

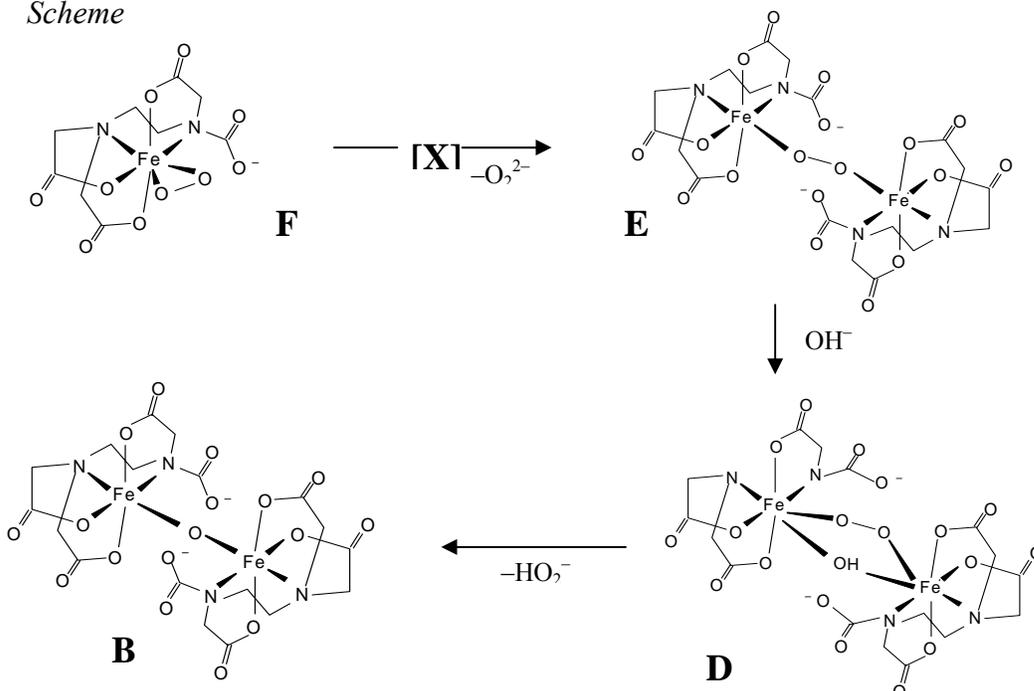
## Electron Paramagnetic Resonance Investigation of Peroxo Species in Fe(III)EDTA-Hydrogen Peroxide System

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A detailed EPR investigation on peroxo species in the Fe<sup>III</sup>-EDTA-hydrogen peroxide was carried out. The EPR measurements were performed on solutions obtained by mixing the ferric ions (500  $\mu$ l, 0.05 mol/l) with EDTA. The amount of EDTA in the mixture was in excess and final molar ratio of EDTA to Fe<sup>III</sup> was 1.3 : 1.0. The pH of the solution was adjusted by using KOH (0.5 mol/l). The reaction of Fe<sup>III</sup>-EDTA with hydrogen peroxide was studied by adding H<sub>2</sub>O<sub>2</sub> to the solution. The concentration of H<sub>2</sub>O<sub>2</sub> in the final solution was in excess. The resultant deep purple solution was quenched at different time intervals to see its formation and then further decomposition. Studies were carried out at different pH (10.5-11.8).

The reaction of the diiron(III)-EDTA complex with H<sub>2</sub>O<sub>2</sub> in alkaline medium forms the six-coordinate [Fe<sup>III</sup>-EDTA]<sup>-</sup> species at acidic pH~1, which is converted to diiron(III)-EDTA complex, [(EDTA)Fe<sup>III</sup>-O-Fe<sup>III</sup>(EDTA)]<sup>4-</sup>, upon raising the pH to~10.4 and the H<sub>2</sub>O<sub>2</sub> reacted with the diiron(III) complex to give peroxide/hydroperoxide related adducts. Interestingly, the reaction tears apart the dimers to result in peroxo adduct, seven-coordinate mononuclear [(EDTA)Fe<sup>III</sup>( $\eta^2$ -O<sub>2</sub>)]<sup>3-</sup> (**F**), which was stable only at very high pH. Moreover, the decomposition of this peroxo adduct can give two species a 6-coordinate  $\mu$ -peroxo diiron(III) complex [(EDTA)Fe<sup>III</sup>-(OO)-Fe<sup>III</sup>(EDTA)]<sup>4-</sup> and a 7-coordinate  $\mu$ -peroxo  $\mu$ -hydroxo diiron(III) complex [(EDTA)Fe<sup>III</sup>-(OO)(OH)-Fe<sup>III</sup>(EDTA)]<sup>5-</sup>.

Scheme



We have also initiated a similar study on the reaction of hydrogen peroxide with other iron(III) complexes, iron(III)-N-hydroxyethylethylenediaminetriacetic acid (HEDTA). Currently, we are analyzing the data to determine ZFS parameters of the species. This will enhance our understanding on the characterization of the species. A paper on this topic of research will be submitted to the *Inorganic Chemistry* in summer, 2008.