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STUDY ON THE IRON COMPLEXES OF EXPANDED PORPHYRINS, PHTHALOCYANINES, AND PORPHYRAZINES

Bir Prakash Mishra
Dept of Chemistry J P Univ Chapra

Jai Ram Singh
Dept of Chemistry J P Univ Chapra

Abstract:

Iron porphyrin complexes, which have the same core structure as the heme cofactor, are perhaps the most widely used compounds in O_2 binding and activation studies. Early efforts were made in stabilizing an Fe–O_2 moiety as a functional mimic of O_2-bound hemoglobin and myoglobin, to gain structural and electronic insights into the nature of the Fe–O_2 bonding in these heme proteins. As early as 1936, Pauling and Coryell determined that the Fe–O_2 group in oxyhemoglobin was diamagnetic. This led to the proposal of several models to describe the nature of Fe–O_2 bonding ,which are detailed in several reviews.

Three limiting electronic descriptions have been considered: low-spin Fe^{II} with a singlet O_2 (the Pauling model), low spin Fe^{III} antiferromagnetically coupled to an $S = 1/2$ superoxide (the Weiss model) and an intermediate-spin Fe^{II} coupled to a triplet O_2 (the McClure–Goddard model). Various spectroscopic techniques, such as Mössbauer, resonance Raman,and X-ray absorption spectroscopies— have now lent credence to the Weiss description for oxyhemoglobin (*i.e.* that it is a ferric superoxo species).

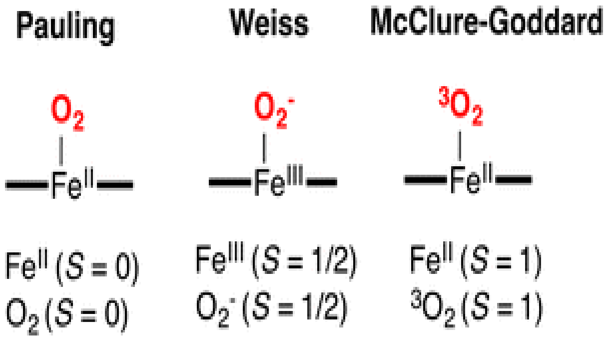

Fig. 1 Different models describing the nature of bonding in the Fe–O_2 intermediate in O_2-binding heme proteins.

A major hurdle in stabilizing the Fe–O_2 moiety for reversible oxygen binding in simple iron(II) porphyrins is the unwanted auto-oxidation reactions that lead to the formation of iron(III) porphyrin μ-oxo/peroxo dimers. Several studies have led to a description of the synthetic requirements needed to stabilize an Fe–O_2 adduct. In synthetic model complexes, reversible O_2 binding often requires an axial ligand, usually an aromatic nitrogen base (*e.g.* pyridine, *N*-methylimidazole), to stabilize the Fe–O_2 adduct against further oxidation and dimerization reactions. The structure of the porphyrin has also been found to directly affect the stability of the O_2 adduct. The axial ligand could be covalently attached to the porphyrin to direct O_2 binding. On the other hand, incorporation of H-bonding groups (such as pivalamide) into the secondary coordination sphere stabilizes the Fe^{III}-superoxo species without the need for an axial ligand. Steric hindrance about the porphyrin ligand also prevents unwanted dimer formation. Perhaps the earliest and most well-known example of

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the application of these synthetic strategies is the "picket-fence" porphyrin discovered by Collman and co-workers The diamagnetic Fe–O_2 adduct of this complex was isolated and characterized using X-ray crystallography, to show the bent, end-on binding of dioxygen to the iron porphyrin. Forty years after the picket-fence, the structural characterization of a five-coordinate Fe–O_2 adduct was achieved with a sterically bare porphyrin site-isolated inside a metal–organic framework. A number of examples since the picket-fence have shown that similar synthetic strategies can be successful for the stabilization of a ferric superoxo complex in a porphyrin scaffold, and these have been summarized in several reviews

