The rebound mechanism in catalytic C–H oxidation by MnO(tpp)Cl from DFT studies: electronic nature of the active species†

David Balcells,[a] Christophe Raynaud,[a] Robert H. Crabtree[b] and Odile Eisenstein*[a]

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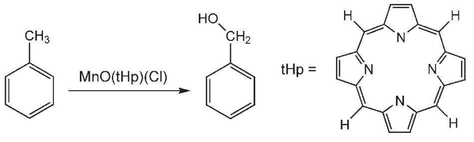
DFT studies show that the rebound mechanism for MnO(tpp)(Cl)-catalyzed C–H hydroxylation is favored for spin states with oxyl character.

C–H bond hydroxylation by high valent metal oxo porphyrin species continues to be an area of great interest in connection with enzymatic oxidation by heme enzymes.[1] Perhaps for this reason the analogous manganese porphyrins have been somewhat less studied, no enzymes containing manganese porphyrins yet being known.[2] From a practical standpoint however, Mn porphyrin complexes have long been known as extremely efficient for C–H bond hydroxylation with a variety of primary oxidants, often more so than the iron porphyrin.[3]

The rebound mechanism[4] (eqn (1), M = Fe,[5] Mn[6] or Ru[7]) commonly proposed for metalloporphyrin-catalyzed oxidations consists of a radical hydrogen abstraction (H-abstraction) followed by the transfer of the resulting hydroxo group from the metal to the intermediate carbon radical (OH-rebound). A related mechanism was described by Strassner and Houk for non-catalytic oxidation with permanganate.[8] Finally, a pathway involving the initial formation of an agostic intermediate was proposed for the iron case.[9] Some key results were recently obtained by Solomon *et al.* who showed experimentally that the singlet state of $[Mn(O)(tdcpp)]^+$ was not able to oxygenate alkanes and suggested that the active species that can do this are probably high spin and may contain an additional ligand *trans* to the oxo.[10]

$$\mathrm{M{=}O + C{-}H \rightarrow M{-}OH + C^{\bullet} \rightarrow M + C{-}OH} \qquad (1)$$

In this paper we present a DFT study on the rebound mechanism for the oxidation of toluene to benzyl alcohol by a model of $[Mn(O)(tdcpp)]^+$ (tdcpp = tetra-(2,6-dichlorophenyl)-porphyrin) in which the phenyl groups of the porphyrin ligand have been replaced by hydrogens (tHp) and a ligand (Cl) *trans* to oxygen has been included (see Scheme 1). The calculations have been carried out with Gaussian 03,[11] at the DFT(BP86) level.[12] Our study shows that the rebound mechanism applies but only in the triplet and quintet spin states, not in the singlet ground state of the system.



Scheme 1 Toluene oxidation by MnO(tHp)Cl.

Several electronic states are accessible for MnO(tHp)Cl. In the singlet state (**S**), both the π(Mn=O) and d_{xy} occupied orbitals are too low in energy to easily undergo thermal electron excitation (see orbital diagrams in the ESI†). These data are consistent with **S** being an oxo complex with no spin density on O. The porphyrin ligand has some π(tHp) orbitals at the frontier level, providing an obvious source for electron excitation leading to higher spin states. The lowest vacant orbitals are π*(Mn=O), which are therefore the best target for hosting promoted electrons. Calculations at the same level on the five coordinate MnO(DCB) complex (DCB = 4,4′-dicarboxy-2,2′-bipyridyl) showed a similar orbital pattern.[13]

The singlet (**S**) and triplet (**T**) states (Fig. 1) are found to have similar energies with **T** being 3.4 kcal mol^{-1} higher in energy. In **T**, two unpaired electrons are localized on Mn, as indicated by the spin density analysis (2.12). Interestingly, this analysis also shows some spin density on oxygen (0.23), which suggests some oxyl radical character. This spin density is the result of partial π*(Mn=O) character in the singly-occupied orbitals. This is also consistent with the elongation of the Mn–O bond in **T** (1.66 Å) relative to **S** (1.57 Å). Because the d_{xy} orbital remains doubly occupied and the spin density of *ca.* 2 is mostly on Mn, the triplet can be described as $Mn^{III}(\uparrow\downarrow\uparrow\uparrow)$ with a small but significant oxyl character. Oxyl character in a similar high valent Mn-oxo intermediate has been proposed by Siegbahn *et al.* for the oxygen-evolving reaction involving photosystem II[14] and with a biomimetic catalyst.[15]

A quintet state, **Q**, has been found 11.1 kcal mol^{-1} above **S**, and thus **Q** is the least stable of the three spin states. A similar energy

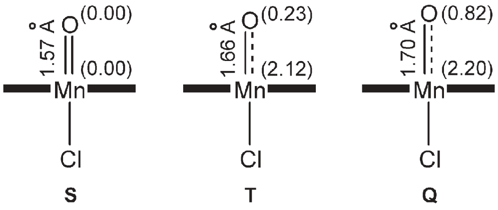


Fig. 1 Spin states of MnO(tHp)Cl. The spin densities on Mn and O are given in parentheses.

