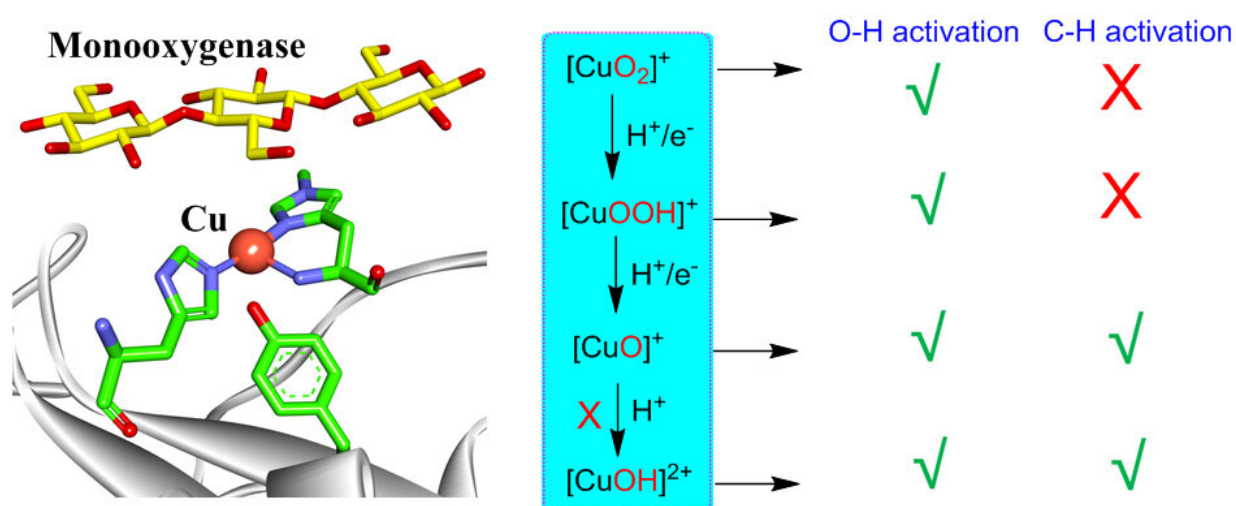


Theoretical perspective on C-H/O-H activation by Cu-O in biological and synthetic systems

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Dioxygen activation by mononuclear copper in biological and synthetic systems may generate various copper-oxygen intermediates including $[\text{CuO}_2]^+$, $[\text{CuOOH}]^+$, $[\text{CuO}]^+$, $[\text{CuOH}]^{2+}$. All these species are able to perform O-H activation, while only $[\text{CuO}]^+$ and $[\text{CuOH}]^{2+}$ are reactive for C-H activation. However, the formation of $[\text{CuOH}]^{2+}$ is highly unfavorable in monooxygenases, leaving $[\text{CuO}]^+$ as the only active intermediate responsible for C-H activation in monooxygenases. These insights can provide consistent understanding on reactivities of various copper-oxygen active species in biological and synthetic systems. Credit: *Chinese Journal of Catalysis*

Dioxygen activations constitute one of the core issues in copper-dependent metalloenzymes. Upon O₂ activation, copper-dependent metalloenzymes, including particulate methane monooxygenases (pMMOs), lytic polysaccharide monooxygenases (LPMOs) and binuclear copper enzymes PHM and DBM, are able to perform challenging C-H/O-H bond activations.

Meanwhile, [copper](#)-oxygen core-containing complexes have been synthesized to mimic the active species of metalloenzymes. Dioxygen activation by mononuclear copper [active site](#) may generate copper-oxygen intermediates, including Cu(II)-superoxo, Cu(II)-hydroperoxo, Cu(II)-oxyl as well as the Cu(III)-hydroxide species.

Intriguingly, all these species have been invoked as the potential active intermediates for C-H/O-H activations in either biological or synthetic systems. Due to the poor understanding of the reactivities of the copper-oxygen complex, the nature of active species in both biological and synthetic systems are highly controversial.

Recently, a research team led by Prof. Binju Wang from Xiamen University, China, gaged the reactivities of various mononuclear copper-oxygen species in both [biological systems](#) and the synthetic systems. The study shows:

- (a) the MN15 functional is highly accurate for mononuclear copper-oxygen complexes, in which the experimental kinetics of various C-H/O-H activations can be well reproduced with MN15.
- (b) Cu(II)-superoxo shows the consistent reactivities in both biological and synthetic systems: It is highly reactive for O-H bond activations but shows low reactivities for C-H bond activations. Thus, Cu(II)-superoxo could not be the active species for C-H activations in both biological and synthetic systems.
- (c) Cu(II)-hydroperoxo is inert for C-H bond activations, but its

radical character on the proximal O enables it to perform HAA from moderate O-H bonds or couple with another Cu(I) to form the dinuclear copper species. Thus, Cu(II)-hydroperoxo represents a key intermediate along the O₂ activation pathways rather than an oxidant for C-H activation in both biological and synthetic systems.

- (d) Cu(II)-oxyl is highly reactive for C-H bond activations and thus could be responsible for C-H activation in mononuclear copper monooxygenases.
- (e) Though the highly reactivities of copper(III)-hydroxide toward C-H [bond](#) activations have been well established, the formation of such species in monooxygenases is highly unfavorable thermodynamically.

These insights are expected to provide the consistent understanding on reactivities of various copper-oxygen active species in both biological and synthetic systems.

The review was published in the *Chinese Journal of Catalysis*.

More information: Peng Wu et al, Theoretical perspective on mononuclear copper-oxygen mediated C–H and O–H activations: A comparison between biological and synthetic systems, *Chinese Journal of Catalysis* (2022). [DOI: 10.1016/S1872-2067\(21\)63974-8](https://doi.org/10.1016/S1872-2067(21)63974-8)

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