Oxygen transfer reactions mediated by diiron complexes

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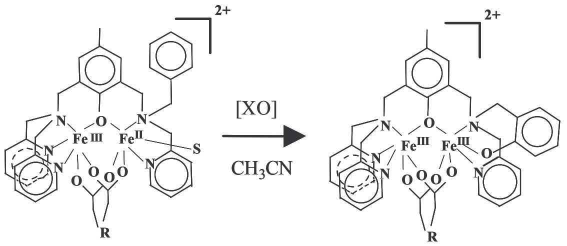
Non heme iron oxygenases catalyze a wide range of oxygen transfer and oxidation reactions, in particular aliphatic and aromatic hydroxylations. Examples include enzymes with mononuclear (eg. phenylalanine hydroxylase) or dinuclear (eg. methane monooxygenase) active sites. A few model systems have been reported to perform aromatic/aliphatic hydroxylations when treated with dioxygen under reducing conditions or with an activated oxygen surrogate. Most of them are or involve mononuclear species.

In the course of our studies of dinuclear iron systems, we reported the characterization of $[Fe^{II}Fe^{III}(L)(mpdp)(H_2O)]$ $(ClO_4)_2$ (mpdp = *m*-phenyldipropionate), a mixed-valent $Fe^{II}Fe^{III}$ complex of a hexadentate phenolato ligand (HL) bearing a dangling benzyl group (Scheme).[1] We report that in the presence of oxygen atom donors (XO, eg. *m*CPBA) the benzyl group of the ligand is almost quantitatively *ortho*-hydroxylated to a phenolate terminally bound to one iron in $[Fe_2(L\text{-}H+O)(mpdp)]^{2+}$. All available experimental evidences concurred to suggest that this reaction involves an oxo-$Fe^{IV}Fe^{IV}$ intermediate.[2] The analogous complex bearing a *t*-butyl group in place of the benzyl reacts similarly.[3] When H_2O_2 is the oxygen donor, the same overall reactions are observed, but they operate along a different mechanism.

Scheme (S=CH_3CN)



References

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[2] F. Avenier, L. Dubois, J.-M. Latour, *New J. Chem.* **2004**, *28*, 782-784.
[3] F. Avenier, L. Dubois, P. Dubourdeaux, J.-M. Latour, *Chem. Comm.* **2005**, 480-482.