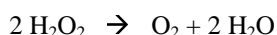


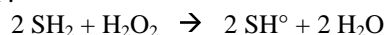
# Catalysis of Oxygen Reduction by Catalase and HRP on Glassy Carbon Electrodes : Comparison of the Mechanisms

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Catalase and horseradish peroxidase (HRP) are both hemic enzymes containing Fe(III)-protoporphyrin as prosthetic group. Both enzymes usually work with hydrogen peroxide as substrate; catalase catalyses the disproportionation of hydrogen peroxide into oxygen and water:



and HRP catalyses the oxidation of numerous substrates (noted SH<sub>2</sub>) by hydrogen peroxide, following the general reaction :



The glassy carbon electrodes (GCE) were used either clean, or after a preliminary electrochemical treatment. Current-potential curves were plotted at 20 mVs<sup>-1</sup> from +0.10 to -1.10 V/SCE with catalase and HRP either dissolved in solution (0.15M NaCl - 0.1M potassium phosphate buffer pH 8.0), or adsorbed on the GCE surface. Adsorption was achieved thanks a 15-minute immersion of the electrode in a DMSO solution that contained the enzyme.

In the absence of enzyme the current-potential curves obtained with clean and with electrochemically treated GCE matched the theoretical curves of oxygen reduction. When catalase or HRP was present in solution, a small current increase was observed at the most negative potential values. These data were compared with the theoretical curves derived from a numerical model, and the effect of the addition of hydrogen peroxide into the solution was investigated. It was concluded that the observed current increases were fully explained by mechanisms where hydrogen peroxide intervenes as an intermediate species. Hydrogen peroxide results from the direct electrochemical reduction of oxygen on the electrode and is further consumed by catalase to form oxygen again. This induces a catalytic current, as represented in Scheme I of Figure 1. In a quite similar way, HRP is able to reduce hydrogen peroxide into water, via a direct electron transfer from the electrode, as represented in Scheme I of Figure 2. This mechanism has already been clearly stated in the literature [1].

On the contrary, when catalase or HRP were adsorbed on the electrode surface, a high catalytic current was observed at potential around -0.10 V/SCE. Actually this catalysis was observed only with clean (i.e. without electrochemical treatment) GCE for catalase, and with both types of GCE for HRP. The demonstration was done that these high current increases can no longer be explained by the classic pathways. A direct electron transfer from the electrode is required as in Schemes II of Figures 1 and 2. The mechanism was discussed with respect to the hydrophobic/hydrophilic properties of the clean and treated GCE, and with respect to the localization of the hemic group in both enzymes: deeply buried in catalase, and easily accessible in HRP. For HRP some possible fine mechanism was suggested with the intervention of different intermediate species of HRP,

according to the thermodynamic data available in the literature. To our knowledge, such a catalysis of oxygen reduction by catalase [2] and HRP [3] represent innovative results, which may give some pertinent contribution to the explanation of aerobic biocorrosion under marine biofilms [4].

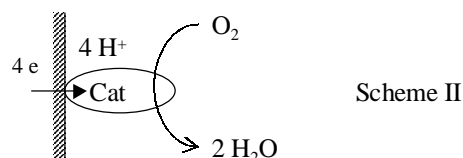
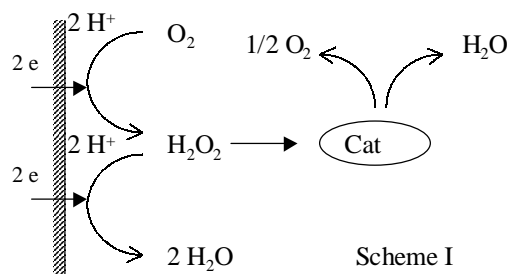


Fig. 1. Proposed mechanisms of the catalase-catalyzed electrochemical reduction of oxygen.

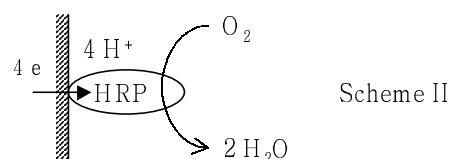
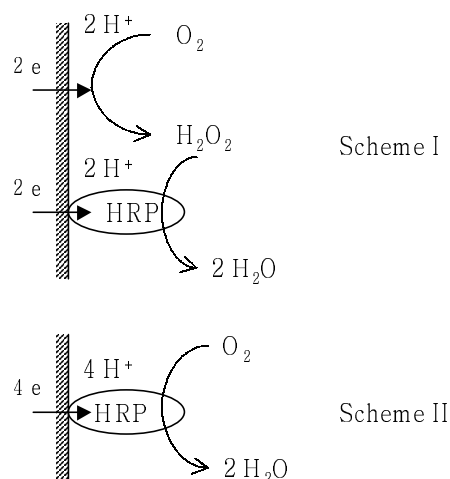


Fig. 2. Proposed mechanisms of the HRP-catalyzed electrochemical reduction of oxygen.

## References

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