講演会のご案内

日時：2014年9月16日（火）13:30～15:00

場所：北海道大学理学部5号館2階5-205号室

講師：John H. Dawson教授

所属：University of South Carolina
Department of Chemistry and Biochemistry

演題：Dioxygen Binding and the Switch to Peroxide Activation by the Globin Sea Worm Peroxidase, *Amphitrite ornata* Dehaloperoxidase

共催：日本生化学会北海道支部

講演概要

The coelomic hemoglobin, dehaloperoxidase (DHP), from the sea worm Amphitrite ornata is the first heme-containing globin possessing physiological peroxidase enzymatic activity. DHP catalyzes the H_2O_2-dependent dehalogenation of halophenols by O-atom addition to generate the corresponding quinones. As both a dioxygen binding globin and a peroxidase, it is a dual function heme protein. With two different starting oxidation states required for reversible O_2 binding (ferrous) and peroxidase activity (ferric), the question arises as to how DHP manages the two functions. In our previous study, the co-presence of substrate 2,4,6-trichorophenol (TCP) along with H_2O_2 has been found to be essential for the activation of enzymatically inactive oxyferrous DHP (oxy-DHP). Based on that study, a functional switching mechanism involving substrate (TCP•) radicals was proposed. To further support this mechanism, we have further examined the H_2O_2-mediated conversion of oxy-DHP to ferric state triggered by both biologically relevant [TCP, 4-bromophenol (4-BP)] and non-relevant (ferrocyanide, etc.) compounds. We also find that all of these conversion reactions are completely inhibited by the presence of ferric heme ligands (KCN, imidazole), indicating an involvement of the ferric oxidation state. Furthermore, the spin-trapping reagent 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) effectively inhibits the TCP/4-BP (but not ferrocyanide)-triggered oxy- to ferric conversion of DHP. Taken together, the results demonstrate that substrate TCP triggers the activation of oxy-DHP into a catalytically active peroxidase through direct oxidation by TCP radicals that are generated and start to accumulate upon H_2O_2-oxidation of TCP catalyzed by trace amounts of ferric DHP initially present in the oxy-DHP sample. The data presented in this study further clarify the mechanism of how halophenol substrate triggers the activation of hemoglobin DHP into a peroxidase. (Funding: NSF MCB 0820456).

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