Catalytic Performance of a Dicopper-Oxo Complex for Methane Hydroxylation

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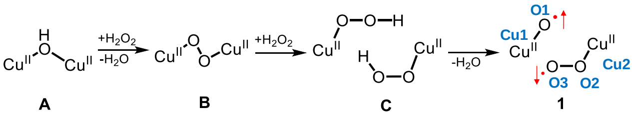
Abstract: A dicopper(II) complex $[Cu_2(\mu\text{-}OH)(6\text{-hpa})]^{3+}$ generates an oxyl radical of $Cu^{II}O^{\cdot}$ and catalyzes the selective hydroxylation of benzene. From the structural similarity to methane-activation catalysts, it is expected to catalyze methane hydroxylation. The catalytic performance for the hydroxylation of methane to methanol by this dicopper complex is investigated by using DFT calculations. The whole reaction of the methane conversion involves two steps without radical species. The activation barrier is calculated to be 10.2 kcal/mol, which is low enough for reactions taking place under normal conditions. DFT calculations show that the dicopper complex has a precondition to hydroxylate methane to methanol.

Keywords: Methane hydroxylation, dicopper-oxo complex, DFT calculation.

1. Introduction

Efficient catalyst design for the selective hydroxylation of methane to methanol with O_2 or H_2O_2 has been one of the most attractive works for industry. Particulate methane monooxygenase (pMMO) with a dinuclear copper site is an enzyme that hydroxylates methane to methanol under mild conditions. Therefore, it is a rational initiative for the catalyst design of methane hydroxylation to focus on the pMMO active site.

In a previous work, a dicopper complex $[Cu_2(\mu\text{-}OH)(6\text{-hpa})](ClO_4)_3$ (**A**) with a dinucleating ligand 1,2-bis[2-[bis(2-pyridylmethyl)aminomethyl]-6-pyridyl]ethane (6-hpa) was synthesized and structurally characterized.[1] Interestingly, it catalyzed the selective hydroxylation of benzene to phenol using H_2O_2. The turnover number after 40 h for the phenol production exceeded 12000 in MeCN at 50°C under N_2. Complex **A** has triplet and open-shell singlet spin states coupled binuclear $Cu^{II}(d^9)$ centers, respectively. The reaction mechanisms were investigated by using density functional theory (DFT).[1] DFT calculations showed that the formation of a $Cu^{II}O^{\cdot}$ species (**1**) occurs in the three steps via intermediates **B** and **C**, as shown in Scheme 1. This complex has a similar structure as the dicopper site of pMMO in that it involves a $Cu^{II}O^{\cdot}$ moiety as the active species. Therefore complex **A** is a possible candidate for the catalysis of methane oxidation. 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]

2. Theoretical

All calculations were performed by using the unrestricted DFT (UDFT) with the B3LYP functional by the Gaussian-09 package. The triplet and open-shell singlet states were computed by using the broken-symmetry approach. We used the Wachters-Hay basis set for the Cu atom and the D95** basis set for the H, C, N, and O atoms.

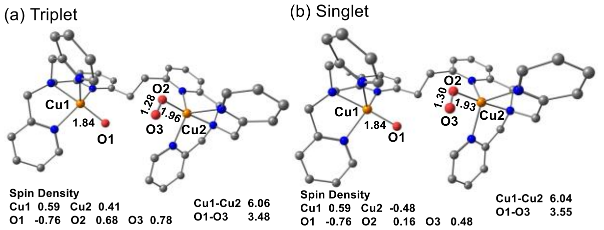


Figure 1. Optimized structures with Mulliken spin densities of **1** in the $[Cu_2O_3]^{+2}$ moiety in (a) the triplet state and (b) open-shell singlet states. The units are in Å.

3. Results and discussion

Figure 1 shows optimized structures of **1** in the triplet and open-shell singlet states. In both states, the long Cu–Cu distance detaches the oxyl and peroxyl radicals and prevents a self-destruction of the $Cu^{II}O^{\cdot}$ and $Cu^{II}O_2^{\cdot}$ radicals by the rebinding.

