Protein-based Radical Intermediates in bi-functional hemeperoxidases

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Catalase-peroxidases (KatGs) are bifunctional heme enzymes with a high structural homology to cytichrome c peroxidase and a catalatic activity comparable to catalases. These unique features of KatGs make them good system to study and understand the role of alternative electron pathways both in heme enzymes. In particular, it is of interest to study the poorly understood role of tyrosyl and tryptophanyl radicals as alternative cofactors in the catalytic cycle of peroxidases and catalses. We have applied a powerful combination of multifrequency (9-285 GHz) EPR spectroscopy, isotopic labeling of Trp and Tyr residues and site-directed mutagenesis to unequivocally identify the reactive intermediates formed by the *Synechocystis* PCC6803 katG. Recent findings on the radical intermediates in *B. pseudomallei* and *M. tuberculosis* KatGs and the selectivity towards substrates will be discussed.

Proposed catalytic cycle of KatGs. Tyrosyl and tryptophanyl radical intermediates were discriminated by using isotopic labeling and High-field EPR spectroscopy.