In my postdoctoral stay in the University of Heidelberg, Germany (June 2007 to Nov 2009), I have modelled several organometallic catalysed reactions including alkane and alkene oxidations using Fe, Ru and Cu based bispidine complexes. The main aim of these projects are to find out the insights of the catalytic mechanism in terms of the preferred spin states and the oxidation states of the key catalyst, as the experimental studies cannot predict the same. This has shed some light on the experimental findings and helped to improve the catalyst model. The calculations have been performed using various methods such as Gaussian suite programs, Jaguar 6.5 and Orca. The basis set and basis functional information can be found in our published papers \(^1\) - \(^6\).

The Key results

The oxidation of cyclohexane by a high valent Fe-bispidine complexes have been modelled computationally to find out the catalytically active oxidant. The computational studies involve the usual putative intermediates and transition states (hydrogen abstraction to a radical intermediate, followed by a radical rebound process) in all possible spin states and including the [(L\(^1\))Fe\(^{IV}\)=O(OH)]\(^+\) and the [(L\(^1\))Fe\(^{V}\)=O(OH)]\(^{2+}\) species (where L\(^1\) = tetradentate bispidine ligand) as possible oxidants (see Figure 1).

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**Figure 1:** Assumed mechanism for the cyclohexane hydroxylation by [(L)Fe\(^{IV}\)=O(OH)]\(^+\) (the same mechanistic pathway was used for [(L)Fe\(^{V}\)=O(OH)]\(^{2+}\)).
The modeled results show that Fe$^{IV}$ complexes are thermodynamically more stable than the Fe$^{V}$ catalysts (by about 50 kJ/mol). However, the activation barriers from the Fe$^{II}$ precatalysts are smaller for the Fe$^{V}$ complex by approximately 20 kJ/mol. The barriers for C-H activation for both oxidation states are smaller (65 kJ/mol for Fe$^{IV}$ and 40 kJ/mol for Fe$^{V}$) than the back reactions (150 and 70 kJ/mol, respectively). From the computed data, it therefore appears that both $[(L^1)Fe^{IV}=O(OH)]^+$ and $[(L^1)Fe^{V}=O(OH)]^{2+}$ (and also $[(L^1)Fe^{IV}=O(OH_2)]^{2+}$, depending on the solvent and the acidity of the solution (the trans to N3 isomers in all cases) are efficient catalysts for C-H activation and oxygen transfer. On the basis of computed results with including error limits of up to 10-20 kJ/mol and appreciable solvent effects, the two pathways may compete. This is exactly what the experiments suggested. The Fe$^{IV}$ route, enforced by a stoichiometric reaction with PhIO as oxidant, seem to involve cyclohexyl radicals of a significant lifetime, while this does not seem to be the case in the H$_2$O$_2$-initiated reaction, which might involve Fe$^{V}$=O as the catalytically active species.

A similar study has been conducted to compare the catalytic efficiency of [Fe(L$^2$)(NCMe)]$^{2+}$/H$_2$O$_2$ and [Fe(L$^3$)(NCMe)]$^{2+}$/H$_2$O$_2$ ($L^{2,3}$ are the pentadentate ligands; isomer of one another) systems with the previously reported [Fe(L$^1$)(NCMe)]$^{2+}$/H$_2$O$_2$ towards the cyclohexane hydroxylation. The results show a strikingly different efficiencies and mechanistic pathways of the tetradentate ($L^1$)- and pentadentate ($L^{2,3}$)-based complexes. With both groups of ligands, there is more than one active pathway. While, for the tetradentate ligand system, there is some indication that an Fe$^{V}$=O-based oxidation might be involved, this is an unlikely scenario for the pentadentate ligands.

The modeling studies have also been carried out for the selectivity in the epoxidation of cis- and trans-b-methylstyrene with the formation of cis and trans products, using the active catalysts $[(L^5)Ru^{IV}=O]^{2+}$ and $[(L^3)Fe^{IV}=O]^{2+}$. The DFT studies indicate that, with both catalysts, the epoxidation is based on a stepwise

\[Figure 2.\] Molecular Structures of $L^1$, $L^2$, and $L^3$ and their Iron Complexes (X is a Solvent Molecule or the Oxo Group).

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mechanism, which, in the first step leads to a radical-based intermediate. This exists in two configurations, which interconvert with a relatively low energy barrier. The product ratio (observed experimentally) depends on the relative energies of the two configurations of the radical intermediate and the height of the energy barriers to the cis- and trans-epoxide products. For the Fe-based system there is, as expected, the additional complication of the availability of various spin levels, and multi-state reactivity is observed. The computed structures and energies can be seen in one of our published articles. Another study have been conducted on the Ru-based system to explain the sulfoxidation mechanism and it was found that the O to S linkage isomerization plays a crucial role to determine the catalytic efficiency.

In addition with the DFT modelling studies, I have also worked with the Molecular Mechanics simulations using momec and MacroModel softwares, which can be used to deal bigger systems such as proteins. I have also developed the force field for the model complex (Cu(II) coordinated cyclic peptide macro cycles) of my interest to do the conformational search.

Overall, during my Post doctoral work, a range of Fe, Ru, and Cu mediated catalytic reactions were modelled in their preferred spin states to investigate their mechanistic insights and also to predict the experimental findings.

Published Papers/References