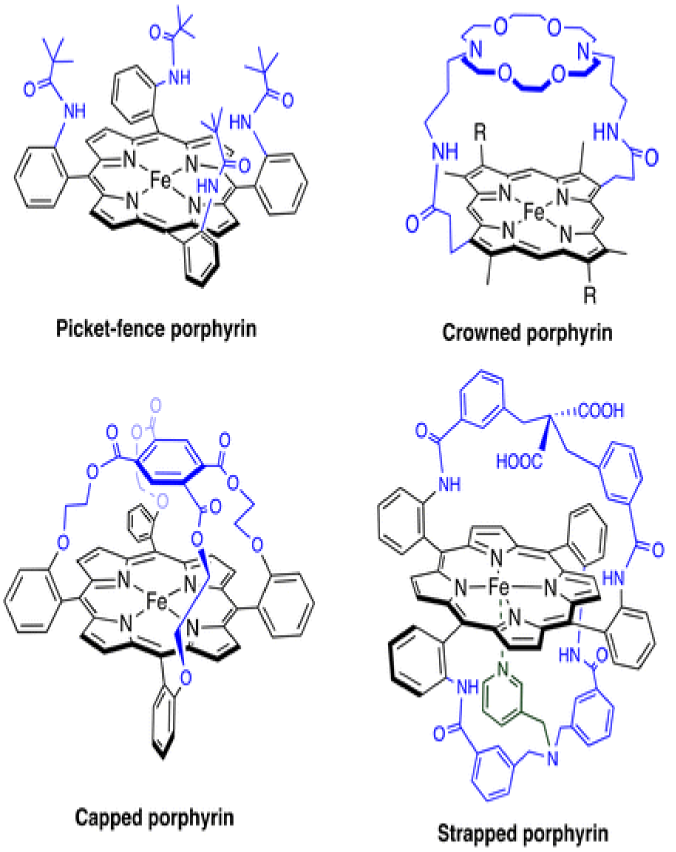

Fig 2 Examples of synthetic iron porphyrin complexes with covalently attached groups for the steric protection of the Fe–O_2 adduct: the picket-fence porphyrin,.

While the inherent reactivity of Fe^{II}(porphyrin) with O_2 is circumvented by synthetic design to mimic O_2 binding, such reactivity can be exploited for oxygenation reactions. One of the early products observed in the reaction between an Fe^{II} porphyrin and O_2 was a ferryl complex, Fe^{IV}(O) porphyrin, which could transfer its O-atom to triphenylphosphine (PPh_3) quantitatively to form triphenylphosphine oxide (PPh_3O) in toluene at −80 °C. This observed substrate reactivity at low temperature opened up the possibility for catalytic turnover at ambient temperatures. Exposure of a solution of Fe^{II}(TPP) (TPP = tetraphenylporphyrin) and excess PPh_3 to a stream of O_2 in toluene at 25 °C resulted in the catalytic formation of PPh_3O (with a turnover number of approximately 27). The catalyst is inactivated by the formation of a μ-oxo dimer, which is unreactive to triphenylphosphine