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[a] *Institut Charles Gerhardt, CNRS, Université Montpellier 2, cc-1501 Place Eugène Bataillon, 34095, Montpellier, France. E-mail: odile.eisenstein@univ-montp2.fr; Fax: +33 467144839; Tel: +33 467143306*
[b] *Yale Chemistry Dept, New Haven, CT, USA. E-mail: robert.crabtree@yale.edu; Fax: +1 203-432-6144; Tel: +1 203-432-3925*

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pattern has been found for the spin states of the Mn^{V}O(salen) species involved in olefin epoxidation.[16] **Q** has spin densities of 2.20 (Mn) and 0.82 (O). This is a result of the higher participation of the π*(Mn=O) orbitals in the singly-occupied orbitals, compared to the **T** case. Unlike the **T** case, spin density on the porphyrin (0.76) arises from participation of π(tHp) in the singly-occupied orbitals. As a consequence, the electronic configuration of the system can be described as Mn^{III}(↑↓↑↑)oxyl-(↑)tHp(↑). Owing to the greater participation of the π*(Mn=O) orbitals, the oxyl character in **Q** is greater than in **T**, which yields an even longer Mn–O bond of 1.70 Å.

These calculations show that all three spin states of the system are accessible with the singlet being the ground state, in good agreement with the experiments reported by Solomon *et al.*[10] A DFT (B3LYP) study on a related cationic system ([Mn(O)-(tHp)(L)]$^+$,with L = H_2O or vacancy) showed a similar pattern with multiple accessible spin states in which the ground state is a quintet.[17]

The reaction path for the formation of benzyl alcohol from toluene and MnO(tHp)Cl was explored for the three possible spin states, starting with H-abstraction. Despite numerous attempts, no transition state for H-abstraction could be located starting from **S**. In contrast, low barrier H-abstraction was found for both **T** and **Q**, which have oxyl character.

Toluene and **T** form an adduct, **T-1**, in which a methyl C–H is 2.10 Å from the oxygen (Fig. 2). The CH···O interaction is weak and **T-1** is only 0.8 kcal mol^{-1} below toluene and **T**. From **T-1** a transition state for H-abstraction, **T-TS1**, has been located 2.7 kcal mol^{-1} above **T-1**. As expected, the H involved in the weak CH···O interaction is transferred to O. At **T-TS1**, the transferring hydrogen is almost midway between C and O (*d*(C···H) = 1.31 Å and *d*(H···O) = 1.25 Å). Relaxation of **T-TS1** towards products leads to intermediate **T-2**, which has a Mn-bound hydroxo group (*d*(Mn–OH) = 1.83 Å) weakly interacting with the benzylic carbon (*d*(OH···C) = 2.09 Å). The high spin density found on the benzylic carbon (−0.63) indicates substantial radical character in the $PhCH_2$ fragment. The spin densities on the metal and the oxygen are also high (2.56 and 0.18 respectively). The H-abstraction (**T-1 → T-TS1 → T-2**) has a low energy barrier of 2.7 kcal mol^{-1} and a favourable ΔE of −4.2 kcal mol^{-1}.

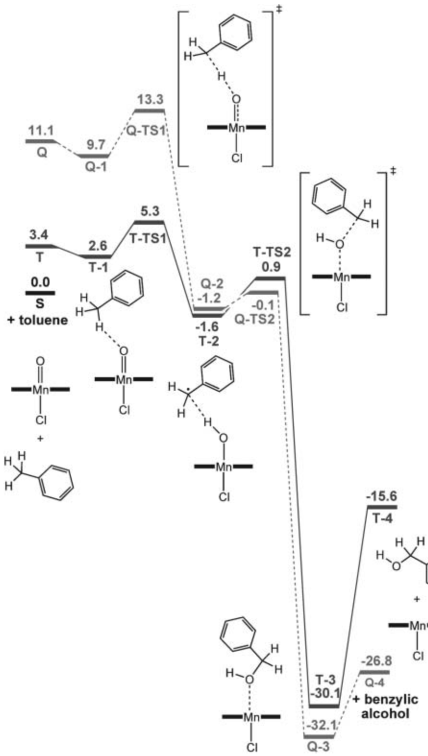

Fig. 2 Potential energy surfaces (kcal mol^{-1}) for toluene oxidation by MnO(tHp)Cl. The solid and dotted lines correspond to the triplet and quintet states respectively.

