

L Que abstract for Girona Seminar 2018 lecture

## **In Pursuit of the Elusive Fe(V)=O Oxidant in Bio-inspired Nonheme Iron-Catalyzed Oxidations**

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It has been 20 years since we initiated efforts to mimic the oxidation chemistry of nonheme iron enzymes and discovered the first example of a nonheme iron complex,  $[[\text{Fe}^{\text{II}}(\text{TPA})(\text{NCMe})_2]^{2+}$ , to be capable of using  $\text{H}_2\text{O}_2$  as oxidant to catalyze the stereospecific hydroxylation of alkanes and the epoxidation and *cis*-dihydroxylation of olefins. Other  $\text{Fe}^{\text{II}}(\text{N}4)$  catalysts have since been identified and developed by a number of groups. The observation that at least some  $^{18}\text{O}$  from labeled water could be incorporated into the oxidation products led us to postulate a water-assisted mechanism involving an  $(\text{N}4)\text{Fe}^{\text{V}}(\text{O})(\text{OH})$  oxidant, strong evidence for which was obtained by Costas and Cronin using cryospray mass spectrometry. However, no experimental insight into the electronic structure of this elusive species could be obtained until more recently. The discovery of White that carboxylic acid additives modulated the chemistry of these catalysts opened new doors for catalyst development and applications in synthetic organic chemistry, as well as for obtaining mechanistic insight. Talsi used EPR to identify a number of fleeting  $S = \frac{1}{2}$  species that could represent the elusive  $\text{Fe}^{\text{V}}(\text{O})$  oxidant. The most intriguing of these was an EPR signal with fairly low  $g$ -anisotropy at  $g = 2.07, 2.01, 1.95$ , which accounted for  $<5\%$  of the Fe in the samples but decayed at a rate dependent on substrate concentration. Serrano-Plana, Company and Costas recently discovered a related  $\text{Fe}^{\text{II}}(\text{N}4)$  catalyst capable of producing this  $g = 2.07$  species in 40-50% yield, corresponding to an intermediate exhibiting the fastest rate for cyclohexane hydroxylation determined to date. Our spectroscopic and computational studies on this intermediate reveal a unique electronic structure that is predominantly  $\text{Fe}^{\text{V}}(\text{O})(\text{O}_2\text{CR})$  in character with some contributions from its  $\text{Fe}^{\text{III}}(\text{OOC}(\text{O})\text{R})$  and  $\text{Fe}^{\text{IV}}(\text{O})(\bullet\text{OC}(\text{O})\text{R})$  electromers mixed in. These details will be elaborated upon in my talk.