Electronic Supplementary Information

Redox activity of nickel and vanadium porphyrins: also a possible mechanism behind petroleum genesis and maturation?

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Figure 1 Total electronic density mapped by the Molecular Electrostatic Potential surfaces of (a) PorH₂, (b) PorFe, (c) PorNi, (d) PorVO (top) and (e) PorVO (side). The scale of color varies from $-2 \times 10^{-2}$ (red) to $2 \times 10^{-2}$ $e$ (blue).
Figure 2 PorVO molecule showing the localization of the unpaired electron over the VO region (total spin density mapped by the molecular electrostatic potential). The spin density varies from 0 (red) to 0.5 (blue).
Figure 3 Reaction path of methanol into methanal conversion catalyzed by one VO porphyrin. 1a is constituted of PorVO ($D_0$) + CH$_3$OH ($S_0$) and 1b is PorVO ($Q_0$) + CH$_3$OH ($S_0$). TS$_{1a-2a}$ is a $D_0$ state. 2a is constituted of PorVOH($T_0$) + *CH$_2$OH ($D_0$) and 2b is PorVOH($S_0$) + *CH$_2$OH ($D_0$). TS$_{2a-3a}$ is a $Q_0$ state whereas TS$_{2a-3a}$ is a $D_0$ state. Finally, 3a is composed of PorVOH$_2$ in $Q_0$ state and CH$_2$O in $S_0$ state whereas 3b is PorVOH$_2$ in $D_0$ state and CH$_2$O in $S_0$. The BDE(nc) marked levels stand for the required energy barriers when no catalyst is present. It means that, to abstract the first hydrogen of the CH$_3$ group, one would need 91.8 kcal.mol$^{-1}$ to do so, whereas one needs 49.2 kcal.mol$^{-1}$ to have it abstracted using a porphyrin molecule. Further on, to abstract the hydrogen of the hydroxyl group, without catalyst, one would need to give 31.7 kcal.mol$^{-1}$ of extra energy (the showed number was renormalized to have 2a as reference) instead of 1.9 only kcal.mol$^{-1}$ when a porphyrin is involved. The gray labels indicate the reaction path passing by another pristine PorVO porphyrin to abstract the hydroxyl hydrogen. TS$_{2a-4a}$ is a $T_0$ state whereas TS$_{2a-4a}$ is the $S_0$ equivalent. They result both 4a or 4b which are composed of either PorVOH ($T_0$) and CH$_2$O ($S_0$) or PorVOH ($S_0$) and CH$_2$O ($S_0$), respectively.
Figure 4 Geometries of the transition states in their lowest energy spin states. (a) $\text{TS}_{1\alpha-2\alpha}$, (b) $\text{TS}_{2\alpha-3\alpha}$ and (c) $\text{TS}_{3\alpha-4\alpha}$. 
Figure 5 Reaction coordinate scan of the PorVO–H dissociation in both $S_0$ and $T_0$ spin states. $S_0$ fails to describe this dissociation curve since it tries to share a single electron in two different atoms far apart (oxygen and hydrogen). The $T_0$ spin state describes the dissociation curve appropriately and indicates a dissociation energy of $\sim 52$ kcal.mol$^{-1}$. The reference is the PorVO system separated from the H$^*$ by an infinite distance.
Figure 6 Molecular orbital 95 (HOMO), relative to vanadium $d_{xy}$. 
Figure 7 Structure de PorNi + ligand: (a) SH$^-$; (b) CH$_3$CH$_2$COO$^-$; (c) Pyridine.
Figure 8 2D PES scan of the PorNi-H$_2$ system.

Figure 9 3D PES scan of the PorNi-H$_2$ system.
Figure 10 $\text{H}_2$ adsorption geometry on top of PorNi.