

Title:

Relativistic and spin effects in quantum mechanical models of aerobic transition metal catalysis

Abstract:

Aerobic oxidation is an emerging frontier of catalysis that is poised to provide green alternatives to existing oxidation reactions. Complete mechanistic understanding of the catalyst-guided,  $O_2$  spin-crossing step is challenging to obtain due to its transitory nature. As a result, first principles computational insight can be highly valuable in resolving the spin-crossing step, as well as other catalyst intermediates. In this work, we use relativistic-Dirac-equation-based electronic structure theories to describe the aerobic oxidation reaction of a Pd complex, [(neocuproine)Pd( $\mu$ -OAc)]<sub>2</sub>[OTf]<sub>2</sub> (**1**), which selectively oxidizes secondary alcohols in geminal diols in the presence of  $O_2$ . In addition to resolving the Pd moderated spin-transition step, relativistic calculations predict that the regeneration of **1** in the catalytic cycle will occur through the formation of  $O_2^{2-}$  and  $H_2O_2$  from disproportionation of two Pd bound  $HOO^-$ . Electronic character for the  $O_2^{2-}$ -palladium system in the Dirac picture shows significant electron donation to the palladium-neocuproine system, which stabilizes the highly reactive oxy-dianion species compared to the non-relativistic case. This donation additionally facilitates  $O_2^{2-}$  abstraction of a proton from the neocuproine ligand methyl site which subsequently leads to the formation of a carboxylic acid and degradation of catalyst function. This and other detailed insights are expected to be useful as a guide to future improvements in aerobic oxidation reactions.