

IRON(III) π -DICATIONS: A KEY INTERMEDIATE TOWARDS BIOINSPIRED UMPOLUNG OF CHLORIDE

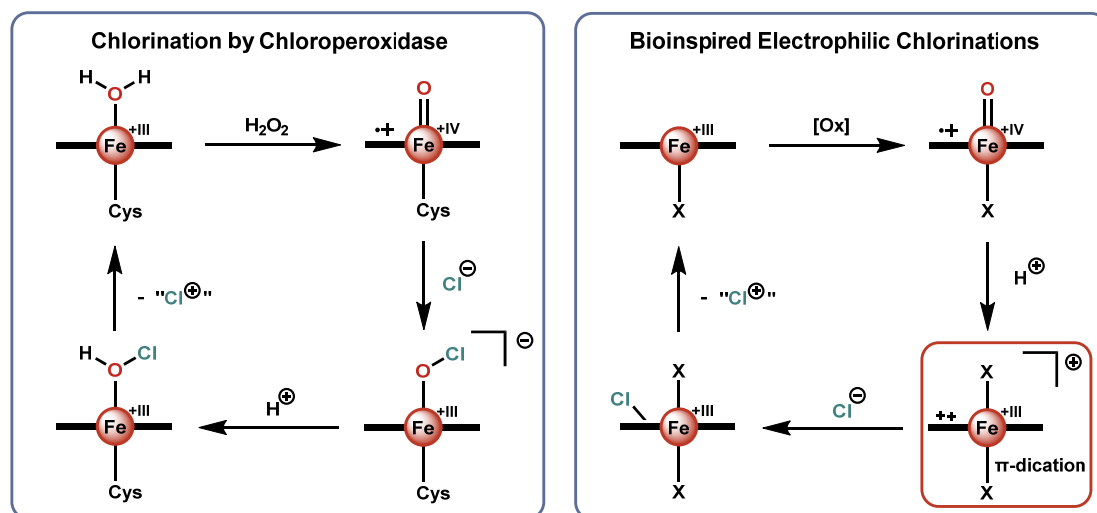
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The heme-containing enzyme Chloroperoxidase performs the umpolung of chloride *via* the formation of an iron(III) hypochlorite intermediate from Compound I and chloride [1]. Inspired by this environmentally benign method for electrophilic chlorinations, chemists have sought to reproduce such reactivity using simple *meso*-substituted porphyrins [1]. A mechanistic divergence was observed wherein stoichiometric chlorinations proceed *via* the formation of a *meso*-chloro-isoporphyrin [2]. A key intermediate to generating this isoporphyrin is an iron(III) π -dication, obtained from the reaction of Compound I with acid [3]. Iron(III) π -dications are a rare find in the literature and little characterization and reactivity has been reported [3, 4]. To further understand these curious species we explored the effect of the *meso*-substituent on the accessibility of a π -dication, allowing us to identify a novel one bearing the *meso*-tetraphenylporphyrin ligand [5]. We performed extensive characterization and investigated the tunability of the system, thereby providing valuable insights for the rational design of catalysts for the bioinspired umpolung of chloride [5].



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