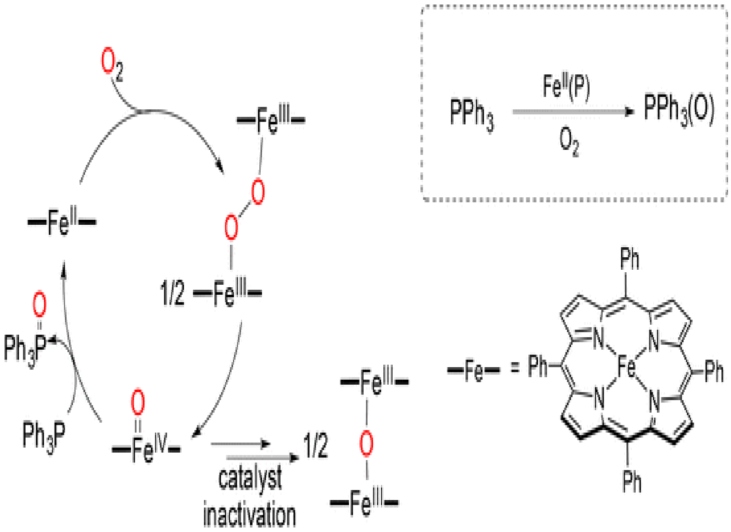

Fig. 3 Proposed mechanism for the catalytic oxygenation of triphenylphosphine by an Fe^{II} porphyrin/O_2 catalyst.

The related ferric peroxo porphyrins, the one-electron reduced analogs of ferric superoxo porphyrins, were synthesized following the addition of 2 equivalents of KO_2 (solubilized in crown ether) to an Fe^{III}(Cl)(TPP) complex *via* the reduced Fe^{II} porphyrin.Alternatively, the ferric peroxo porphyrin can be generated by electrochemical reduction of the ferric superoxo complex. Reactivity studies performed on these complexes showed that they are not electrophilic and are instead nucleophilic (*i.e.* they are capable of oxidizing electron-poor alkenes). Naruta and co-workers demonstrated that a ferric hydroperoxo species can be selectively prepared by different synthetic routes. The ferric peroxo complex $Fe^{III}(O_2)$(TMPIm) (TMPIm = imidazole-tethered trimesitylporphyrin) was prepared by either addition of O_2 and 1 equiv of cobaltocene ($CoCp_2$) in methanol, or addition of KO_2 to a solution of Fe^{II}(TMPIm). EPR and resonance Raman spectroscopies show results consistent with a side-on bound, η^2-peroxo ferric species. Protonation of this complex results in a spin-state change from high-spin to low-spin Fe^{III}, with a concomitant change from an η^2 to an η^1 O_2 binding mode for the ferric hydroperoxo complex, Fe^{III}(OOH)(TMPIm). Interestingly, porphyrin modification using a bulky xanthene group to provide steric hindrance results in the transient formation of an η^1, end-on bound ferric peroxo porphyrin complex

The ability to mimic efficient catalytic alkane oxygenations performed by heme monooxygenases using simple metalloporphyrins and O_2 has been an active field of research, due to its enormous industrial potential. A primary requirement for these catalysts is the formation of a metal–oxo species, which is the key oxidizing species in the heme enzymes. While catalytic C–H bond oxidation has been demonstrated with iron porphyrins and O_2 congeners such as PhIO, mCPBA and H_2O_2, oxidation with O_2 remains a significant challenge, in part due to the need for protons and exogenous reductants to cleave the O–O bond. Ellis and Lyons have reported the catalytic oxidation of light alkanes, propane and isobutene, with β-halogenated (Br, Cl) Fe^{III} porphyrins and O_2. An increase in the oxidation activity was observed with an increase in the number of halogens in the porphyrin ring. In particular, the perhalogenated complex, Fe^{III}(Cl)(TPPF$_{20}$β-Br$_8$), showed the highest activity with a TON (turnover number) of >13 000 in in the hydroxylation of isobutane to *t*-butanol at room temperature (25 °C). A mechanism was proposed), similar to the catalytic oxygenation of triphenylphosphine, where the active oxidant is a ferryl species activated by the electron-withdrawing halogen substituents. Subsequent studies by Labinger and Gray have shown that this mechanism is not viable, due to the stability of the Fe^{II} species of the perhalogenated porphyrins ($Fe^{III/II}$ = 0.31 V *vs.* AgCl/Ag) toward O_2. Instead, a radical-chain autoxidation mechanism was proposed (wherein the Fe^{III} porphyrin complex catalyzes the decomposition of the alkyl hydroperoxide that was formed over the course of the radical chain reaction with O_2. Moreover, the oxidative activity of this catalyst was inhibited upon addition of a radical trap. This mechanism is different in that it does not undergo a pathway analogous to those found in heme enzymes, but instead relies on the redox power and durability of the catalyst in reacting with alkyl hydroperoxides that are formed in the process.

