

To rebound or dissociate? This is the mechanistic question in C-H hydroxylation by heme and nonheme metal-oxo complexes

Kyung-Bin Cho,^{*a} Hajime Hirao,^{*b} Sason Shaik^{*c} and Wonwoo Nam^{*a}

Electronic Supplementary Information

^a Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760, Korea. Email: workforkyung@ewha.ac.kr, wwnam@ewha.ac.kr

^b Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Republic of Singapore. Email: hirao@ntu.edu.sg

^c Institute of Chemistry and The Lise Meitner-Minerva Center for Computational Quantum Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel. Email: sason@yfaat.ch.huji.ac.il

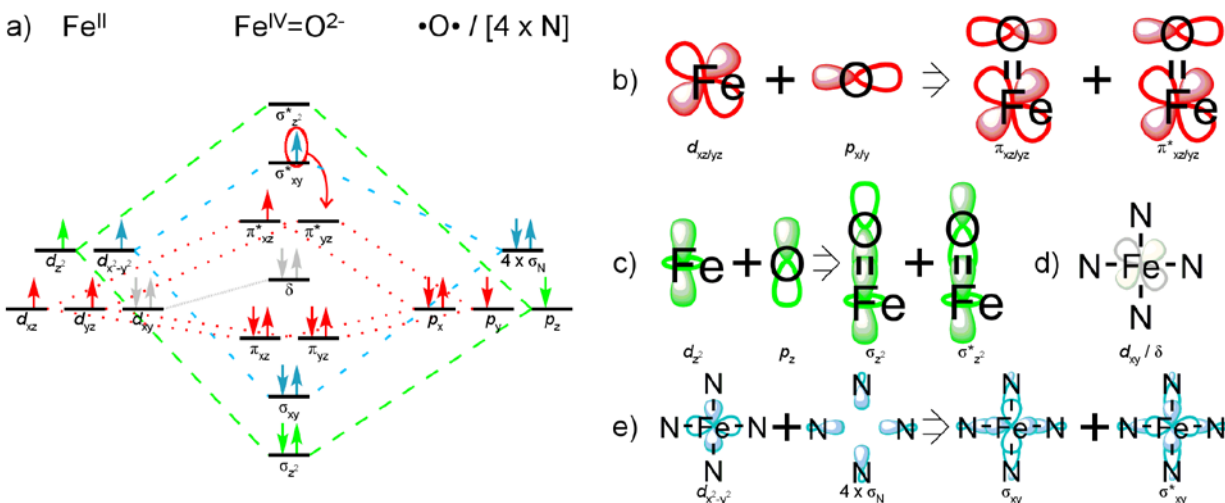


Figure S1. Combining the d -orbitals on Fe^{II} with p -orbitals on monooxygen or four equatorial nitrogen ligand atoms to form tetragonal pyramidal (octahedral without an axial ligand) $\text{Fe}^{\text{IV}}\text{O}$ species. The electron occupation is corresponding to $\text{Fe}^{\text{IV}}\text{O}$ species, but the orbital mixing concept is applicable to any metal-oxo species. a) Schematic changes of the energy levels during the formation (or dissociation) of the $\text{Fe}^{\text{IV}}\text{O}$ species from (to) the Fe^{II} orbitals on the left and $\text{O}/4\text{xN}$ orbitals on the right. b) The d_{xz} and d_{yz} orbitals on Fe combines with p_x and p_y on O, respectively, to form the bonding π_{xz} and π_{yz} orbitals, as well as their antibonding counterparts (π^*_{xz} and π^*_{yz}). c) d_{z^2} combine with p_z to form σ_{z^2} and $\sigma^*_{z^2}$ orbitals. d) The d_{xy} orbital is the only orbital that is not interacting with any ligand atoms. e) The $d_{x^2-y^2}$ orbital interacts with the equatorial ligand atoms to form σ_{xy} and σ^*_{xy} , and is therefore independent of any reactions involving the Fe-O bond.

