# [P2] Theoretical study for methane oxidation by dicopper complex

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Efficient catalyst design for the selective hydroxylation of methane with O_2 or H_2O_2 has been attractive works for industry. In a previous work, a dicopper complex $[Cu_2(\mu\text{-}OH)(6\text{-}hpa)](ClO_4)_3$ (**A**) was synthesized and characterized[1]. It catalyzed the selective hydroxylation of benzene to phenol using H_2O_2. DFT calculations showed the reaction mechanisms and the formation of a $Cu^{II}O^{\bullet}$ species (**1**) occurs in the three steps, as shown in Scheme 1. Since this complex has a similar structure as the dicopper site of particulate methane monooxygenase (pMMO), the complex is a possible candidate for the catalyst of methane hydroxylation. In this study, we performed a numerical assessment of the catalytic performance of **1** for the hydroxylation of methane to methanol using DFT.
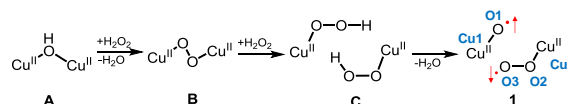
Scheme 1. A proposed mechanism of H_2O_2 activation catalyzed by dicopper species[1].

Figure 1 shows a computed energy diagram for the conversion of methane to methanol by **1**. Since complex **1** has the $Cu^{II}O^{\bullet}$ and $Cu^{II}O_2^{\bullet}$ species, we considered the two types of transition states for the C–H bond cleavage of methane, as shown in Figure 2. Since the calculated activation energies for **TS1** is lower than that for **TS1'**, the methane hydroxylation is initiated by the C–H bond cleavage of methane by the $Cu^{II}O^{\bullet}$ moiety. The **TS1** activation energy is small compared with the C–H bond dissociation energy of methane and similar to the value of the C–H bond dissociation by pMMO.
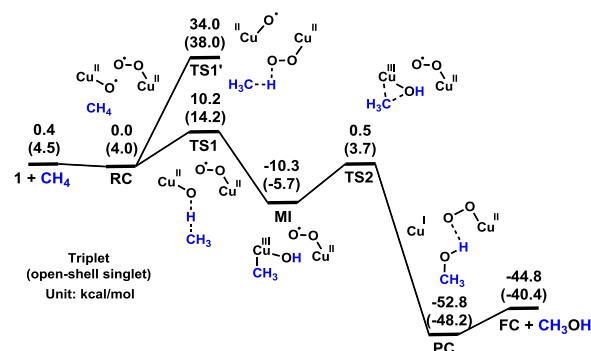

Figure 1. Computed energy diagram for the methane hydroxylation catalyzed by **1**. Relative energies respect to reactant complex (**RC**), measured from **1** and methane in the triplet state, are in kcal/mol.

The energy diagram connects **MI** and **PC** in the C–O bond formation step and the energy barrier is lower than that in the Cu–C bond cleavage. Therefore no radical species is formed in the two-step mechanism.

A calculated energy difference of **PC** and **FC** + CH_3OH is 8.0 kcal/mol. Since the value corresponds to the binding energy between methanol and **FC**, the produced methanol would be removed easily from the complex without overoxidation.
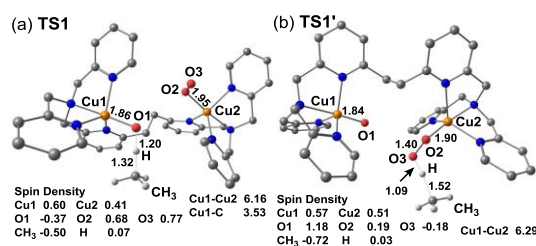

Figure 2. Optimized structures with Mulliken spin densities of (a) **TS1** by the $Cu^{II}O^{\bullet}$ species and (b) **TS1'** by the $Cu^{II}O_2^{\bullet}$ species in the $[Cu_2O_3]^{+2}$ moiety in the triplet state. The units are in Å.

Bibliography:

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