

Bioinspired Electron Transfer Catalytic Systems

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In the respiratory chain, electrons relay from NADH to O₂ via the redox carriers such as ubiquinone and cytochrome *c* oxidase in the inner mitochondrial membrane in eukaryotes or in the plasma membrane in bacteria. On the other hand, the activation of O₂ and the oxygenation of substrates are one of the most important chemical and industrial processes. Alternatively the two-electron oxidation of substrates may also result in the oxygenation of substrates using water as an oxygen source.

We report herein bioinspired electron transfer (ET) catalytic systems: the four-electron reduction of O₂ by ferrocene derivatives and NADH analogs catalyzed by a cofacial dicobalt porphyrin and the photocatalytic oxygenation of olefins using pentaamminechlorocobalt(III) complex ([Co(III)(NH₃)₅Cl]Cl₂) as an oxidant and water as an oxygen source.

The selective four-electron reduction of O₂ ferrocene derivatives¹ and NADH analogs² occurs using a cofacial dicobalt porphyrin as a catalyst. Mechanisms of the catalytic four-electron reduction of O₂ by ferrocene derivatives and NADH analogs have been elucidated on the basis of detailed kinetic studies on the overall catalytic reactions as well as on each redox reaction in the catalytic cycle.

Substrate oxygenation occurs by high-valent manganese-oxo porphyrins ([$(P)Mn^V(=O)]^+$) which are generated by the ET oxidation of $(P)Mn^{III}(OH)$ with $Ru(bpy)_3^{3+}$ (bpy = 2,2'-bipyridine) as a one-electron oxidant, in which water is used as the oxygen source. Addition of $Ru(bpy)_3^{3+}$ to an MeCN solution of olefins (styrene, cyclohexene) containing water and a catalytic amount of $(P)Mn^{III}(OH)$ affords epoxides, diols and aldehydes efficiently. Alkanes (ethylbenzene, adamantane) are also converted to the hydroxylated products with an appropriate $(P)Mn^{III}(OH)$. The photocatalytic oxygenation of olefins is initiated by photoinduced ET from $Ru(bpy)_3^{2+}$ to [Co(III)(NH₃)₅Cl]Cl₂ to produce $Ru(bpy)_3^{3+}$, which can oxidize (TMSP) $Mn^{III}(OH)$ to the high-valent manganese-oxo porphyrin, leading to the photocatalytic oxygenation of olefins. The oxygen source in the substrate oxygenation was confirmed to be water using ¹⁸O labeled water.

References

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