Peroxidase Electron Transfer in Lipid Films: What's going on?

James Rusling,[1] Zhe Zhang,[2] Salem Chouchane[3] and Richard Maggliozzo[3]

[1]University of Connecticut
Department of Chemistry
55 N. Eaqleville Rd.
Storrs, CT 06269-3060
USA

[2]Nature's Sunshine Products
1655 N Main Street
Spanish Fork, UT 84606
USA

[3]Brooklyn College, City Univ. of New York,
Department of Chemistry
2900 Bedford Ave.
Brooklyn, NY 11210-2889
USA

Stable films of the lipid dimyristoylphosphatidylcholine (DMPC) and M. tuberculosis catalase-peroxidase (KatG), several other peroxidases, myoglobin and catalase showed direct, reversible Fe(III)/Fe(II) voltammetry on pyrolytic graphite electrodes. All of these enzymes showed cathodic electrochemical responses to hydrogen peroxide and oxygen. Amperometric responses for these films to hydrogen peroxide at 0 V are likely to contain significant contributions from catalytic reduction of oxygen produced during the catalytic cycles by reaction of peroxide with peroxidase compound I. Relative apparent turnover rates at pH 6 based on steady-state currents at 0 V vs. SCE in the presence of hydrogen peroxide were in the order horseradish peroxidase (HRP) ¿ cytochrome c peroxidase (CcP) ¿ soybean peroxidase (SP) ¿ myoglobin (Mb) ¿ KatG ¿ catalase. Lower currents for the very efficient peroxide scavengers KatG and catalase may be related to the instability of their compounds I in the presence of hydrogen peroxide. KatG catalyzed the electrochemical reduction of oxygen more efficiently than catalase and CcP, but less efficiently than the other peroxidases. DMPC films incorporating glucose oxidase and peroxidases gave good analytical responses to glucose, demonstrating the feasibility of dual enzyme-lipid films for biosensor fabrication. Mechanistic implications of our results will be discussed.