

Spin-State Energetics and Oxyl Character of Mn-Oxo Porphyrins by Multiconfigurational *ab initio* Calculations: Implications on Reactivity

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Important electromeric states in manganese-oxo porphyrins MnO(P)^+ and $\text{MnO(PF}_4\text{)}^+$ (porphyrinato or *meso*-tetrafluoroporphyrinato) have been investigated with correlated *ab initio* methods (CASPT2, RASPT2), focusing on their possible role in multi-state reactivity patterns in oxygen transfer (OAT) reactions.[1] Due to the lack of oxyl character, the Mn^{V} singlet ground state is kinetically inert. OAT reactions should therefore rather proceed through thermally accessible triplet and quintet states that have a more pronounced oxyl character (Figure 1). Two states have been identified as possible candidates: a Mn^{V} triplet state and a $\text{Mn}^{\text{IV}}\text{O(L}^{\bullet}\text{a}_{2\text{u}})^+$ quintet state. The latter state is high-lying in MnO(P)^+ but is stabilized by the substitutions of H by F at the *meso* carbons (where the π $\text{a}_{2\text{u}}$ orbital has significant amplitude), as shown in Table 1. Oxyl character and Mn-O bond weakening in these two states stems from the fact that the Mn-O π^* orbitals become singly (triplet) or doubly occupied (quintet). Moreover, an important role for the reactivity of the triplet state is also likely to be played by the π bond that has an empty π^* orbital, because of the manifest diradical character of this π bond, revealed by the CASSCF wave function. Interestingly, the diradical character of this bond increases when the Mn-O bond is stretched, while the singly occupied π^* orbital loses its oxygen radical contribution. The RASPT2 results were also used as a benchmark for the description of excited state energetics and Mn-O oxyl character with a wide range of pure and hybrid density functionals. With the latter functionals both the $\text{Mn}^{\text{V}} \rightarrow \text{Mn}^{\text{IV}}$ promotion energy and the diradical character of the π bond (with empty π^*) are found to be extremely dependent on the contribution of exact exchange. For this reason, pure functionals are to be preferred.

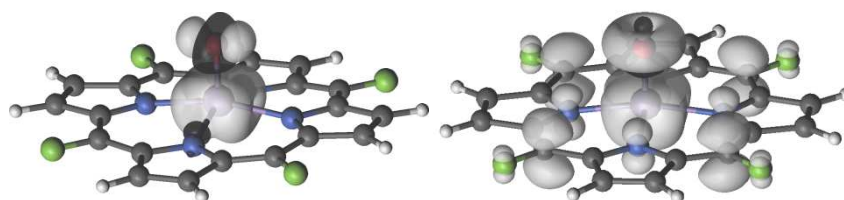


Figure 1. Spin density from CASSCF in the $\text{Mn}^{\text{V}}\ ^3\text{B}_1$ state (left) and the $\text{Mn}^{\text{IV}}\ ^5\text{A}_2$ state (right) of $\text{MnO(PF}_4\text{)}^+$.

Table 1. RASPT2 energies in kcal mol^{-1} relative to Mn^{V} singlet ($^1\text{A}_1$) ground state. Calculations performed considering solvation by PCM with $\epsilon = 53.54$ to model $\text{H}_2\text{O/CH}_3\text{CN}$ 7/3 in mol.

	$\text{Mn}^{\text{V}}\text{O(L)}^+$	$\text{Mn}^{\text{IV}}\text{O(L}^{\bullet}\text{a}_{2\text{u}})^+$			$\text{Mn}^{\text{IV}}\text{O(L}^{\bullet}\text{a}_{1\text{u}})^+$		
L	$^3\text{B}_1$	$^5\text{A}_2$	$^3\text{B}_1$	$^1\text{B}_1$	$^5\text{A}_1$	$^3\text{B}_1$	$^1\text{B}_1$
P	4.5	11.7	18.9	18.9	13.3	19.5	19.6
PF ₄	5.4	3.7	9.4	9.5	19.9	25.1	25.3

Reference: [1] Jannuzzi, S. A. V.; Phung, Q. M.; Domingo, A.; Formiga, A. L. B.; Pierloot, K.; *Inorg. Chem.* **2016**, 55, 5168. (Cover of issue 11, June 6th).