Theoretical study of the reduction of nitric oxide in bacterial nitric oxide reductase

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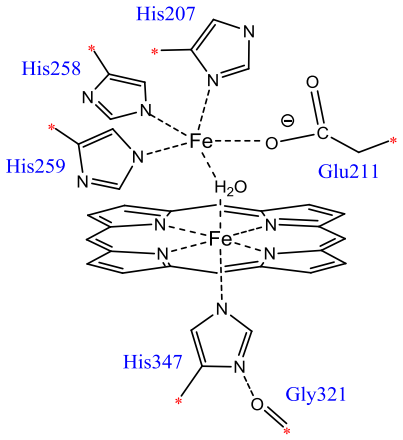
Nitric oxide reductase (NOR) is a bacteriological enzyme which catalyzes the reduction of nitric oxide (NO) to nitrous oxide (N_2O) during anaerobic respiration.

$$2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O$$

The active site of NOR has a particular structure which contains a heme Fe and a non-heme Fe [1]. This structure is quite similar to that of cytochrome oxidase which catalyzes the reduction of O_2 to H_2O during aerobic respiration [2]. Because of the similarity of their structures, NOR is considered to be an evolutionary progenitor of cytochrome oxidase. In other words, NOR has the key to clarify the evolutionary history of acquirement of the aerobic respiration system.



In this work, the catalytic mechanism of NOR has been studied using DFT and ONIOM(DFT:MM) methods. Firstly, the catalytic cycle of model complex was calculated using DFT and AFIR (Artificial Force Induced Reaction) methods. According our calculations, the reaction starts with NO-addition to heme Fe. The second NO attacks the N atom of the NO coordinated to heme Fe and forms a five-membered ring intermediate. After the N-O bond cleavage, an non-heme Fe(IV)=O / heme Fe-N_2O intermediate is formed. The N-O bond cleavage step is the rate-determining step, but its barrier is higher than the experimental value. Secondly, the effect of surrounding protein was studied using ONIOM(DFT:MM) method. The specific protein environmental effects on the catalytic cycle will be discussed in detail.

References

[1] T. Hino, *et al*., *Science* **330**, 1666 (2010). [2] S. Buschmann et al., *Science* **329**, 327 (2010).