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Computational Study of Acetylene Hydration by Bio-inspired Group Six Catalyst Models

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Abstract

A combination of density functional theory and natural bond orbital analysis was employed to study two bio-inspired catalyst models that mimic the acetylene hydratase active site. The Group 6 metals (Cr, Mo, W) and substituents (CN, H, CH₃) on the dithiolate supporting ligands were used to evaluate the effect of metal identity and supporting ligand on free energy barriers and the thermodynamics of the reaction. In catalyst model **1**, a metal-bound hydroxo ligand (M^{IV}-OH) acts as a general base, while in catalyst model **2**, a propionate plays the role of general base. The calculations showed that in both chromium complexes **1** and **2**, acetylene does not bind to the metal in the reactant catalysts, suggesting that Cr is not a soft enough acid in the 4+ formal oxidation state to bind acetylene. The comparison of calculated free energies for molybdenum and tungsten complexes reveals that for models **1** and **2**, Mo complexes have lower free energy barriers and are more exergonic as compared to the W variant. Comparing the energy profiles of complexes **1** and **2** indicates that on average, complex **2** has lower barrier energies in comparison to **1**, while model **1** has a more exergonic ΔG_{rxn} for acetylene hydration. NBO analysis suggests a metalocyclopropene constitutes the more faithful representation of the Mo and W reactants rather than a π -acetylene. Furthermore, calculations indicate that for both complexes **1** and **2**, using electron withdrawing substituents such as CN on dithiolate supporting ligands lowers the activation free energies compared to CH₃ and H substituents. Analysis of the impact of polarity through use of different continuum solvents on the reaction coordinate suggest that a less polar active site is more favorable for acetylene hydration.

Keywords: Acetylene hydration; Bio-inspired catalyst; DFT; Group six metals; NBO

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