

Rapid freeze quench ENDOR studies of the compound I of heme peroxidases

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The formation of compound I is the first step in the reaction mechanism of heme peroxidases. This intermediate stores two oxidizing equivalents from hydroperoxide as an oxyferryl iron center and a radical. This reactive intermediate radicals are thought to be as ferryl porphyrin radical cations. However, recent findings indicate that the electronic structure of these compound I may depend on the nature of the axial ligand. Therefore, it is very important to elucidate the electronic structure of these compound I with different axial ligands. We have been currently using Rapid-freeze quench ENDOR to reveal the electronic structure of compound I of chloroperoxidase (CPO) and horseradish (HRP). The axial ligands of CPO and HRP are cysteine and histidine, respectively. Q-band CW and Pulsed ENDOR coupled with rapid freeze quench technique have been proven to be the powerful tool to characterize this intermediate compound I. This work will provide direct evidence for the electronic structure of compound I.