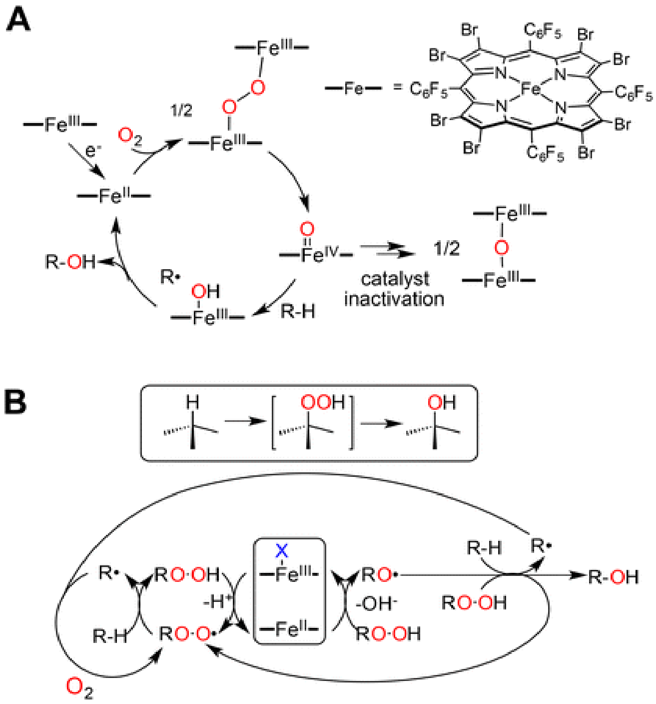

Fig. 4 Proposed mechanisms of the catalytic oxygenation of light alkanes by an Fe^{III} porphyrin/O_2 catalyst

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Iron(III) porphyrin, by itself, does not react with O_2. Catalytic turnover with O_2 is typically achieved by the addition of external co-reductants to generate Fe^{II}(porphyrin) and initiate the reaction, as shown in . Catalytic substrate oxidation has been previously demonstrated with Fe^{III}(porphyrins) and reductants, such as H_2 in colloidal Pt. Another possible point of entry into a catalytic oxygenation cycle is *via* the photolytic cleavage of a bis-iron(III)-μ-oxo porphyrin. Nocera and coworkers have shown that the use of Pacman porphyrin systems enables facile turnover due to greater substrate access to the photogenerated Fe^{IV}(O) species Irradiation of a solution of a bis-iron(III)-μ-oxo pacman porphyrin (DPDF)Fe_2O (DPDF = fluorinated Pacman porphyrin with a dibenzofuran spacer) in the presence of 1 atm of O_2 and hydrocarbons, such as toluene, cumene, diphenylmethane, and fluorene, results in the catalytic oxidation of these substrates with modest turnover numbers of up to 287. The key oxidizing species upon photolysis is proposed to be an Fe^{IV}(O) species, and the Fe^{II} porphyrin product after substrate oxidation reverts back to the bis-iron(III)-μ-oxo porphyrin upon exposure to O_2. This photocatalytic oxidation cycle using Pacman systems has also been used to oxidize O-atom acceptors such as phosphines, sulfides, and olefins.

Iron phthalocyanines, and the related iron porphyrazines, can also perform the same bioinspired catalytic oxidation reactions with O_2 typically associated with porphyrin complexes. For example, the catalytic oxygenation of PPh_3 has been observed with iron phthalocyanine catalysts and O_2. The catalytic substrate oxidation properties of iron phthalocyanines and other related complexes have been discussed in detail in several reviews. Interestingly, there have been no examples of structurally characterized O_2 adducts of iron phthalocyanines or iron porphyrazines. Fitzgerald and coworkers showed that iron(II) tetraanthracenotetraazaporphyrin (Fe^{II}(TATAP)), shows no affinity for O_2, and this was explained in terms of an unusually positive $Fe^{III/II}$ redox potential. For comparison, the highly electron-withdrawing species Fe^{II}($TPFPBr_8$) ($TPFPBr_8$ = octabromotetrakis(pentafluorophenyl)porphyrin), which undergoes O_2-mediated alkane oxidation *via* a radical chain autoxidation mechanism, was also shown to be inert towards O_2.

