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Reactions of iron(III) porphyrins with peroxides and hydrogen peroxide: Mechanistic insights

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Iron(III) porphyrin catalysed oxidations of different substrates by hydroperoxides and hydrogen peroxides have been the choice of many research groups in the recent years, the reasons being their easy availability and the eco-friendly by-products. Intermediates in such oxidation reactions have been the subject of intensive debate [1]. Various research groups have adduced evidence in favour of homolytic and hetrolytic cleavage of the peroxo-bond; there are also reports suggesting a unified mechanism for all oxidants [2,3].

$$\begin{array}{ccccc} [\mathrm{PFe(III)}]^{+} + \mathrm{Ox} & \xrightarrow{\text{fast}} & [\mathrm{PFe(III)\text{-}Ox}] & \xrightarrow{\text{rds}} & \left[\begin{array}{l}\text{Reactive}\\ \text{intermediate}\end{array}\right] \\ & & & & \downarrow \mathrm{S} \\ & & & & [\mathrm{PFe(III)}]^{+} + \mathrm{SO} \end{array} \qquad (1)$$

Thus a generalized equation for such a oxidation reaction shown in (1) where P is the porphyrin dianion, Ox is the oxidant, S is the substrate and SO is the oxidized product. Recent studies in our laboratory have indicated that formation of such intermediate(s) in solution is highly dependent on the choice of the solvent and the catalyst involved. Generation, identification and reactivity of such intermediate(s) and the protocol for the activation of the catalyst are discussed.

References

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