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K05 VANADIUM PEROXIDASES : STRUCTURE AND FUNCTION.

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Vanadium haloperoxidases form a new class of enzymes that contain vanadium as a prosthetic group. The bromoperoxidases from seaweeds, catalyze the oxidation of bromide and the chloroperoxidases which have recently been discovered in fungi catalyze also effectively the oxidation of chloride. The prosthetic group in these enzymes has structural features similar to vanadate and the metal oxide can be removed which renders the enzyme inactive. It is possible to reactivate the peroxidases by the addition of vanadate. This property in combination with the results of a variety of biophysical techniques suggests an active site in which vanadium is ligated to at least 4 oxygen functions and one or two nitrogen atoms possibly from histidines [1]. Addition of substrates does not affect the redox state of the metal and further in the reduced state the enzyme is inactive. Our results suggest that no redox changes occur during catalysis and that the metal is involved in the binding of hydrogen peroxide and subsequent formation of an activated peroxo-intermediate by acting as Lewis acid [2]. Extensive steady-state studies have been carried out which show that the chloroperoxidase reacts sequentially with its substrates and is able to produce HOCl at high concentrations [3]. The vanadium enzyme exhibited a high thermostability and displayed high stability in organic solvents. We recently succeeded in sequencing the gene coding for the chloroperoxidase (68 kDa) and its derived amino acid sequence [4]. We have compared this sequence with that available for the vanadium bromoperoxidase from a seaweed [5]. There is a large sequence homology with this vanadium enzyme. However, sequence similarity with other known peroxidases was not found except for a small region which shared limited similarity with bacterial haloperoxidases and other α/β -hydrolase-fold enzymes. Some of the structural properties in relation to the catalytic properties will be discussed.

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