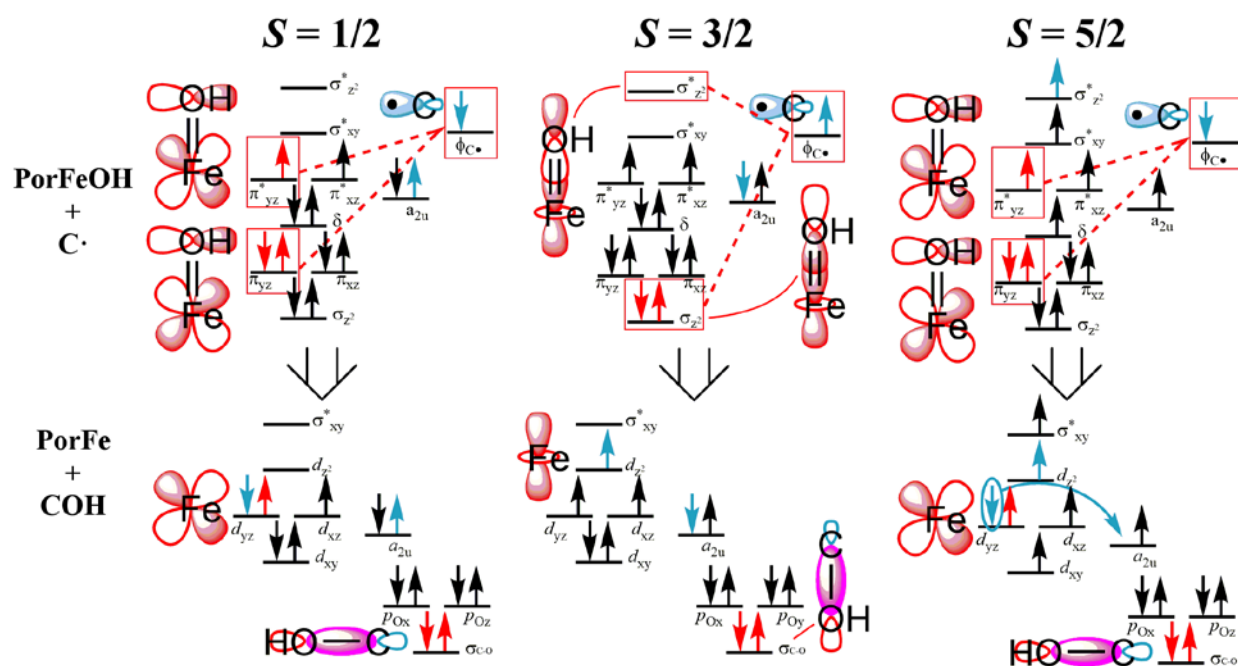


Figure S2. Occupations and electron shift patterns for the rebound step of P450 reactions. Blue arrows represent the electrons that originate from the substrate $\phi_{C\cdot}$ orbital. This orbital interacts with either the π_{yz}/π^*_{yz} or $\sigma_{z^2}/\sigma^*_{z^2}$ orbitals (red squares) to form the C-O bonding orbital σ_{C-O} (consisting of $\phi_{C\cdot}$ and one p orbital from O) and the corresponding d orbital on Fe. These orbitals are filled with electrons from the original orbitals (red arrows). The other orbitals form the rest of the d orbitals on Fe and the two other p orbitals on O. In the $S = 5/2$ state, a final step is to move the α -electron in d_{yz} to the lower-lying orbital a_{2u} .

