Regulation Mechanism of a Novel Heme-Containing Aldoxime Dehydratase, OxdB

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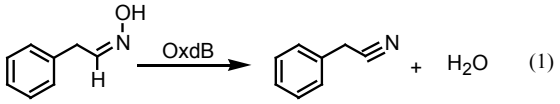
Phenylacetaldoxime dehydratase from *Bacillus* sp. strain OxB-1 (OxdB) catalyzes the dehydration reaction from Z-phenylacetaldoxime (PAOx) to phenylacetonitrile (PAN) (eq 1).



(1)

OxdB is a 40kDa monomer protein which contains a protoheme. The activity of ferrous OxdB was 1150-fold higher than that of ferric OxdB, indicating that the ferrous heme was the active site for OxdB catalysis. In this work, the structure and function relationships of OxdB were studied by spectroscopic and mutagenesis methods. Electronic absorption and EPR spectroscopies revealed that the coordination structure of the heme in OxdB was similar to that of myoblobin. Although ferric OxdB was inactive, PAOx bound to the protoheme. EPR spectroscopy revealed that PAOx bound to the ferric heme via its oxygen atom. On the other hand, ferrous OxdB bound PAOx via a nitrogen atom. These results show a novel mechanism by which the activity of a heme enzyme is regulated, that is, the redox-dependent change in the coordination structure of a substrate-heme complex controls enzymatic activity. Site-directed mutagenesis revealed that His306 located in the substrate-binding heme pocket was a catalytic residue.