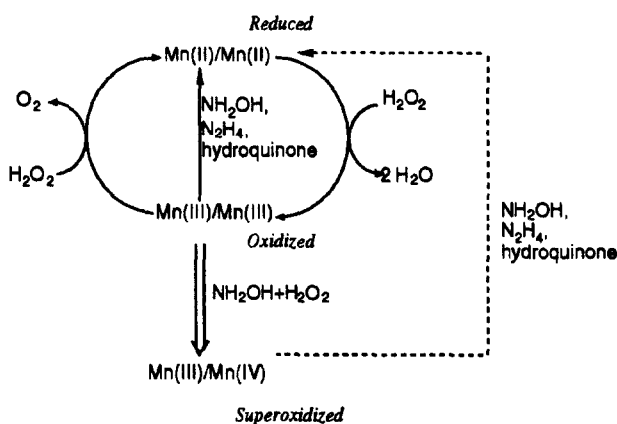


## B074 CHARACTERIZATION OF THE MANGANESE SITES IN MANGANESE REDOX ENZYMES: CATALASE AND SUPEROXIDE DISMUTASE.

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Mn plays a key role in a variety of redox proteins, including superoxide dismutase (mononuclear Mn site), catalase (dinuclear Mn site) and the photosynthetic oxygen evolving complex (tetranuclear Mn site). Recent work on the structural, kinetic, and spectroscopic characterization of the Mn sites in the catalase and in Mn and Fe superoxide dismutase will be described.

For Mn catalase, a combination of activity measurements, EPR and x-ray absorption spectroscopy [1,2] has led to the kinetic model shown in Fig. 1,



**Figure 1.** Oxidation state interconversions of Mn catalase.

with the active enzyme cycling between  $Mn^{II}/Mn^{II}$  and  $Mn^{III}/Mn^{III}$  oxidation states. An inactive, superoxidized  $Mn^{III}/Mn^{IV}$  derivative can be prepared by  $NH_2OH + H_2O_2$  treatment. This inactive derivative has is structurally [2] and spectroscopically [3] similar to the active  $S_2$  state of the photosynthetic oxygen evolving complex. Azide is a competitive inhibitor of Mn catalase and NMR data suggest that azide binds to the  $Mn^{II}/Mn^{II}$  enzyme with displacement of a bound water. Azide binding to the  $Mn^{III}/Mn^{IV}$  derivative causes only minor perturbations to its EPR spectrum.

The Mn and Fe superoxide dismutases are highly homologous proteins, with very similar metal binding sites (3 His + 1 Asp + (possibly) 1 water). EXAFS and XANES data [4] for the native ferric enzyme show a 5 five coordinate metal site (i.e., confirm the presence of a coordinated solvent molecule) Data for the native+azide and the high-pH forms of the enzyme show that here the metal site is six coordinate, demonstrating that these anions bind without displacement of the solvent molecule.

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