

TRAPPING A HIGHLY REACTIVE NON-HEME IRON INTERMEDIATE THAT OXYGENATES STRONG C-H BONDS WITH STEREORETENTION

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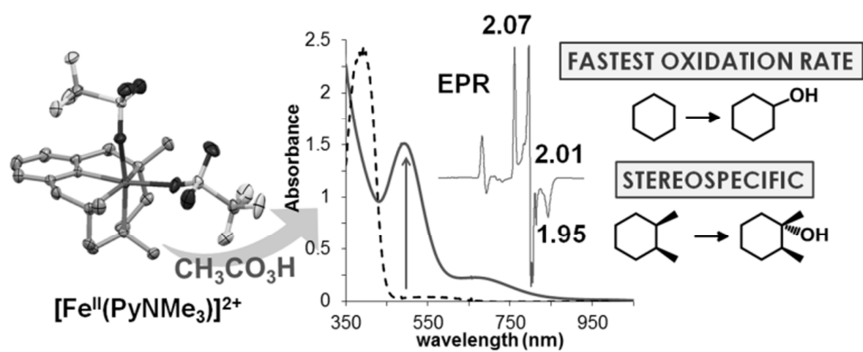
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Mononuclear iron(III)-peroxo species are key intermediates in the catalytic cycle of many iron enzymes that carry out O₂ activation including cytochrome P450, Rieske dioxygenases, lipoxygenases or alpha-ketoglutarate-dependent oxygenases¹. These enzymes are involved in many essential processes and their malfunction is related to several illnesses, such as inflammatory diseases or cancer. Due to their biological relevance there is an intrinsic interest in understanding the chemistry of iron(III)-peroxo compounds.²⁻⁵ Of particular importance are reactions that involve breakage of the O-O bond, and reaction of these peroxide species with substrates difficult to oxidize such as alkanes and arenes.

In the present work,⁶ a metastable mononuclear ferric peracetate complex Fe^{III}-OOCOMe (**2**) has been generated at cryogenic temperatures by reaction of excess peracetic acid with a new nitrogen-based tetradentate iron(II) precursor [Fe(CF₃SO₃)₂(PyNMe₃)] (**1**). This intermediate species has been spectroscopically characterized by UV-Vis, cryospray mass spectrometry (CSI-MS) and EPR, the latter revealing the presence of two S = 1/2 species associated with the chromophore of **2**. Compound **2** is kinetically competent to perform stereospecific and site selective hydroxylation of strong C-H bonds of alkanes (BDE ~ 100 kcal·mol⁻¹) through a Hydrogen Atom Transfer (HAT) mechanism with reaction rates higher than those attained with the most reactive oxoiron(IV) described up to date. Thus, this work constitutes the first example where synthetic non-heme iron species responsible for stereospecific and site selective C-H hydroxylation are spectroscopically trapped, and its catalytic reactivity against C-H bonds can be directly interrogated by kinetic methods.



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