COMPUTATIONAL STUDY ON THE REVERSE REACTION OF FORMATE OXIDATION BY MOLYBDENUM-CONTAINING FORMATE DEHYDROGENASE

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As a biological catalyst, Molybdenum-containing formate dehydrogenases (Mo-FDHs) plays an essential role in the formate oxidation. Nowadays, due to the dramatic increase in atmospheric CO_2 levels, more and more experimental and computational studies are turning to CO_2 reduction and effective mechanisms for carbon capture. One of the pathways for the latter is the inverse reaction of formate oxidation [1, 2]. However, the underlying mechanism is still under debate, namely whether the formate directly connects to Mo or the SeCys ligand dissociates from the metal center. In this work, a large QM region of two selected enzymes is chosen to obtain detailed information on the Mo surroundings, a model used previously by Ryde and coworkers [3]. First, we study the full mechanism of the forward reaction of Mo-FDHs. Ligands modifications during the reaction and their contribution to the potential energy are addressed. Further, based on the results for the forward reaction, interactions between substrate and Mo and the ligands change will be investigated.

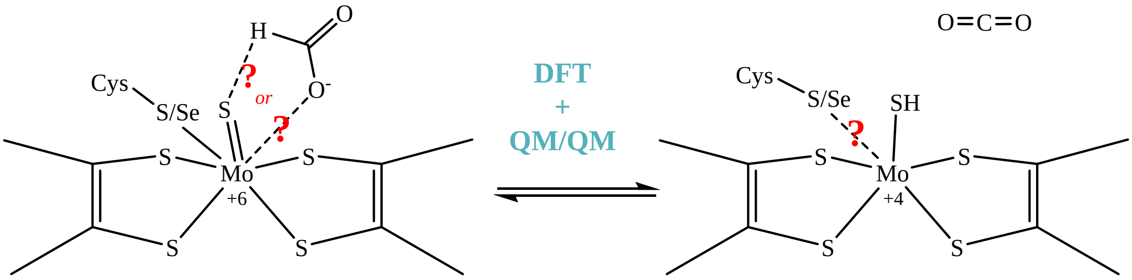

Figure 1. Mechanisms of reverse and forward reactions catalyzed by Mo-FDHs.

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[1] Maia, L. B., Moura, I., and Moura, J. J., Environment and Energy, 29-81 (2021).

[2] Siegbahn, P. E., J. Phys. Chem. B, 126, 1728 (2022).

[3] Dong, G., and Ryde, U., J Biol Inorg Chem, 23, 1243 (2018).