Iron Corroles and Corrolazines

In contrast to iron(II) porphyrins, which readily react with dioxygen, O_2 reactivity with iron corroles and corrolazines remains relatively unexplored. Examples of characterized Fe–O_2 adducts in corroles are non-existent in the literature, perhaps arising from the stabilization of the high-valent redox states in corroles, which is the opposite of what is required for O_2 reactivity (*i.e.* an electron rich metal center). Reduction to the anionic Fe(II) corrole may be performed electrochemically to access the iron(II) state for O_2 binding. Kadish and coworkers have shown that reduction of Fe^{III}(oec) (oec = octaethylcorrole) to $Fe^{II}(oec)^-$ occurs in a reversible manner at −0.68 V *vs.* SCE (saturated calomel electrode) in benzonitrile, however the reactivity of this species with O_2 was not studied. Murakami has shown that Fe^{III} corroles can be reduced to the Fe^{II} state by the addition of hydroxide ion (OH^-) in the presence of olefins but in the presence of O_2 at 25 °C, the Fe^{II} species undergoes outer-sphere electron transfer with O_2 to revert back to the Fe^{III} corrole complex.

Iron(III) corroles, in concentrated solutions, react with O_2 to form bis-corrole-diiron(IV)-μ-oxo dimer complexes. The mechanism by

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which the μ-oxo dimer forms has not been investigated, but is presumed to proceed through a mechanism similar to that of the formation of the μ-oxo dimer of the iron porphyrins, wherein an iron–superoxo species is transiently formed. Catalytic oxygenation of olefins and hydrocarbons has been reported by Newcomb using the formally tetravalent bis-corrole–diiron μ-oxo dimer complex $(TPFC)Fe_2O$ (TPFC = tris(pentafluoro)corrole).[101] Photolysis of this complex by irradiation with a 355 nm laser pulse results in the formation of a putative $Fe^{V}(O)$ corrole complex that oxidizes cyclooctene to cyclooctene oxide with *ca.* 200 turnovers in the presence of excess O_2 (The iron(IV) complex $Fe^{IV}(Cl)(TPFC)$ is also capable of oxidizing the C–H bonds of hydrocarbons such as cyclohexane and adamantane in the presence of *tert*-butyl hydroperoxide (*t*-BuOOH). Based on mechanistic studies, a radical-chain autoxidation mechanism was proposed, similar to that of the analogous $Fe^{III}(Cl)$ porphyrins. Although corroles are known to stabilize formally high-valent oxidation states, the possibility of ligand non-innocence in these systems complicates electronic structure assignments. For example, recent X-ray absorption spectroscopy studies on Fe(X)(tpc) (X = Ph, Cl, NO; tpc = triphenylcorrole) suggest that their iron centers can be described as Fe^{III}-like for X = Cl, NO, consistent with an $Fe^{III}(X)(tpc^{\cdot +})$ configuration, or Fe^{IV}-like for X = Ph, which is closer to an $Fe^{IV}(X)(tpc)$ description.

