

Summary and Conclusions

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The main scope of the present Ph.D. thesis is to understand the electronic structures of metal complexes, formation of high valent metal-oxo and reaction mechanism of the oxygen atom transfer, C-H and O-H bond activation by different high valent metal-oxo/hydroxo/superoxo complexes. The specific problems chosen here are listed below

1. In the first section, we have focused on the exploration of electronic structures of TAML derivate iron monomer and dinuclear species. We have also explored the magnetic exchange coupling constant of μ -oxo and μ -1,2-peroxo diiron TAML derivate species. NBO plots show the ionic and covalent character of the metal-oxygen bond. The nitrogen atom coordinated to the iron metal gains electrons density via the electron delocalization mechanism. The significant spin density at the oxygen atom can be a witness for C-H/O-H/N-H bond activation.
2. In the second section, we have focused on the mechanistic study of allylic oxidation of cyclohex-2-enol to cyclohex-2-enone by using iron(V)-oxo as the oxidant. Here, we have proposed two pathways (*pathway a* and *pathway b*), from the computed energy it is found that, barrier height of the C-H bond is small as compare to O-H bond and the second step is barrier-less i.e. C-H bond activation is more favorable than O-H bond activation (*pathway b*). From the computed eigenvalue plot and bond angle it is found that C-H/O-H bond activation occurs via the proton coupled electron transfer mechanism followed by the π pathway. Along with we have also studied the oxygen atom transfer mechanism (epoxidation) that leads to the formation of cyclohexane epoxide, and found that the barrier for oxygen atom transfer is higher than *pathway a* and *pathway b*. This is the first computational study to discuss a comparative study on C-H vs. O-H bond activation along with oxygen attack towards cyclohex-2-enol by Fe(V)-oxo species. A significant exchange of metal electrons and

change in structural parameters during transition states can influence reactivity and help to design a potential oxidant for catalytic transformation reactions.

3. In the third section, we have studied the electronic structure of metal-superoxo species with chromium, manganese, iron, and cobalt-superoxo species with two different ring size TMC ligand and also tested their reactivity towards C-H bond activation. From the calculations it is predicted that the 13-TMC ligated superoxo species are more reactive towards C-H bond activation except for iron-superoxo species and first hydrogen abstraction is the rate-determining step in all the studied species, occurs via proton-coupled electron transfer mechanism. The computed bond angles $\angle N1-M-N3$ and $\angle N2-M-N4$ show more contraction with 13-TMC species than the 14-TMC which in turn pushes the metal out of the plane and hence increase the reactivity of electrophilic reaction. Our calculations show that the ring size of the TMC ligand plays an important role to control reactivity. By tuning the ring size one can alter the reactivity of metal-superoxo species towards organic substrates.
4. In the fourth section, we have attempted to explore the reason behind the formation of oxo wall in between group 8 and group 9. Metal-oxo species are formed from O---O bond cleavage of metal-hydroperoxo. Here, we have taken the Cr, Mn, Fe, Co, Ni, and Cu with two different geometry octahedral (14-TMC) and trigonal bipyramidal (buea), and it is found that the barrier for O---O bond cleavage is higher with late transition metal hydroperoxo (Co, Ni, and Cu). This is due to enhance exchange reactivity (EER). As the pairing of electrons starts in the late transition series by which enhance exchange reactivity decreases and the bond order of metal-oxo bond also decreases. This is also supported by 4*d* and 5*d* transition metals (Ru, Rh, Os, and Ir). Computed spin density at oxo and metal-oxo bond distance suggests that the earlier transition metal forms metal-oxo while the late transition metal forms metal-

oxyl. Metal-oxo of the late transition metal series exists as metal-oxyl. Metal-oxo species acts as a reactive intermediate in the oxidation reaction, along with these are also involved in O-O bond formation. The formation of metal-oxyl seems to be important for O-O coupling. These reactive intermediates are involved in many metal-mediated catalytic nucleophilic and electrophilic reactions which are familiar in biology and chemistry. The study of these species with structure and function relations may lead to a general system that functionalizes the C-H bond or carry group transfer reactions.

To this end, our findings on metal complexes and biomimetic catalytic reactions will provide clues to experimentalists to enhance the reactivity/selectivity/efficiency and can be able to predict better high valent non-heme metal catalysts which can be used in several catalytical transformation reactions.