Dioxygen Activation Mechanism in Fe^{3+} Catechol Dioxygenase: Importance of Multi-Configurational Character

Naoki Nakatani, Yoshihide Nakao, Hirofumi Sato, and Shigeyoshi Sakaki*

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University

E-mail: sakaki@qmst.mbox.media.kyoto-u.ac.jp

Catechol dioxygenase, found in diverse range of soil bacteria, activates molecular oxygen to catalyze aromatic bond cleavage of catechol (1,2-dihydroxylbenzene) and its derivatives. Its active center consists of a non-heme-iron complex.

Based on a lot of spectroscopic and theoretical studies, two different mechanisms were proposed in the Fe^{3+} catechol dioxygenase; one is "substrate activation" and the other is "oxygen activation". In the "substrate activation" mechanism, the electron-transfer from catechol to Fe^{3+} leads to formation of a Fe^{2+}-semiquinone radical species, and then O_2 directly reacts with the catechol carbon (**Scheme 1a**). In the "oxygen activation" mechanism, O_2 first attacks Fe^{3+} to form Fe-O_2 direct bond (**Scheme 1b**). However, it has not been clarified which mechanism is correct.

As for the preliminary reported theoretical studies, they carried out by using density functional theory, which is not enough to qualitatively evaluate the Fe-O_2 interaction because of its multi-reference character. We employed here the CASSCF method to explicitly consider a multi-reference character. Our purpose is to investigate the activation mechanism of O_2 in Fe^{3+} catechol dioxygenase.

Our computational results support the "oxygen activation" mechanism in which the Fe^{2+}-semiquinone radical species is not included. According to the detailed analyses, electron transfer from catechol to dioxygen moiety occurs when the Fe-O_2 distance becomes 2.4 Å. The oxidation state of Fe is always 3 through the oxygen activation. This is because that the Fe-O_2 interaction stabilizes the energy level O_2 to take place the electron transfer from catechol to O_2.

Scheme 1.