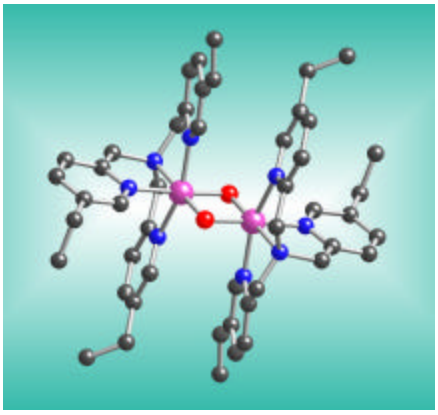
Size Discrimination in the Activation of Aliphatic C-H Bonds by an $Fe^{III}Fe^{IV}(\mu\text{-}O)_2$ Oxidant

Oleksandr P. Pokutsa, Antoni Mairata I Payeras, and Lawrence Que, Jr.
Chemistry Department and Center for Metals in Biocatalysis, University of Minnesota
oleksandr@chem.umn.edu

Methane is the best substrate for soluble methane monooxygenase (MMO) despite the fact that it has the strongest aliphatic C-H bond among alkanes. This selectivity has been attributed to a molecular sieving effect that provides greater access of the smaller methane to the diiron active site. Herein we report studies of substrate oxidation by $[Fe^{III}Fe^{IV}(\mu\text{-}O)_2(5\text{-}Me_3\text{-}TPA)_2]^{3+}$ (5-Me_3-TPA = tris(5-methyl-2-pyridylmethyl)amine), a complex with a core structure (see analog $[Fe^{III}Fe^{IV}(\mu\text{-}O)_2(5\text{-}Et_3\text{-}TPA)_2]^{3+}$) similar to that proposed for MMO oxidizing intermediate **Q**,[1] and by the analogous mononuclear $[Fe^{IV}(O)(5\text{-}Me_3\text{-}TPA)]^{2+}$ complex.[2] As previously observed for related oxoiron(IV) complexes,[3] the latter oxidant exhibits bond cleavage rates that correlate systematically with the strength of the substrate C-H bond, e.g. Ph_3CH > cyclohexanol > methanol. Surprisingly for $[Fe^{III}Fe^{IV}(\mu\text{-}O)_2(5\text{-}Me_3\text{-}TPA)_2]^{3+}$, the order of reactivity is opposite, with the more inert methanol (BDE = 93 kcal/mole) being oxidized six times faster than Ph_3CH (BDE = 81 kcal/mole). We speculate that this trend relates to the restricted access of the target C-H bond to the Fe_2O_2 core.



Supported by NIH GM-38767

1. Y. Dong, H. *et al.*, *J. Am. Chem. Soc.* **1995**, *117*, 2778-2792.
2. Lim, M. H.; Rohde, J.-U.; Stubna, A.; Bukowski, M. R.; Costas, M.; Ho, R. Y. N.; Münck, E.; Nam, W.; Que, L., Jr., *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3665-3670.
3. Kaizer, J.; Klinker, E. J.; Oh, N. Y.; Rohde, J.-U.; Song, W. J.; Stubna, A.; Kim, J.; Münck, E.; Nam, W.; Que, L., Jr., *J. Am. Chem. Soc.* **2004**, *126*, 472-473.