

Chemistry Colloquium

Wednesday, November 3, 12pm

Virtual Event

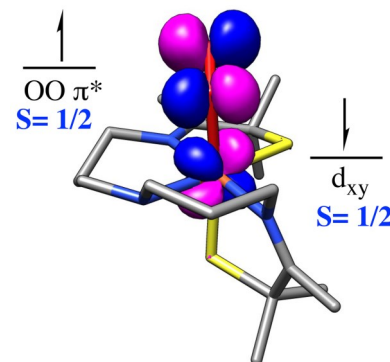
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“Cleavage of Strong C-H Bonds by a
Thiolate-Ligated Fe(III)-Superoxo Complex ”

Abstract: Thiolate (RS⁻) ligands have been shown to lower the activation barrier to O₂ binding, and facilitate peroxy O-O bond cleavage, and the cleavage of strong C-H bonds. We will describe an alkyl thiolate-ligated Fe(II) complex that reacts with dioxygen (O₂) to form an unprecedented example of a reactive iron superoxo (RS-Fe(III)-O₂) intermediate that is capable of cleaving strong C-H bonds. A thiolate-ligated iron superoxo is proposed to play a key role in the biosynthesis of β-lactam antibiotics, as well as the prevention of cancerous tumor metastases. Isopenicillin N-synthase (IPNS) catalyzes the former, and cysteine dioxygenase (CDO) the latter. Very few iron superoxo compounds have been reported, and none are capable of cleaving strong CH bonds. Spectroscopic characterization, and calibrated DFT and TD-DFT calculations, show that the frontier orbitals of our RS-Fe(III)-O₂ consist of two strongly coupled unpaired electrons of opposite spin, one in a superoxo p*(O-O) orbital, and the other in an Fe(d_{xy}) orbital. Both the calculated and experimental electronic absorption spectrum of our RS-Fe-O₂ are similar to that of the putative IPNS superoxo intermediate, as well as an intermediate involved in the catalytic cycle of CDO. The rate at which our superoxo converts to a putative iron hydroperoxo (Fe(III)-OOH), is shown to depend on the C-H bond strength of the solvent or sacrificial H-atom donor, and a deuterium isotope effect ($k_H/k_D=4.8$), comparable to that of IPNS ($k_H/k_D=5.6$), is observed. As demonstrated by the presence of a low energy thiolate → Fe-O₂ charge transfer transition, the electron-rich alkyl thiolate likely plays a role in increasing reactivity by creating a more basic superoxo. The bond dissociation energy (BDE) of the C-H bonds cleaved by our RS-Fe-O₂ superoxo compound (92 kcal/mol) are comparable to those cleaved by the enzyme IPNS (93 kcal/mol).



Zoom Link: <https://rochester.zoom.us/j/93379813487>

Website: https://events.rochester.edu/event/chemistry_inorganic_colloquium_kovacs

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