

[L3] Quantum Chemical Studies on Methane Hydroxylation by Transition-Metal-Oxo Species

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The bond dissociation energy and bond length of a parent molecule producing a radical are useful measures in considering the stability of a free radical. We have discussed a non-radical mechanism for methane hydroxylation by the bare MO^+ complex and methane monooxygenases (sMMO and pMMO) using DFT calculations.^{1,2} This mechanism is applicable when metal-oxo species are coordinatively unsaturated. Direct interaction between methane and a metal active center can form a weakly bound methane complex in the initial stages of the reaction. Subsequent C–H bond cleavage to form an intermediate with an HO–M–CH_3 moiety in a non-radical manner and recombination of the resultant OH and CH_3 ligands take place at a metal active center to form a final methanol complex. The fact that methyl radical is 10–20 kcal/mol less stable than secondary and carbon radicals and benzyl radicals leads us to reasonably propose this non-radical mechanism. This mechanism is widely applicable to enzymatic and metal-exchanged zeolite systems.^{2,3} Metal-exchanged zeolites are known to exhibit catalytic activity in the direct conversion of methane to methanol. The influence of different metals on this reaction is theoretically investigated by using DFT calculations on a periodic system of MO^+ -ZSM-5 zeolite ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{and Cu}$).³ The results indicate a high dependency of the reaction on the metals, where the reactivity towards C–H bond dissociation is predicted to increase in the order of CoO^+ -ZSM-5 < NiO^+ -ZSM-5 < FeO^+ -ZSM-5 < CuO^+ -ZSM-5. The role of ZSM-5 zeolite in the catalytic activity is also investigated by comparing our calculation results with those reported for the reaction by the bare MO^+ species in the gas phase.⁴ We found that the nanopores of ZSM-5 zeolite exert a confinement effect, which destabilizes the adsorption of methane and can lower the activation energy for the C–H bond dissociation.

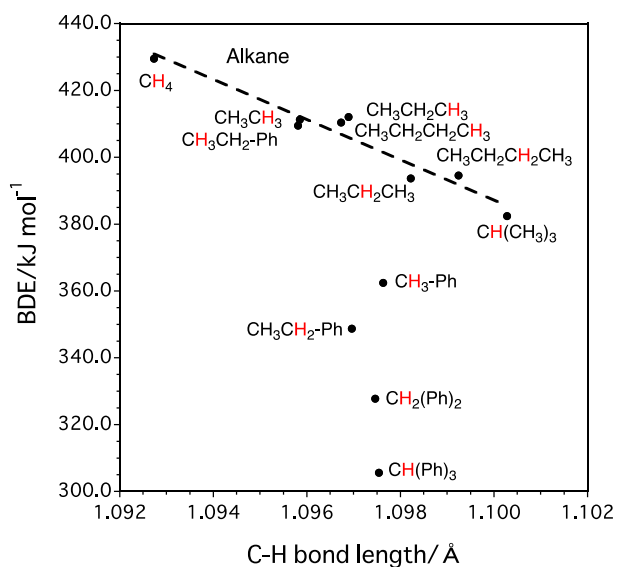


Fig. 1. Correlation between C–H bond dissociation energies and bond lengths calculated at the B3LYP/6-311++G** level of tertiary theory.

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