Electronic Supplementary Information

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

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February 1, 2019

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Figure 1 Total electronic density mapped by the Molecular Electrostatic Potential surfaces of (a) PorH$_2$, (b) PorFe, (c) PorNi, (d) PorVO (top) and (e) PorVO (side). The scale of color varies from -2.10^{-2} (red) to 2.10^{-2} e (blue).
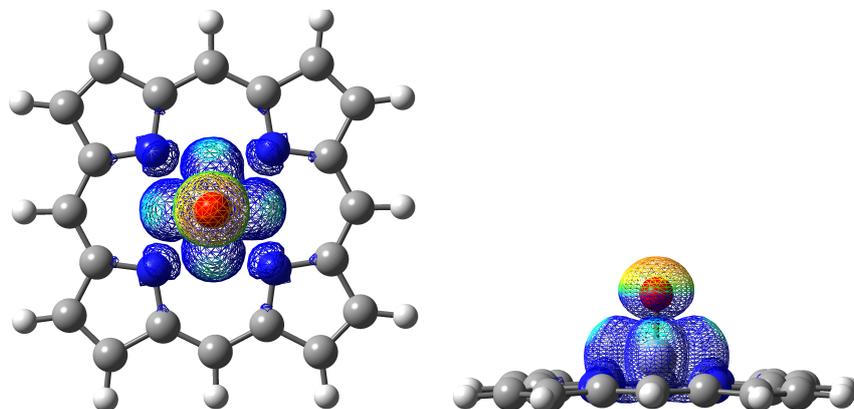
Figure 2 PorVO molecule showing the localization of the unpaired electron over the VO region (total spin density mapped by the molecular electrostatic potential). The spin density varies from 0 (red) to 0.5 (blue).

$$E^T_{\mathrm{CH_3OH}} - (E^T_{\bullet\mathrm{CH_2OH}} + E^T_{\bullet\mathrm{H}})$$

100.7

$$E^T_{\bullet\mathrm{CH_2OH}} - (E^T_{\mathrm{CH_2O}} + E^T_{\bullet\mathrm{H}})$$

73.7

$[\mathrm{Por(VO)\text{-}H\text{-}CH_2OH}]^{\bullet\dagger}$

49.2 (42.3)

$\mathbf{TS}_{1a-2a}$

$[\mathrm{Por(VO)\text{-}H\text{-}OCH_2}]^{\dagger}$

48.8 (47.8)*

$\mathbf{TS}_{2a'-3a'}$

43.9 (38.7)

$\mathbf{TS}_{2a-3a}$

42.0 (45.8)

2a

$\mathrm{Por(VOH)} + {}^\bullet\mathrm{CH_2OH}$

$[\mathrm{Por(VOH)\text{-}H\text{-}OCH_2}]^{\bullet\dagger}$

35.0 (38.9)

3a

$\mathrm{Por(VOH_2)}^\bullet + \mathrm{CH_2O}$

17.1 (14.6)*

3a'