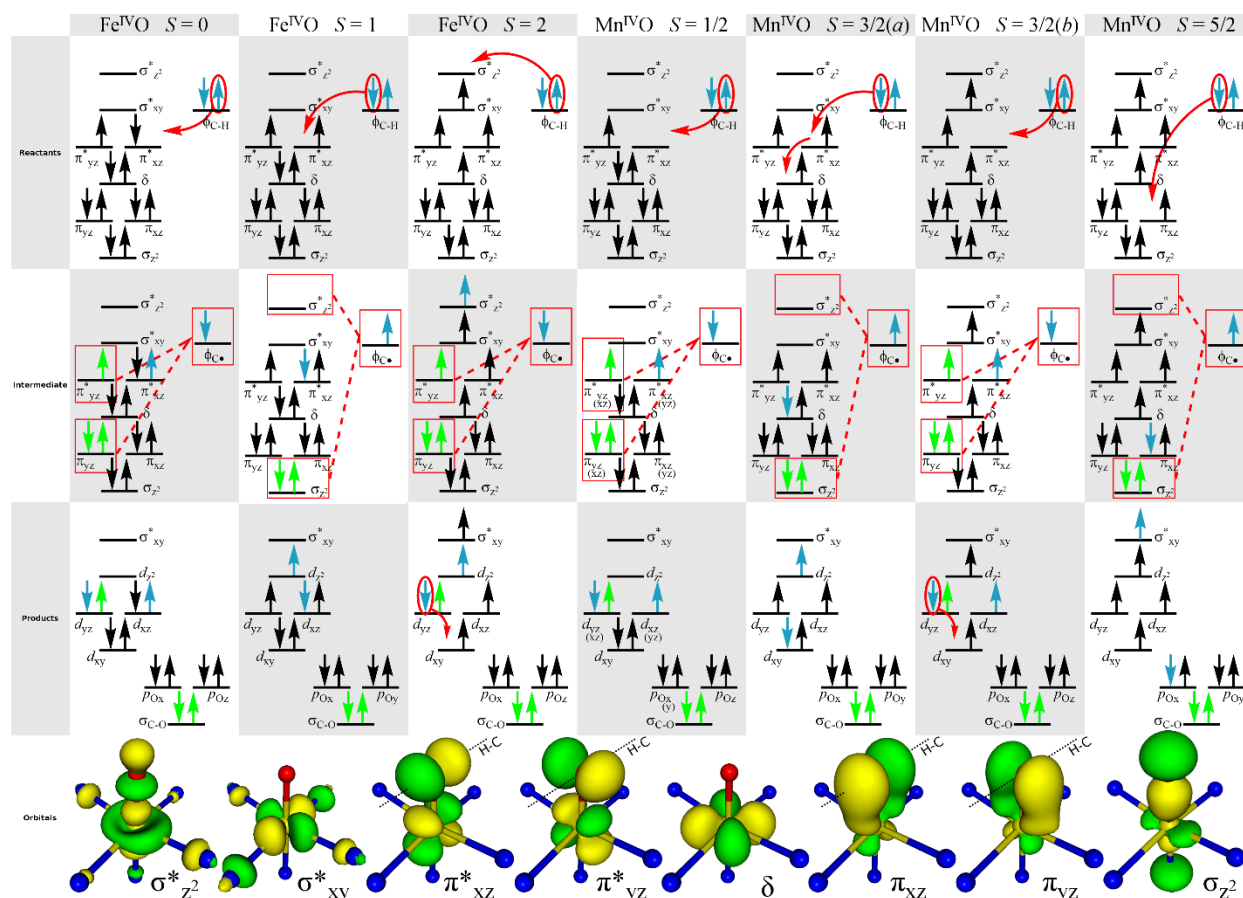


Figure S3. Possible valence electron configurations of Fe^{IV}O and Mn^{IV}O. The one electron movement, which reduces the metal-O during the H-abstraction step, is shown (first row, blue arrows indicate electrons originating from the substrate). At the intermediate step (second row), the substrate radical orbital now interacts (red squares) with either the $\sigma_{z2}/\sigma^*_{z2}$ or π_{yz}/π^*_{yz} pair of orbitals (in the case of Mn^{IV}O $S = 1/2$, there was an example found in which the radical interacts with the π_{xz}/π^*_{xz} pair, ref. 34 in the main text). The metal-oxygen bond cleavage causes the σ and π orbitals to break up into their constituent orbitals (Figure S1, b and c), leaving behind the d orbitals on the metal and the p orbitals on O. The interaction with the substrate creates a bonding orbital σ_{C-O} filled with electrons from the interacting orbitals (green, third row). The shapes of the starting valence orbitals are also shown (fourth row).