

## Effects of Meso Ligands and Metal Center on the Catalytic Efficiency of Mn(III) and Fe(III) Meso-Tetrakis Porphyrins

Araújo-Chaves, J.C.<sup>1</sup>, Pessoto, F.S.<sup>1</sup>, Inada, N.M.<sup>2</sup> and Nantes, I.L.<sup>1</sup>

<sup>1</sup>CIIB-UMC Mogi das Cruzes-SP, Brazil

<sup>2</sup>IFSC-USP São Carlos-SP, Brazil

In this study, the rates of *tert*-BuOOH consumption ( $k_2/[tert\text{-BuOOH}].\text{min}^{-1}$ ) at pH 8.5 were obtained for the anionic Fe(III) and Mn(III) *meso-tetrakis (para-sulfonatophenyl)* porphyrin (TPPS<sub>4</sub>) and for the cationic *meso-tetrakis 4-N-methyl pyridinium* (TMPyP) as a function of  $[tert\text{-BuOOH}]$ . The dissociation constants ( $K_s$ ) and the maximal rates ( $k_2$ ) were obtained and thus, it was possible to determine the respective catalytic efficiencies:  $k_2/K_s$  (MnTPPS<sub>4</sub>) =  $1.2 \times 10^4 \text{ M}^{-1}.\text{s}^{-1}$ ,  $k_2/K_s$  (FeTPPS<sub>4</sub>) =  $10 \times 10^4 \text{ M}^{-1}.\text{s}^{-1}$ ,  $k_2/K_s$  (MnTMPyP) =  $0.012 \times 10^4 \text{ M}^{-1}.\text{s}^{-1}$ ,  $k_2/K_s$  (FeTMPyP) =  $1.3 \times 10^4 \text{ M}^{-1}.\text{s}^{-1}$ . The lower catalytic efficiency of both manganese porphyrins relative to the iron porphyrins can be assigned to two factors: low reactivity of hydroperoxides as oxygen donor to manganese(III) porphyrins and the incapacity of oxomanganese to use peroxide as reducing agent for recycling. Accordingly, the presence of 150  $\mu\text{M}$  GSH duplicated the peroxide consumption by the manganese porphyrins. Differently of the parallel direct reaction of GSH with *tert*-BuOOH, in the presence of manganese porphyrins, crescent amounts of GSH did not lead to linear increase of peroxide consumption, probably due to direct reduction of the metal center by the thiol group. The lower catalytic efficiency of cationic porphyrins could be assigned to the retention of OH<sup>-</sup> ions impairing the coordination with the metal that favors the catalytic efficiency. Contrary to Fe(III) meso tetakis porphyrins, the manganese partners cleave peroxides predominantly by heterolytic scission of O-O bond. Taken together, these results point out the manganese porphyrins as catalysts able to mimic the activity antioxidant of glutathione peroxidase.

Key words: TMPyP, TPPS<sub>4</sub>, *tert*-BuOOH, catalysis

Supported by: FAPESP, CNPq, FAEP-UMC