$\mathrm{Por(VOH)} + \mathrm{CH_2O}$

0 kcal.mol^{-1}

1a

$\mathrm{Por(VO)}^\bullet + \mathrm{CH_3OH}$
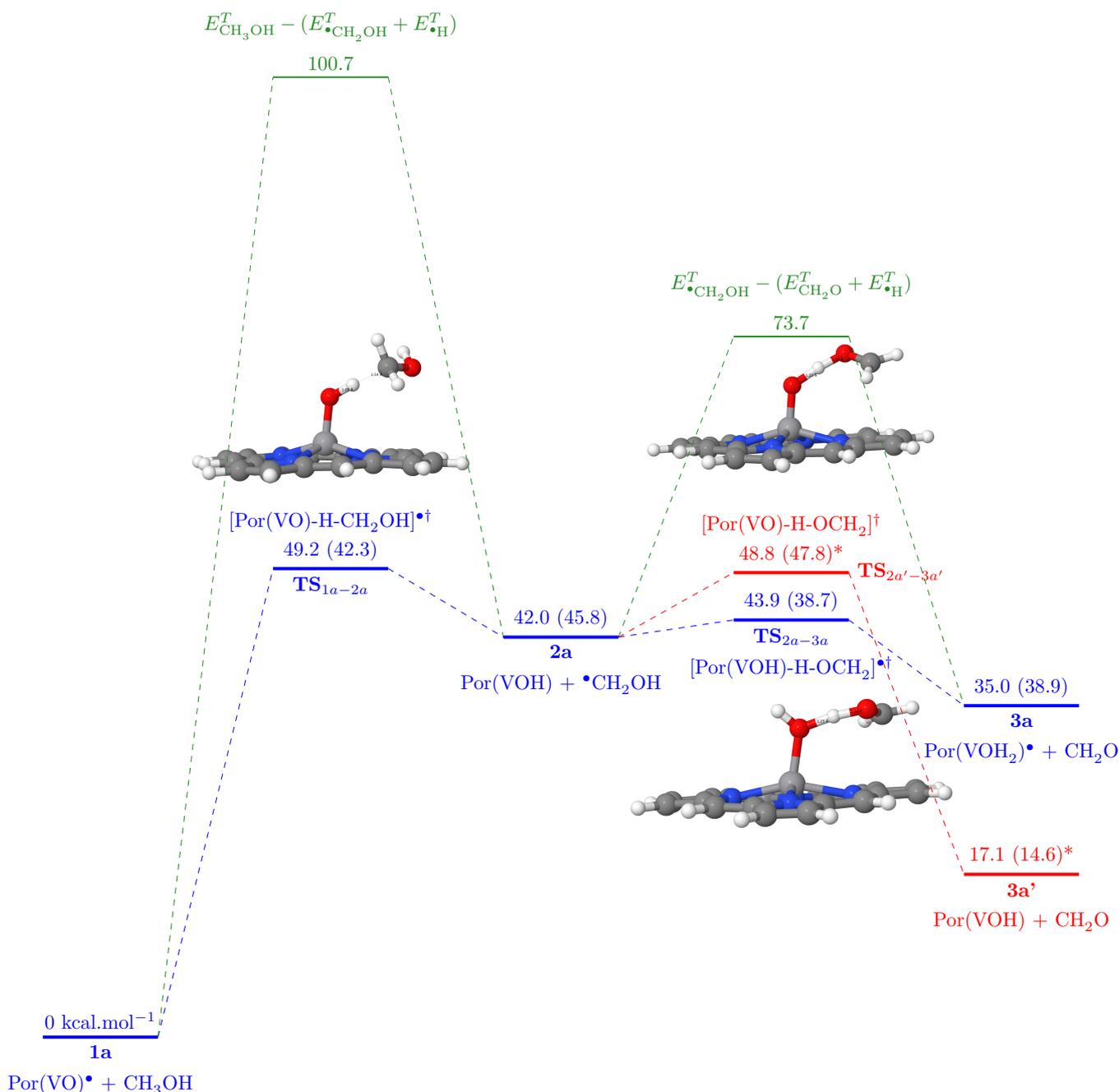
Figure 3 Reaction path of methanol into methanal conversion catalyzed by one VO porphyrin. $1a$ is constituted of PorVO (D_0) + CH$_3$OH (S_0) and $1b$ is PorVO (Q_0) + CH$_3$OH (S_0). TS$_{1a-2a}$ is a D_0 state. $2a$ is constituted of PorVOH(T_0) + $^\bullet$CH$_2$OH (D_0) and $2b$ is PorVOH(S_0) + $^\bullet$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(n.c) 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.

(a)

(b)

(c)

