Making and Breaking the O-O Bond at Molecular Iron Catalysts

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The formation and cleavage of the O-O bond is arguably the most important reaction in living organisms. Reductive O-O breakage takes place in cytochrome C oxidase.[1] This reaction constitutes the basic constituent of cellular respiration in aerobic organisms, and represents a primary source of energy. O-O cleavage also takes place in oxygenases,[2] and results in the generation of highly electrophilic high valent metal-oxo species, responsible for oxidative transformations. On the other hand, O-O bond formation takes place at a Mn_4Ca cluster in the Oxygen Evolving Center of Photosystem II (PSII) of green plans and some bacteria. In both oxidative and respiration enzymes, metal ions adopting high oxidation states result from reductive O-O cleavage reactions while in PSII they are responsible for O-O bond formation.[3]
Selected coordination complexes that reproduce structural aspects of enzymatic active sites have been shown to catalyze analogous reactions, and recently some of these complexes have turned into very attractive tools for organic synthesis.[4-8] In addition, the study of the mechanisms of action of these catalysts has shed light into the molecular details of enzymatic systems. Our research group undertakes this approach and aims at studying the chemistry of iron coordination complexes with chemically robust nitrogen-based ligands, and which can sustain high oxidation states.[5-8]

[1] S. Ferguson-Miller, G. T. Babcock, *Chem. Rev.* **1996**, *96*, 2889-2907.
[2] a) M. Costas, M. P. Mehn, M. P. Jensen, L. Que, Jr., *Chem. Rev.* **2004**, *104*, 939-986. B) B. J. Wallar, J. D. Lipscomb, *Chem. Rev.* **1996**, *96*, 2625-2658. C) E. I. Solomon, et al. *Angew. Chem. Int. Ed.* **2001**, *40*, 4570. d) S. Shaik, et al. *Chem. Rev.* **2010**, *110*, 949-1017. e) E. G. Kovaleva, J. D. Lipscomb, *Nat. Chem. Biol.* **2008**, *4*, 186-193.
[3] Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, Nature **2011**, 55.
[4] a) L. Que, W. B. Tolman, *Nature* **2008**, *455*, 333-340. b) A. Company, et al. in Iron-Containing Enzymes, Versatile Catalysts of Hydroxylation Reactions in Nature (S. P. De Visser, D. Kumar), RSC, Cambridge, 2011.
[5] a) A. Company et al. *J. Am. Chem. Soc.* **2007**, *129*, 15766. b) L. Gomez et al *Angew. Chem. Int. Ed.* **2009**, *48*, 5720.
[6] a) O. Cusso et al. *J. Am. Chem. Soc.* **2013**, *135*, 14871 b) O. Cussó et al. *Angew. Chem. Int. Ed.,* **2015**, *54(9)*, 2729.
[7] O. Cussó et al. *Org. Lett.* **2013**, *15*, 6158
[8] a) J. Lloret-Fillol *Nat. Chem.* **2011**, *3*, 897, b) Company et al. *J. Am. Chem. Soc.* **2014**, *136*, 4624, c) Codola et al. *Nat. Commun.* **2015**, *6*, 5865