



On the Mechanism of COS Hydratation by Carbonic Anhydrase

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Decades ago, it has been shown that COS consumption of the vegetation is accompanied by metabolic production of H₂S and other sulfur volatiles. Carbonic Anhydrase (CA) has been identified as the key enzyme for this process. In order to provide understanding for the catalytic path at a molecular scale, studies employing model compounds have been performed. The reaction was modeled using the complex $\text{Tp}^{\text{Ph,Me}}\text{Zn-OH}$, a mimic for the catalytic centre of CA. It was shown that in the course of the reaction of COS with zinc-bound hydroxide, CO₂ is formed; the hydroxide ligand is converted to hydrosulfide, resulting in the complex $\text{Tp}^{\text{Ph,Me}}\text{Zn-SH}$.

We investigated the mechanism of the CA-mediated COS hydration using density functional calculation. It is widely similar to CO₂ hydration, apart from the fact that a hydrosulfide complex is obtained which represents a minimum on the free energy hypersurface. We also found that COS as well as CO₂ are not capable to react further with this modified catalyst. As a consequence, the normal catalytic cycle can not proceed as long the hydrosulfide ligand is present. However, this is in contrast to the finding that CA is not inactivated by COS.

Further computational studies revealed that reactivation of CA, that is, replacement

of the hydrosulfide ligand with hydroxide thereby yielding H_2S , is possible just by protonation and ligand exchange. This result was corroborated by a model experiment and an *in vivo* study.

Thus, we conclude that CA is perfectly equipped by nature to fulfill the task of COS hydrolysis. In biological systems, H_2S is transformed readily into cysteine by the cysteine synthase complex; COS fixation is therefore directly connected to the plant's sulfur metabolism. The sulfur from COS is thus readily available for the plant's sulfur supply.