

Probability of Oxygen Activation at the Ferric Center: Oxygen Activation Mechanism for Catechol Dioxygenases and Model Systems

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Iron proteins involved in direct processing of dioxygen (O₂) generally require the ferrous center for binding and/or activation of O₂. Thus, presence of the electron transfer process is essential for the ferric systems. Intradiol catechol dioxygenases, however, are interesting exemptions, since they keep the ferric state throughout the catalytic cycle and insert dioxygen atoms into the aromatic ring via catecholatoiron(III) intermediates. Substrate activation mechanism, which involves the initial binding of O₂ to the catecholate ligand before the dioxygen insertion, has been proposed as an alternative to the oxygen activation mechanism and accepted as a probable mechanism. However, we have preferred the oxygen activation process at the ferric center and tried to accumulate the theoretical¹ and experimental²⁻⁴ supporting data. Following data support that the unusual process is probable regardless of the presence of the vacant site for the oxygen binding. The successful observation of the reversible oxygen binding to [Fe^{III}(Me₃TACN)(3,6-DTBC)]BF₄² indicates that the presence of a vacant site on the ferric center is effective to accelerate the formation of the Fe-O₂ bond. The extraordinary low reactivity of [Fe^{III}(TPA)(3,6-DTBC)]BF₄³ in the series of [Fe^{III}(TPA)(R-Cat)]BF₄ indicates the effect of the steric interaction between the TPA and 3,6-DTBC ligands in the binding process of O₂ to the ferric center. The low reactivity of the high- and low-spin admixture complex, [Fe^{III}((NO₂)₂-TPA)(4Cl-Cat)]BF₄⁴ in the series of [Fe^{III}((R),(R')-TPA)(4Cl-Cat)]BF₄ is ascribed to the lower reactivity of the low-spin iron center than the high-spin iron center with O₂.

It seems probable that spin-delocalization from Fe^{III}-Cat towards Fe^{II}-SQ plays a key role in this mechanism, but it will be interesting to discuss if this type of mechanism is specific to catechol dioxygenases and model systems or applicable to other systems.

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