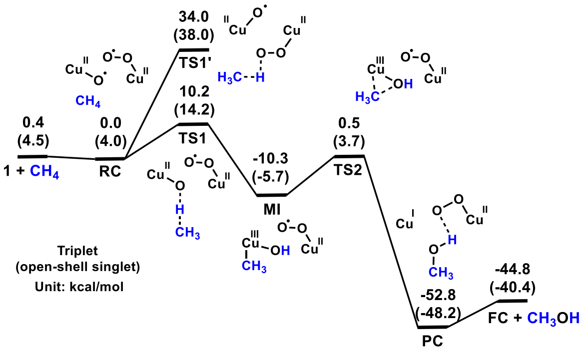


Figure 2. Computed energy diagram for the methane hydroxylation catalyzed by **1**. Relative energies respect to reactant complex (**RC**), measured from **1** and methane in the triplet state, are in kcal/mol.

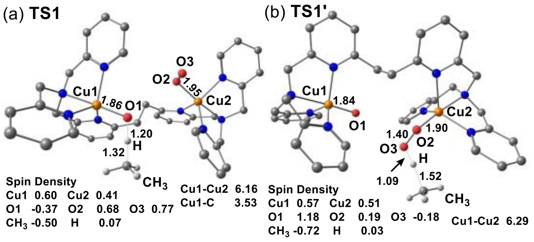


Figure 3. Optimized structures with Mulliken spin densities of (a) **TS1** by the $Cu^{II}O^{\cdot}$ species and (b) **TS1'** by the $Cu^{II}O_2^{\cdot}$ species in the $[Cu_2O_3]^{+2}$ moiety in the triplet state. The units are in Å.

Figure 2 shows a computed energy diagram for the conversion of methane to methanol in the triplet and singlet states. Since the triplet potential energy surface lies well below the singlet one is endothermic, the triplet state should play a dominant role in this reaction. Since complex **1** has the $Cu^{II}O^{\cdot}$ and $Cu^{II}O_2^{\cdot}$ species, we considered the two types of transition states (**TS1** and **TS1'**) for the C–H bond cleavage of methane, as shown in Figure 3. Calculated activation energies for **TS1** and **TS1'** in the triplet state are 10.2 and 34.0 kcal/mol, respectively. Therefore the methane hydroxylation is initiated by the C–H bond cleavage of methane by the $Cu^{II}O^{\cdot}$ moiety. The calculated **TS1** activation energy is not only small compared with the C–H bond dissociation energy of methane but also similar to the value of the C–H bond dissociation by pMMO. This result indicates that complex **1** possesses ability enough for the C–H bond activation of methane.

The energy diagram connects **MI** and **PC** via the second transition state (**TS2**) in the C–O bond formation step. DFT calculations show that a calculated energy of transition state in the Cu–C bond cleavage is higher than that for **TS2**. Therefore no radical species is formed in the two-step mechanism at the species relative to the reaction.

A calculated **PC** energy relative to **RC** is −52.8 kcal/mol, which is twice more exothermic than that for pMMO. A calculated energy of **FC** that includes the complex where methanol is removed from **PC** and the released methanol is −44.8 kcal/mol relative to **RC**, the energy difference of **PC** and **FC** + CH_3OH is 8.0 kcal/mol. Since the value of 8.0 kcal/mol corresponds to the binding energy between methanol and **FC**, the produced methanol would be removed easily from the complex without overoxidation. The $Cu^{II}O_2^{\cdot}$ species can be utilized in the regeneration of **B**. A calculated energy from **FC** to **B** is –6.0 kcal/mol and the energy difference from **B** to **C** in Scheme 1 is –10.2 kcal/mol. These results indicate that **FC** obtained from the methanol production can lead to **B** and **C** that catalyze a next methane hydroxylation.

4. Conclusions

In this work, we have investigated the catalytic performance of a dicopper complex for methane hydroxylation using DFT calculations. Complex **1** has a $Cu^{II}O^{\cdot}$ species that performs the C–H bond activation of methane and the activation energy is lower than that of benzene. The methane hydroxylation should take place in a two-step manner without radical species. In addition, since the value of the binding energy of produced methanol and **FC** is small, the produced methanol is expected to be released easily from the complex without overoxidation. Complex **FC** can lead to **B** to turn the next catalytic cycle. The DFT calculations show that complex **A** has a necessity precondition to hydroxylate methane to methanol under mild conditions. We conclude that complex **A** possess the capability for methane hydroxylation.

References

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