Towards Understanding the O_2 Chemistry of Mononuclear Non-Heme Iron Enzymes: Intra- and Extradiol Dioxygenases

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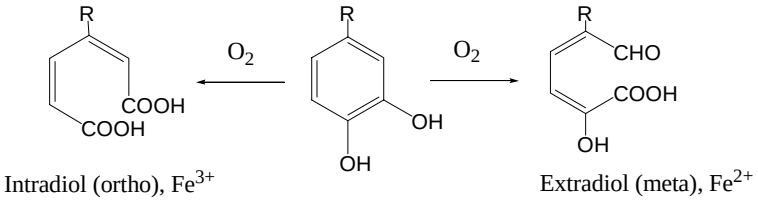
Both intra- and extradiol dioxygenases are found in a number of soil bacteria and participate in the degradation of catecholic rings. However, there is a striking difference in the position of ring cleavage and reaction mechanism. Intradiol dioxygenases employ a Fe^{3+} center which has been proposed to activate substrate for direct attack by O_2. In contrast, extradiol dioxygenases use a Fe^{2+} center and substrate binding has been proposed to activate the Fe^{2+} site for O_2 binding and reaction.

To identify the factors governing the different chemical behaviour towards O_2, we have studied the active site geometric and electronic structures of these two classes of enzymes with a combination of spectroscopic methods, and complemented these spectral studies with DFT calculations. Substrate activation by the Fe^{3+} center in intradiol dioxygenases is investigated through spectroscopic and computational studies on the enzyme-substrate complex. The interaction of O_2 with the Fe^{2+} site upon substrate binding in extradiol dioxygenases is probed by binding a small molecule O_2 analog, NO, to the enzyme-substrate complex.



Intradiol (ortho), Fe^{3+}
3,4-PCD; R=COOH

Extradiol (meta), Fe^{2+}
2,3-CTD; R=H

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