DFT Calculations Reveal a Concerted Asynchronous Mechanism for Nitrite Reduction by Copper Complex

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Nitrite (NO_2^-) anion plays a crucial role in the natural nitrogen cycle and physiological control. The human body uses NO_2^- as a resource of nitric oxide (NO), which works as a pathogen killer and a signaling transmitter.

Kundu and co-workers reported the phenol-mediated reduction of NO_2^- to NO catalyzed by the copper(II) complex supported by the tripodal heteroditopic-cryptand ligand (**L**).[1] The reaction of 2,4-di-*tert*-butylphenol with the nitrite copper(II) complex ($[Cu^{II}(\mathbf{L})(\kappa^2\text{-}O_2N)]^+$) forms the corresponding *o,o'*-biphenol and NO with the hydroxyl copper(II) complex ($[Cu^{II}(\mathbf{L})(OH)]^+$). In this study, DFT calculations were performed to clarify the nitrite reduction by the copper(II) nitrite complex.

Figure 1 shows optimized geometries in the copper active site and a computed energy diagram for the nitrite reduction by the copper complex. The ground state is the doublet state during the reaction. First, the reactant complex (**RC**) is formed due to the interaction between the copper nitrite complex $[CuONO]^+$ and the phenol. Then, the O–H bond alternation and the O–N bond cleavage in **RC** occur simultaneously at a transition state (**TS**), resulting in the formation the product complex (**PC**). Finally, phenoxyl radicals undergo coupling to produce biphenol.

To characterize the property of electron transfer, we performed IBO analyses, a kind of localized molecular orbitals.[2] We focused on the five IBOs corresponding to five steps. As a result, we can conclude that the concerted reaction with the five steps proceeds asynchronously.

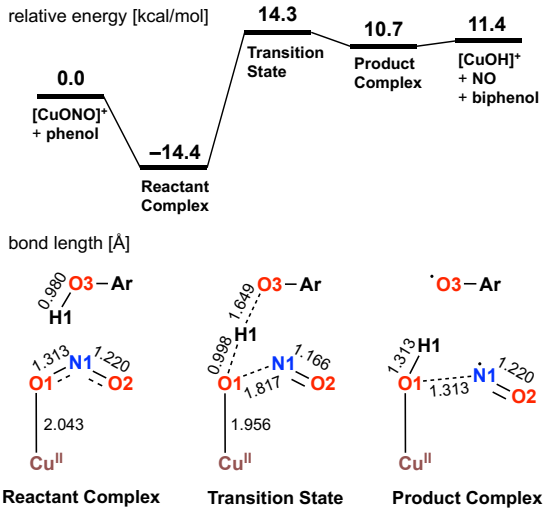

Figure 1. Energy diagram for the nitrite reduction and optimized geometries of **RC**, **TS**, and **PC**.

1) A. Mondal, K. P. Reddy, J. A. Bertke, and S. Kundu, *J. Am. Chem. Soc.*, **2020**, *142*, 1726–1730.
2) G. Knizia, *J. Chem. Theory Comput.*, **2013**, *9*, 4834–4843.