Figure 4 Geometries of the transition states in their lowest energy spin states. (a) TS$_{1a-2a}$, (b) TS$_{2a-3a}$ and (c) TS$_{2a-4a}$.
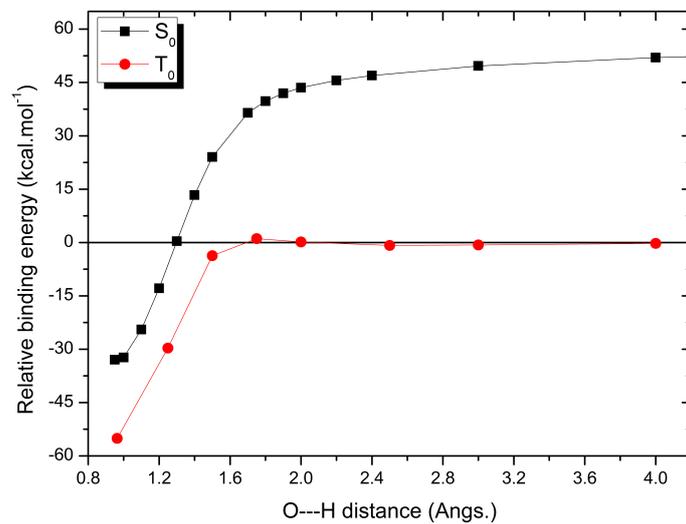
Figure 5 Reaction coordinate scan of the PorVO—H dissociation in both S_0 and T_0 spin states. S_0 fails to describe this dissociation curve since it tries to share a single electron in two different atoms far apart (oxygen and hydrogen). The T_0 spin state describes the dissociation curve appropriately and indicates a dissociation energy of ~ 52 kcal.mol^{-1}. The reference is the PorVO system separated from the H$^\bullet$ by an infinite distance.
