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 FeIVO and FeVO 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 FeIVO complexes has been widely studied, reaction mechanisms by less common FeVO 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 FeVO 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 FeVO species, [FeVO(OH)(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 FeVO 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 FeIVO and FeVO reactivity in alkane C-H oxidation reactions will also be highlighted.