

Unveiling the active species for oxygen atom transfer reactions promoted by manganese porphyrins

André Luiz Barboza Formiga

Institute of Chemistry – University of Campinas, P.O.Box 6154, 13083-970, Campinas, SP, Brazil

Abstract: Cytochrome P450 is a class of monooxygenases present in a variety of living organisms playing an important role in oxygen atom transfer (OAT) reactions to hydrophobic substrates. Generally, their catalytic sites contain a prosthetic iron porphyrin group coordinated to a cysteine residue in a hydrophobic pocket. Over the years, several biomimetic manganese counterparts revealed to be also active for OAT and, in some cases, with catalytic activities similar to those found in natural enzymes. Despite the similarity in geometry and catalytic activities, manganese porphyrins react differently from iron porphyrins and the nature of the active species is yet to be determined. A high-valent Mn complex was claimed to be responsible by the OAT. This is mainly due to the experimental detection of a diamagnetic Mn(V)-Oxo species in 1997 with a remarkable stability in alkaline medium.[1] This stability contrasts with the expected high reactivity an active species should have. However, DFT calculations confirmed the possibility of a diamagnetic state for this Mn(V)-Oxo species and the inertness toward OAT was claimed to be a consequence of a low oxyl character for this state.[2] This debate on the nature of the active species is still open and two important questions must be answered. What is the role of the oxyl character for reactivity? If the diamagnetic Mn(V)-Oxo ground state is unreactive, what is the true nature of the active species? Recently, we have used two model systems to investigate the relative energies of low-lying electromeric states of these Mn-Oxo species using the multiconfigurational ab initio CASPT2 and RASPT2 methods.[3] We have found that two states are possible candidates to be the active species, a $\text{Mn}^{\text{V}}\text{O}(\text{P})^+$ triplet state and a $\text{Mn}^{\text{IV}}\text{O}(\text{P}^{\bullet})^+$ quintet state. We have also showed that *meso* substitution is responsible to change the energy difference between these two states showing that a multistate reactivity pattern cannot be ruled out. We have used the RASPT2 results as a benchmark for a variety of pure and hybrid functionals in DFT calculations. From this benchmark study we have extended our investigation to more complex molecules with *meso*-substituted groups like phenyl and penta-*fluoro*-phenyl groups.

Key-words: manganese porphyrin, CASSCF, spin state energetics

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