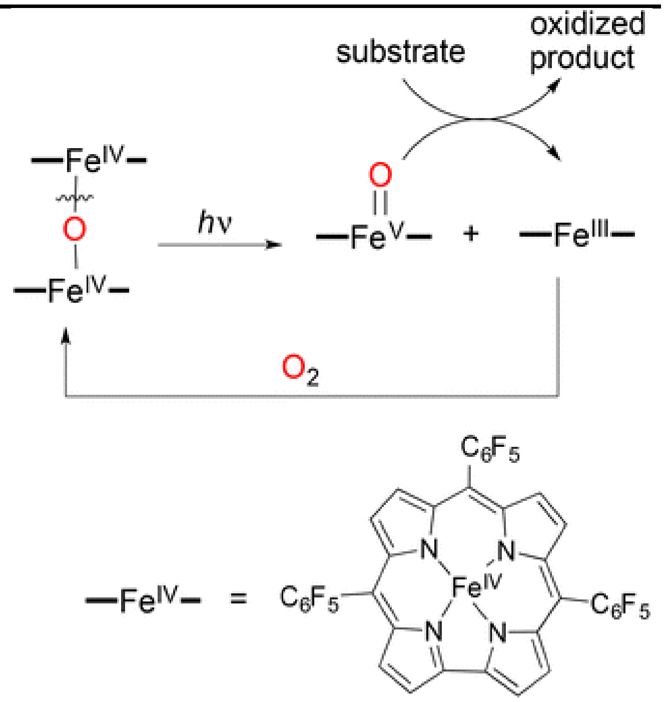

Fig. 5 Proposed mechanism for the photocatalytic oxygenation of substrates with $(TPFC)Fe_2O$ and O_2.

While iron(III) corroles form μ-oxo dimers in the presence of O_2, iron(III) corrolazine $Fe^{III}(TBP_8Cz)$ (TBP_8Cz = octakis(*tert*-butylphenyl)corrolazine) is remarkably unreactive towards dioxygen. However, in the presence of the oxidant H_2O_2, catalytic oxygenation of sulfides has been observed. Performing the oxygenation reaction of thioanisole with $Fe^{III}(TBP_8Cz)/H_2O_2$ in the presence of a large excess of $H_2{}^{18}O$ resulted in no incorporation of ^{18}O into the methylphenyl sulfoxide product, indicating that a high-valent iron–oxo species was not formed in the catalytic process. A competing pathway was indicated, where disproportionation of H_2O_2 to O_2 was observed. A mechanism was proposed that accounts for all of the observations, which suggests the formation of an iron(III)–hydroperoxide Fe^{III}–OOH adduct as the key oxidizing species in the sulfoxidation reaction.

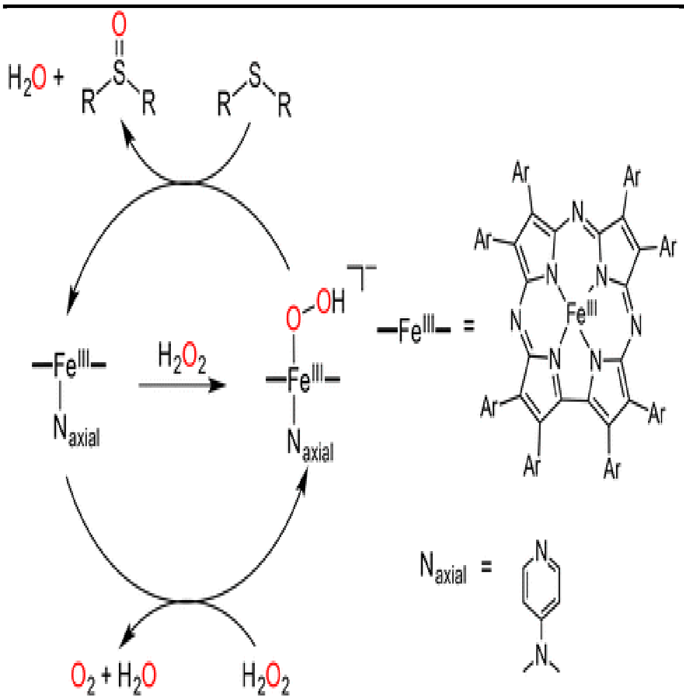

Fig. 6 Proposed catalytic sulfoxidation and catalase activity for $Fe^{III}(TBP_8Cz)$ and H_2O_2

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