 mW).

Given all the above observations, *i.e.*, (i) a direct conversion between **1^{II}** and **1^{IV}-O**, (ii) first-order kinetics in both Fe^{II} and H₂O₂, (iii) activation parameters consistent with O-O bond heterolysis and (iv) the implication of both protons and the amine in the second coordination sphere, one can suggest that the formation of **1^{IV}-O** is initiated by the heterolytic cleavage of an Fe^{II}-H₂O₂ intermediate promoted by the dialkylamine group acting as an acid-base relay. The role of this latter moiety being similar to the one assigned to distal histidine or glutamate residues in heme peroxidases.^[22,33,34]

To gain more insight into the mechanism of the binding and activation of H₂O₂ on **1^{II}**, a series of DFT calculations were performed. We started from the ^{1,3,5}[Fe^{II}(H₂O₂)(^{NH}Bn-tpen)]²⁺



Scheme 1. Influence of the second coordination sphere on the formation of Fe^{IV}O and Fe^{III}OOH intermediates as observed in this work. (with S = H₂O or MeOH)

(^{1,3,5}**1^{II}-H₂O₂**) complexes in either the singlet, triplet or quintet spin state. First, **1^{II}-H₂O₂** was optimized in various orientations of H₂O₂ with respect to the metal center and dialkylamine group. In particular, orientation (a) has the distal OH group of H₂O₂ in hydrogen bonding interaction with the pendant amine group (**1^{II}-H₂O₂-a**), whereas in the alternative structure the proximal OH group was hydrogen bonded to the amine (**1^{II}-H₂O₂-b**) (Fig. 4 and S.I., Fig. S10). Test calculations with a range of density functional methods were performed including the full reaction mechanism with B3LYP and PBE1PBE DFT methods. Both density functional methods give virtually the same reaction mechanism and the only difference relates to the relative energies of the various complexes. Our results are consistent with a recent benchmark study that showed these methods to reproduce experimental free energies of activation for the reaction of nonheme Fe^{IV}-oxo with substrates to within 3 kcal mol⁻¹.^[35,36] Finally, as the spin-state ordering of the Fe^{IV}-oxo species is sometimes sensitive to the choice of the density functional method, we calculated the Fe^{IV}-oxo species with several methods and procedures (S.I. Table S9). With all methods, apart from BP86, the triplet spin **1^{IV}-O** is the ground state in agreement with the Mössbauer studies reported above. Despite these fluctuations in spin-state energies, previous studies of ours; however, showed that changing the density functional method generally does not change regio- and stereo-selectivities of a chemical reaction but only affects the relative energies.^[37,38]

In the triplet and quintet spin states, the **1^{II}-H₂O₂-a** and **1^{II}-H₂O₂-b** structures are close in energy with a small preference of the latter at B3LYP level of theory. Well higher in energy than these quintet spin H₂O₂ complexes are the triplet spin states. Therefore, the triplet spin ³**1^{II}-H₂O₂** will not play a role in the reaction mechanism leading to the formation of the Fe^{IV}-oxo species. Subsequently, we investigated the proton transfer from H₂O₂ to the dialkylamine group to form an Fe^{II}-hydroperoxo intermediate, which is negligible from complex **1^{II}-H₂O₂-b** (Fig. 4) at B3LYP and PBE1PBE level of theories.

