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Mechanistic studies of the decay of a group of nonheme diiron(III)-peroxo complexes

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The investigation of dioxygen binding and activation in dinuclear iron complexes has attracted recent interest because of the presence of carboxylate bridged dinuclear iron sites in several biologically important proteins, such as the R2 protein of ribonucleotide reductase, the hydroxylase component of methane monooxygenase and fatty acid desaturases [1]. In the first step of oxygen activation, the diiron(II) centre binds oxygen to form a diiron(III)-peroxo adduct which then undergoes O–O bond cleavage to form different active intermediates depending upon the protein. The lifetime of the peroxo intermediate varies widely from protein to protein.

Structures for three diiron(III)-peroxo complexes have been reported in recent years. Although the structures and related studies have greatly enhanced our understanding about the formation of the peroxide intermediate in the proteins, the process of breaking the O–O bond and interaction with substrate is far from understood. In this report we present kinetic studies of the decomposition of a group of closely related diiron(III)-peroxo complexes and their interaction with triphenylphosphine as a substrate. Kinetic studies of the decomposition of $[Fe^{III}_2(O_2)(hptp)(O_2CR)_n]^{2+/1+}$ (hptp = anion of N, N, N¢ N¢tetrakis(2-pyridylmethyl)-2-hydroxy-1,3-diaminopropane; RCO_2^- = various substituted benzoic acid; $n = 1$ or 2) at low temperature shows a pseudo first order rate of decay. The rate of decay depends both on the pK_a of the bridging benzoate and the concentration of PPh_3 present in the solution. Our data show the formation of a 1:1 adduct between the peroxo complex and PPh_3 before decomposition. The major finding of this work is the remarkable stability of the peroxo complex generated from $[Fe^{III}_2(O_2)(hptp)(O_2CPh)_2]^+$ which decomposes roughly two orders of magnitude slower than the corresponding mono benzoate complex. This is in contrast with an earlier finding from this group which showed that increased electron donation to the core facilitates cleavage of the peroxo species. The present report discusses the effect of coordination site saturation compared to the electronic effect on extending the lifetime of the peroxo species.

References

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