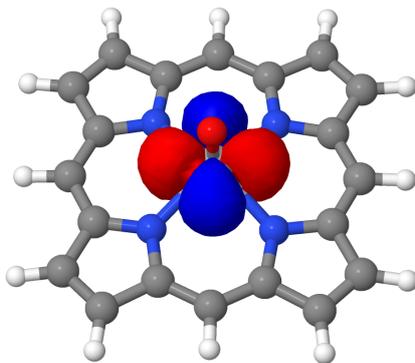
Figure 6 Molecular orbital 95 (HOMO), relative to vanadium d_{xy}.
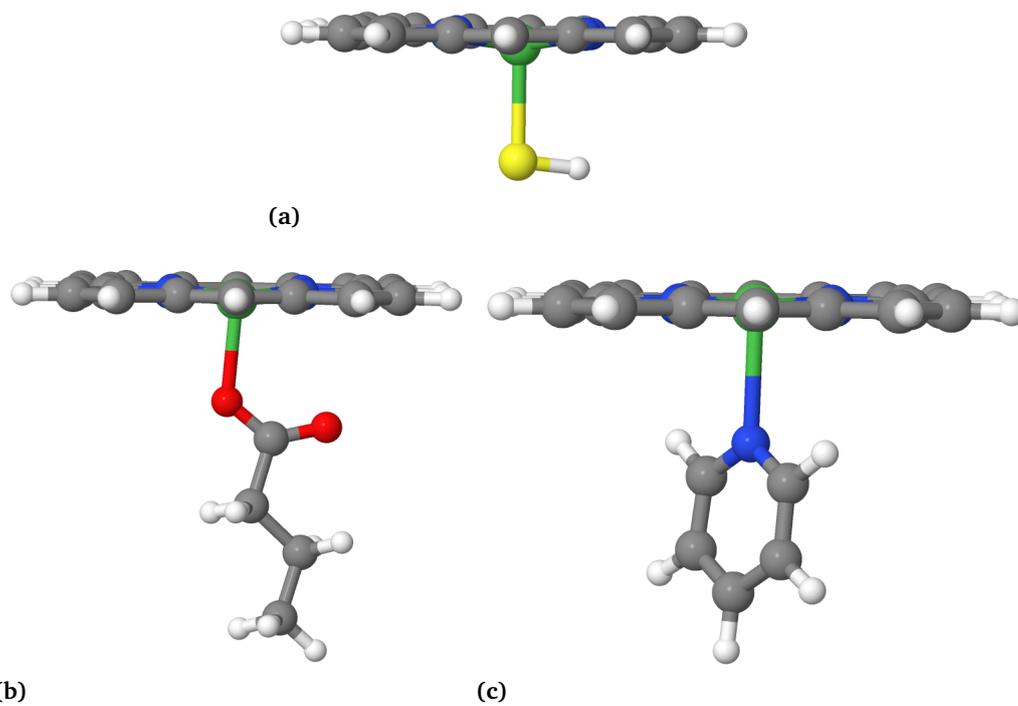
Figure 7 Structure de PorNi + ligand: (a) SH^-; (b) $CH_3CH_2COO^-$; (c) Pyridine.
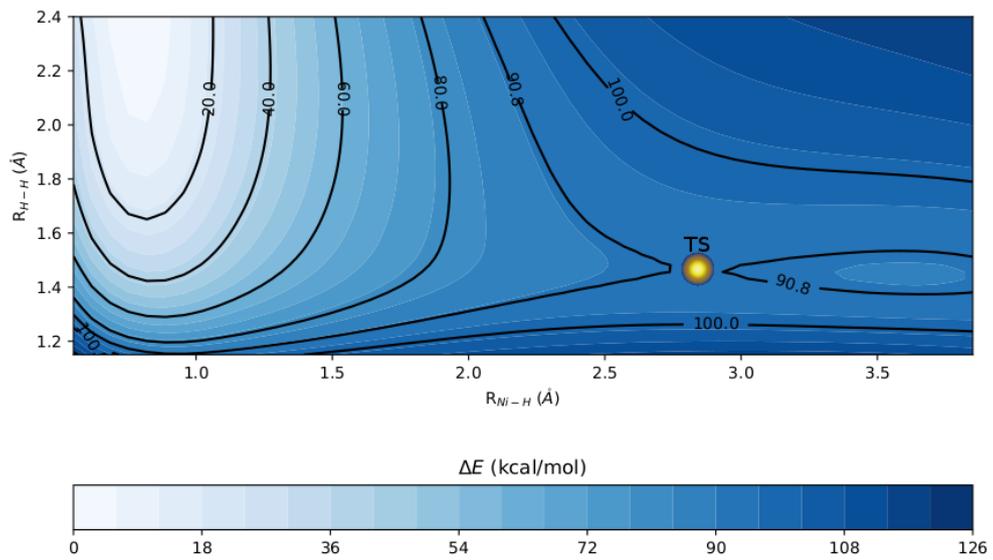
Figure 8 2D PES scand of the PorNi-H_2 system.
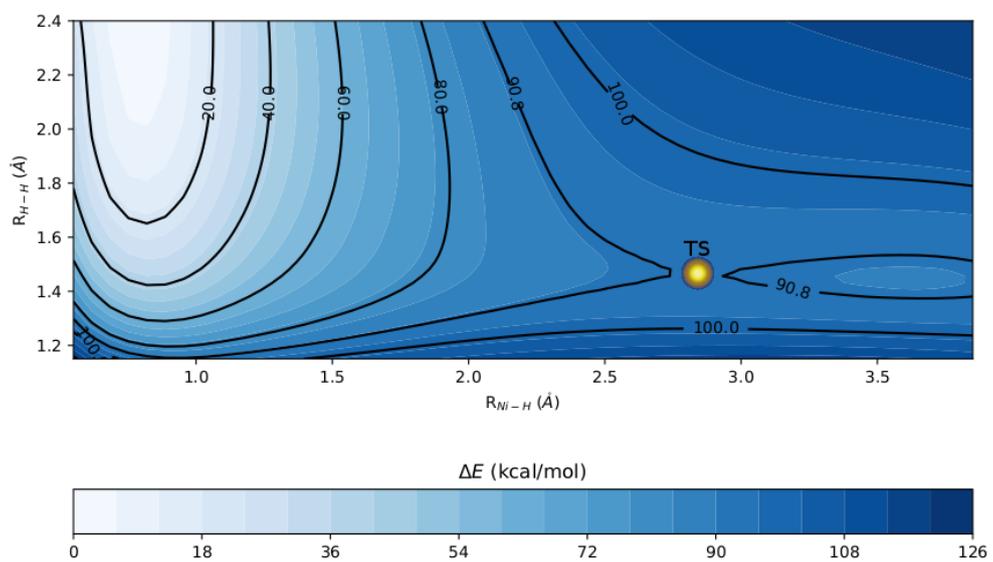
Figure 9 3D PES scand of the PorNi-H_2 system.
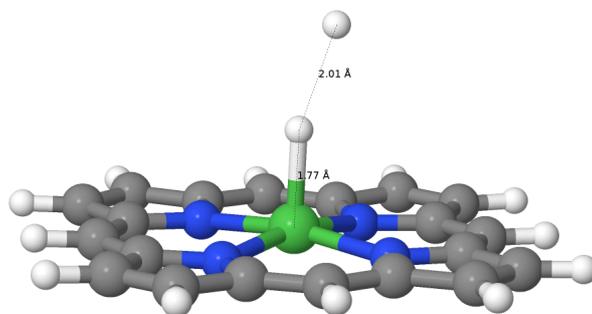
Figure 10 H_2 adsorption geometry on top of PorNi.