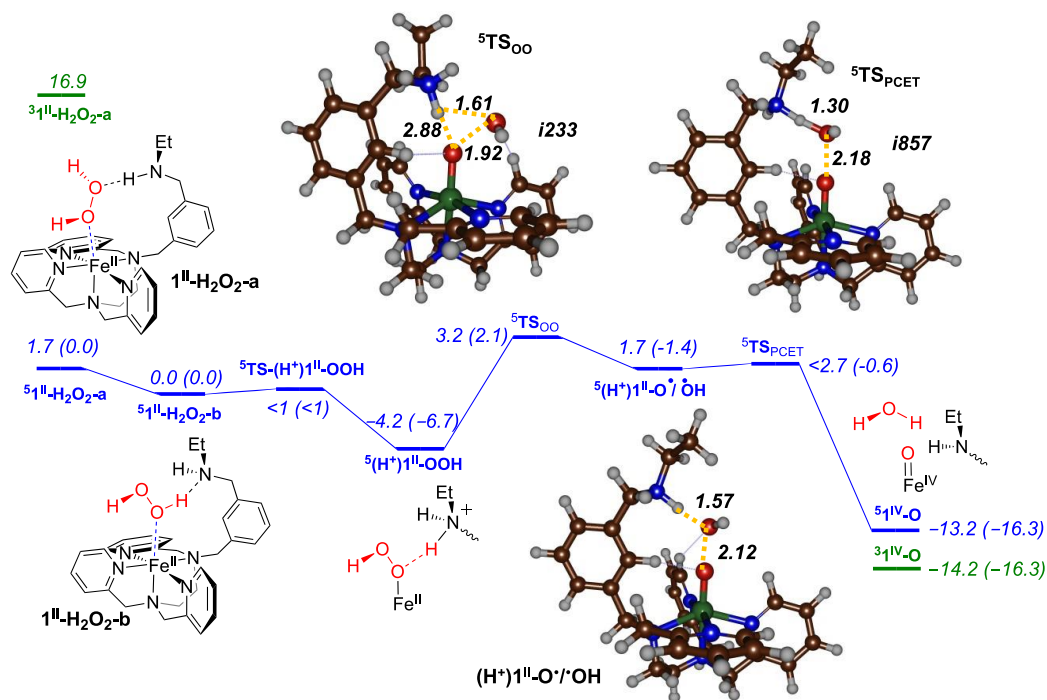


Figure 4. Potential energy landscape for the formation of the $\text{Fe}^{\text{IV}}\text{-O}$ species 1^{IV}-O from the $\text{Fe}^{\text{II}}\text{-H}_2\text{O}_2$ adduct $1^{\text{II}}\text{-H}_2\text{O}_2$ as calculated at UB3LYP/BS2//UB3LYP/BS1 level of theory. Energies are in kcal.mol^{-1} with $\Delta E_{\text{BS2}}+\text{ZPE}$ data outside parenthesis and ΔG_{BS2} data in parenthesis

However, in the case of $1^{\text{II}}\text{-H}_2\text{O}_2\text{-a}$ no direct proton transfer from the terminal OH group could be located. Instead, an internal rotation occurs during the geometry scan and changes structure $1^{\text{II}}\text{-H}_2\text{O}_2\text{-a}$ into $1^{\text{II}}\text{-H}_2\text{O}_2\text{-b}$.

The geometry scan converges to a proton transfer intermediate $(\text{H}^+)1^{\text{II}}\text{-OOH}$ that shows a hydrogen bond between the nascent ammonium group and the proximal oxygen atom. The next step leads to the cleavage of the hydroperoxo bond in $(\text{H}^+)1^{\text{II}}\text{-OOH}$. Similarly to previous calculations on nonheme Fe complexes,^[39] we find a homolytic bond breaking to give a formal $\text{Fe}^{\text{II}}\text{-oxyl}$ complex and an OH radical (S.I., Table S4). In particular, we find an electronic configuration with a spin density of 4.2 on the Fe-oxo unit and a down-spin electron (spin density of -0.6) on the leaving $\cdot\text{OH}$ in support of our characterization of $(\text{H}^+)1^{\text{II}}\text{-O}'/\text{OH}$. The calculated reaction barrier for the homolytic cleavage of the O-O bond is $\Delta G^\ddagger = 8.8$ (B3LYP) and 15.3 (PBE1PBE) kcal.mol^{-1} via $5^{\text{TS}}_{\text{OO}}$. The latter free energy of activation is in perfect agreement with the experimental Eyring values at 298 K of 16.7 kcal.mol^{-1} (Fig. 4). Attempts to swap molecular orbitals to find an $\text{Fe}^{\text{IV}}\text{-oxo}$ and an OH^- anion converged back to a radical situation in all cases and hence corresponds to a higher energy pathway.

In the final reaction step the $\text{Fe}^{\text{IV}}\text{-oxo}$ or 1^{IV}-O is formed through a simultaneous electron and proton transfer process: namely proton transfer from the pendant ammonium group to the OH radical and electron transfer from the $\text{Fe}^{\text{II}}\text{-oxyl}$ to $\cdot\text{OH}$. This pathway has a small barrier of less than 1 kcal mol^{-1} above $(\text{H}^+)1^{\text{II}}\text{-O}'/\text{OH}$. Interestingly, the energy surface from TS_{OO} to TS_{PCET} is almost flat (the $\text{Fe}^{\text{II}}\text{-oxyl } \cdot\text{OH}$ intermediate $(\text{H}^+)1^{\text{II}}\text{-O}'/\text{OH}$ is high in energy), which indicates that these steps will