Intermediate **T-2** undergoes OH-rebound generating complex **T-3**. The hydroxo group of **T-2** is transferred to the benzylic carbon yielding benzyl alcohol. In **T-3** the benzyl alcohol remains weakly bound to the metal with a Mn–O distance of 2.09 Å. The transition state of the rebound step, **T-TS2**, has a reactant-like structure with a short Mn–OH distance of 1.86 Å and a long HO···C distance of 2.41 Å. The main difference between **T-2** and **T-TS2** is a change of position of H which moves away from the carbon allowing the benzyl radical to interact with the oxygen. Starting from **T-2**, the OH-rebound has a very low energy barrier of 2.5 kcal mol^{-1} and is strongly exothermic by −28.5 kcal mol^{-1}. This indicates that OH-rebound is much more exothermic and faster than the prior H-abstraction step.[18] The reaction product is released in a subsequent dissociative step, **T-3 → T-4** + benzyl alcohol, with an energy cost of 14.5 kcal mol^{-1} relative to **T-3**.

The toluene hydroxylation pathway was also studied for the quintet state, **Q** (Fig. 2). The overall reaction is similar to that found for the triplet. After association between **Q** and toluene to form **Q-1** (*d*(CH···O) = 2.24 Å), H-abstraction through **Q-TS1** (in which H is midway between C and O; *d*(C···H) = 1.24 Å and *d*(H···O) = 1.39 Å), forms **Q-2** in which the spin density on the benzyl radical carbon is 0.65. This step is exothermic by 10.9 kcal mol^{-1} and has an energy barrier of 3.6 kcal mol^{-1}. Subsequent OH-rebound through **Q-TS2** leads to intermediate **Q-3**, in which the benzyl alcohol interacts weakly with Mn (*d*(Mn–O) = 2.42 Å). This strongly exothermic reaction (ΔE = −30.9 kcal mol^{-1}) has a very low barrier of 1.1 kcal mol^{-1}. A facile subsequent dissociative step, **Q-3 → Q-4**, yields benzyl alcohol.

The energy profiles for the reaction paths *via* the triplet and quintet are thus very similar. Nevertheless, because **Q** is 7.7 kcal mol^{-1} less stable than **T**, the quintet potential energy surface is at a higher energy for the H-abstraction step. In contrast, the OH-rebound step is slightly more favoured for the quintet than for the triplet. This suggests that the reaction may start on the triplet surface and finish on the quintet by spin crossover before the final dissociation step. However, there might be no real advantage in this crossing because the minor energy gain in the OH-rebound step for the quintet state could be compensated by the barrier for spin crossover. However, a detailed analysis of the spin crossover requires a complex calculation of minimum energy crossing points,[19] that is beyond the scope of the present communication.

In summary, the calculations show that, regardless of the spin state, OH-rebound is more favoured than H-abstraction both at the thermodynamic and kinetic levels. The very low barrier for the

OH-rebound step suggests that the hydroxo-Mn intermediate is unlikely to have sufficient lifetime to be characterized.

The computational study presented here suggests that the rebound mechanism is a feasible pathway for catalytic C–H oxidation by MnO(tHp)(Cl). Our calculations show that the singlet state of the oxo species, MnO(tHp)Cl, is not active in the hydroxylation of toluene. In contrast, after being excited to a higher spin state (a process which should be thermally accessible), either the triplet or the quintet, the reaction proceeds with very low barriers. These computational results agree with the experimental observations that the singlet state is not reactive in this reaction.[10] Furthermore a number of diamagnetic singlet 5-coordinate square pyramidal manganese(V)-oxo complexes having an axial oxo group are known to be stable and thus to lack exceptional reactivity.[20] A corrolazine example, that is rather close in structure to the present MnO(tpp) system can only abstract H atoms from very easily oxidized substrates such as phenols.[21] Unexpectedly, even a small oxyl character is sufficient to make the H-abstraction feasible, as shown by the equal energy barriers calculated for both **T** and **Q**. The critical influence of the spin on the reactivity of MnO species has been also reported in catalytic epoxidation.[22]

The influence both of the metal coordination mode (five- *vs.* six-coordinate) and the nature of the ligand on the relative energies of the spin states of the system is crucial for a better understanding of Mn-catalyzed oxidation. Our theoretical studies on Mn-catalyzed C–H activation are being extended to other catalytic systems and substrates, notably with MnO(tHp)X, where $X \neq Cl$.

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