

EFFECT OF THE SUBSTRATE AND SOLVENT INTO THE ALKANE-HYDROXYLATION MECHANISM BY NON-HEME $\text{Fe}^{\text{V}}(\text{PYTACN})=\text{O}$ CATALYST

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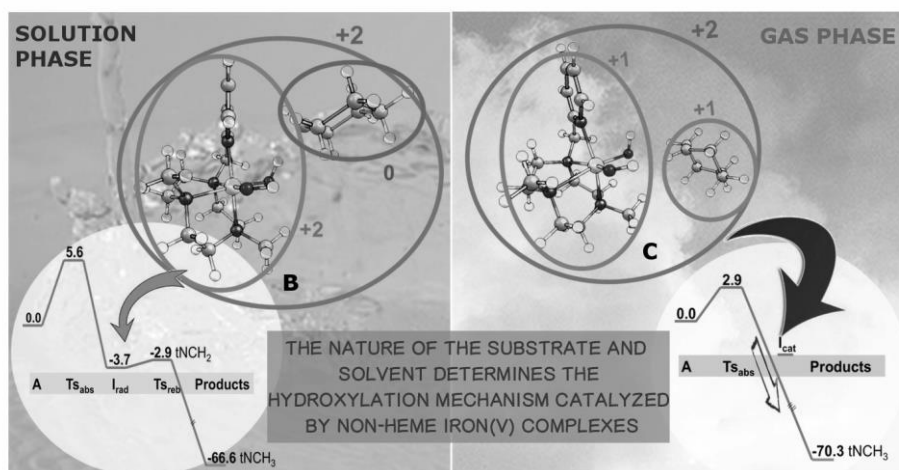
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Alkane hydroxylation processes (AHP) have importance in enzymatic oxidations that participate in metabolic paths, xenobiotic detoxifications and biodegradation, among others reactions.^[1] Furthermore, alkane C-H oxidation reactions find major interest in organic synthesis.^[2] The preparation of $\text{Fe}^{\text{IV}}\text{O}$ and Fe^{VO} complexes has represented a step forward reproducing the chemistry taking place at non-heme iron dependent oxygenases, and has prompted the investigation of their reactivity in alkane C-H oxidation.^[3]

Although the reaction mechanism for alkane oxidation processes by $\text{Fe}^{\text{IV}}\text{O}$ complexes has been widely studied, reaction mechanisms by less common Fe^{VO} complexes presented in literature present some controversies. In all cases the reaction starts with a hydrogen-atom transfer (HAT) from the C-H bond by the Fe^{VO} group, and then reaction mechanisms vary from a rebound stepwise to a concerted highly asynchronous process.^{[4],[5],[6]} The origin of these important differences is still not completely understood. In order to clarify this apparent inconsistency, the stereospecific hydroxylation of a series of alkanes (methane and substrates bearing primary, secondary, and tertiary C-H bonds) through a Fe^{VO} species, $[\text{Fe}^{\text{V}}(\text{O})(\text{OH})(\text{PyTACN})]^{2+}$, (PyTACN=(1-(2'-pyridylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane)), has been computationally examined at gas phase and in acetonitrile solution. Thus, solvent and substrate's nature effects in the reaction mechanism are considered.^[7]

The study shows that: i) to properly describe alkane hydroxylation processes mediated by Fe^{VO} species, it is essential to take into consideration the solvent effects during geometry optimizations; ii) the use of gas-phase geometries (with or without solvent effects) explains the variety of different mechanisms for the hydroxylation of alkanes reported in the literature.

The most important differences between $\text{Fe}^{\text{IV}}\text{O}$ and Fe^{VO} reactivity in alkane C-H oxidation reactions will also be highlighted.



- 1) P.R. Ortiz de Montellano, *Chem. Rev.* **2010**, 110, 932.
- 2) M. Costas, *Coord. Chem. Rev.* **2011**, 255, 2912.
- 3) A.R. McDonald, L. Que, *Coord. Chem. Rev.* **2013**, 257, 414.
- 4) A. Bassan, M.R.A. Blomberg, P.E.M. Siegbahn, L. Que, *Chem. Eur. J.* **2005**, 11, 692.
- 5) P. Comba, M. Maurer, P. Vadivelu, *Phys. Chem. A.* **2008**, 112, 13028.
- 6) I. Prat, A. Company, V. Postils, X. Ribas, L. Que, J.M. Luis, M. Costas, *Chem. Eur. J.* **2013**, 19, 6724.
- 7) V. Postils, A. Company, M. Solà, M. Costas, J.M. Luis, *Computational Insight into the Alkane-Hydroxylation Mechanism by Non-Heme Fe(PyTACN) Iron Complexes. Effect of the Substrate and Solvent.* Submitted.