be seen as synchronous and the electron/proton transfer may be seen as coincidental with the initial homolytic O-O bond scission. The structures of $5^{\text{TS}}_{\text{OO}}$, $(\text{H}^+)1^{\text{II}}\text{-O}'/\text{OH}$ and $5^{\text{TS}}_{\text{PCET}}$ are displayed in Fig. 4 alongside the reaction profile. Clearly seen, particularly in $5^{\text{TS}}_{\text{OO}}$, are H-bond interactions of the ammonium group with the distal (1.61 Å) and proximal (2.88 Å) oxygen atoms. As such, O-O bond cleavage will be affected by H/D replacement and should lead to a KIE as observed experimentally. In conclusion, the computational modeling reveals that the activation of H_2O_2 indeed occurs *via* an overall heterolytic cleavage of the initial $\text{Fe}^{\text{II}}\text{-H}_2\text{O}_2$, as inferred from the experimental data (S.I., Fig. S11). However, the heterolytic cleavage is initiated by a homolytic O-O bond cleavage immediately followed by a proton/electron-transfer from the ammonium/ $\text{Fe}^{\text{II}}\text{-oxyl}$ that forms the $\text{Fe}^{\text{IV}}\text{-oxo}$ species and releases water.

Finally, we tested the same reaction mechanism under low pH conditions, *i.e.* starting from the H_2O_2 bound complex with protonated dialkylamine chain, $(\text{H}^+)\text{-}1^{\text{II}}\text{-H}_2\text{O}_2\text{-b}$. Thus, these calculations start from $5,3(\text{H}^+)\text{-}1^{\text{II}}\text{-H}_2\text{O}_2\text{-b}$ and a homolytic O-O bond cleavage barrier of $\Delta G^\ddagger = 8.2$ kcal mol^{-1} splits H_2O_2 into two OH radicals directly in an exergonic step of 3.6 kcal mol^{-1} to form $5(\text{H}^+)1^{\text{III}}(\text{OH})'/\text{OH}$ (S.I., Fig. S12). The electronic configuration of the latter consists of an $\text{Fe}^{\text{III}}\text{-hydroxo}$ with five unpaired electrons on the metal antiferromagnetically coupled to an OH radical (S.I., Table S15). Subsequently, a proton-coupled electron-transfer barrier gives the $\text{Fe}^{\text{IV}}\text{-oxo}$ species and a water molecule in a highly exergonic reaction step. These results are in line with the experimental work reported above. In the presence of acid, the substantial barrier for the PCET indicates that the nascent free

*OH may be easily scavenged by the MeOH solvent leading to the Fe^{III} species rather than yielding the Fe^{IV}-oxo directly. Our findings are consistent with those reported by Hirao et al. for the reaction of [Fe^{II}(TMC)]²⁺ with H₂O₂ in the absence of base.^[21]

In summary, we demonstrate that the introduction of a pendant amine group in the second coordination sphere of a non heme Fe^{II} complex modifies its reactivity toward H₂O₂ and allows the direct formation of an Fe^{IV}-oxo intermediate instead of the Fe^{III}OOH usually observed for related complexes lacking this second sphere moiety. To our knowledge, this is the first time that such an effect is demonstrated in an intra-molecular fashion. Activation parameters measured during the process correlate with the values previously associated to heterolytic O-O bond cleavage in the literature. The large (k_H/k_D) KIE is also in good agreement with the involvement of the amine group as an acid/base relay. Our mechanism is supported by density functional theory calculations, which shows that the mechanism involves a proton transfer from the proximal OH group of H₂O₂ towards the distal one, *via* the transient protonation of the pendant amine group. More precisely, the initial proton transfer to the alkylamine is followed by a homolytic O-O bond cleavage accompanied by proton-coupled electron transfer to form the Fe^{IV}-oxo species.

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Keywords: Fe complex • O-O bond breaking • Fe^{IV}-oxo • mechanism • N ligand

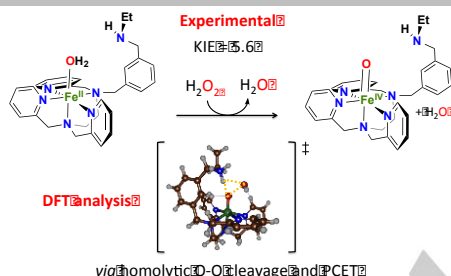
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Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

A novel synthetic iron(II) complex bearing a second sphere intramolecular base efficiently forms an iron(IV)-oxido species in the presence of H_2O_2 . Mechanistic studies demonstrate an overall heterolytic cleavage of the O-O bond constituted of an homolytic cleavage with a concerted proton coupled electron transfer.



Khaled Cheaib, Muhammad Qadri Effendy Mubarak, Katell Sénéchal-David, Christian Herrero, Régis Guillot, Martin Clémancey, Jean-Marc Latour, Sam P. de Visser, * Jean-Pierre Mahy, Frédéric Banse, * Frédéric Avenier*

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Selective formation of an $\text{Fe}^{\text{IV}}\text{O}$ or an $\text{Fe}^{\text{III}}\text{OOH}$ intermediate from $\text{Fe}^{\text{II}}-\text{H}_2\text{O}_2$: controlled heterolytic vs homolytic O-O bond cleavage by