# COMMUNICATION

## Oxygen-Atom Transfer by a Naked Manganese(V)–Oxo–Porphyrin Complex Reveals Axial Ligand Effect

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Dedicated to the Centenary of the Italian Chemical Society

High-valent transition-metal–oxo complexes are electrophilic oxidants implicated in a variety of biological processes and chemical transformations.<sup>[1]</sup> Manganese(V)–oxo species are suggested to be crucial intermediates in the epoxidation of a wide range of alkenes and they provide useful functional models for the active species of heme-containing monooxygenases, including cytochrome P450 enzymes. Manganese– oxo units are also found at the core of photosystem II, performing oxidation of water to oxygen.<sup>[2]</sup>

 $Mn^{V}$ -oxo-porphyrin complexes are analogous to the socalled Compound I intermediate, described as an Fe<sup>IV</sup>-oxoporphyrin radical cation complex. They were first prepared by Groves in aqueous solution and characterised as diamagnetic low-spin d<sup>2</sup> ground state.<sup>[3]</sup> Other examples of complexes bearing a  $Mn^{V}$ -oxo unit bound to macrocyclic and salen ligands have also been described.<sup>[4]</sup>

Interestingly, the oxygen-atom-transfer (OAT) reactivity of  $Mn^{v}$ -oxo-porphyrin complexes soluble in water is found to be strongly pH-dependent. The pronounced enhancement observed at low pH has been explained by the effect of the axial ligand *trans* to the  $Mn^{v}$ -oxo unit on the electron promotion energy required to access the reactive high-spin states and by the existence of the prototropic equilibria in water depicted in Equation (1).

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[a] Prof. M. E. Crestoni, Prof. S. Fornarini, Dr. F. Lanucara Dipartimento di Chimica e Tecnologie del Farmaco Università di Roma "La Sapienza" P.le A. Moro 5, 00185, Roma (Italy) Fax: (+39)06-4991-3602 E-mail: mariaelisa.crestoni@uniroma1.it The stable form, observed at a high pH as well as with excess base in organic solvents, is relatively inert and has been characterised recently as the first example of a *trans*-dioxomanganese(V),  $Mn^{V}O_{2}^{-}$ , species.<sup>[5]</sup> At lower pH the prototropic equilibria shift in favour of oxo-hydroxo,  $Mn^{V}O(OH)$  and oxo-aqua,  $Mn^{V}O(H_{2}O)^{+}$ , species.<sup>[6]</sup> The highest reactivity of the  $Mn^{V}O(H_{2}O)^{+}$  complex is accounted for by the small low-spin/high-spin promotion energy contributing to lower the energy barriers in a two-state energy profile linking the reactant singlet to the product quintet state, as shown by DFT calculations.<sup>[7]</sup> Laser flash photolysis methods have allowed the formation of high-valent manganese–oxo–porphyrin complexes and rate constants have been measured for their reactions with a variety of substrates.<sup>[8]</sup>

The current evidence on high-valent manganese–oxo complexes is even more complicated when one considers the multiplicity of different factors that may affect their reactivity behaviour, such as the influence of axial ligands, the nature of the active form of the catalyst and the presence of counterions.<sup>[9]</sup>

We have now succeeded in obtaining a ligand-free  $Mn^{V}$ oxo-porphyrin complex generating a naked species in the gas phase. This ultimate catalytic intermediate (**1**, in which the porphyrin ligand represented by the oval is the 5,10,15,20-tetrakis(pentafluoro-

phenyl)porphinato dianion, TPFPP) is found to perform efficient OAT to an array of sampled olefins.

To this end we have exploited mass spectrometric techniques,

suitable to provide a direct view of highly reactive metal complexes.<sup>[10]</sup> Working in a highly dilute environment the lifetime of transient intermediates may be rendered adequately long to allow unveiling of both structural details and elementary steps of their catalytic activity. By these means Fe<sup>IV</sup>–oxo–porphyrin radical cation complexes and their in-



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trinsic reactivity features have been characterised in the gas  $\ensuremath{\mathsf{phase}}\xspace^{[11]}$ 

The naked  $Mn^{V}$ -oxo-porphyrin cation **1**, [(TPFPP) $Mn^{VO}$ ]<sup>+</sup>, has been obtained in the gas phase by electrospray ionisation (ESI) of a solution prepared by controlled treatment of the porphynatomanganese(III) chloride [(TPFPP) $Mn^{III}$ ]Cl with iodosylbenzene in methanol at -20 °C. The ion chemistry of **1** has been assayed by Fourier transform ion cyclotron mass spectrometry (FT-ICR).

A high-resolution mass spectrum shows the isotopic peak cluster centred at m/z 1043.0116 (calculated 1042.9754), as expected for the neat addition of an oxygen atom to the reagent [(TPFPP)Mn<sup>III</sup>]<sup>+</sup> ion (**2**) at m/z 1027.0148 (calculated 1026.9805) (Figure 1). Carefully controlled experimental



Figure 1. ESI(+) FT-ICR mass spectrum from a solution of  $[(TPFPP)Mn^{III}]Cl (5 \mu M)$  and iodosylbenzene  $(6 \times 10^{-4} M)$  in methanol. The inset shows an enlargement of the isotopic pattern at m/z 1043 (ion 1).

conditions were adopted to optimise the formation of the oxidised intermediate. In particular, the choice of the protic solvent methanol was a critical factor.<sup>[8c]</sup>

When the so-obtained ion at m/z 1043 is mass selected and allowed to react with olefins (L) in the FT-ICR cell at room temperature, the ensuing ion chemistry conforms to the reactivity behaviour expected from a Mn<sup>V</sup>-oxo-porphyrin cation **1**. In fact the reaction leads to the reduced product ion **2**, implying that an OAT process has occurred [Eq. (2)].

$$[(TPFPP)Mn^{V}O]^{+} + L \rightarrow [(TPFPP)Mn^{III}]^{+} + LO$$
<sup>(2)</sup>

However, the reaction never goes to completion, leaving a steady fraction of unreacted ion at m/z 1043. In analogy with previous findings and reasoning about the corresponding iron complex,<sup>[12]</sup> we ascribe this result to the presence of an isomeric species unfit to release an oxygen atom, most likely a species oxidised on the porphyrin ligand that may be depicted as [(TPFPP-O)Mn<sup>III</sup>]<sup>+</sup> (**3**). Such a species, bearing a four-coordinate manganese, is expected to display addition reactivity to ligands stronger than olefins. This reactivity is indeed observed towards 2-fluoropyridine (2Fpy). The key experiment takes the following course. The overall ion population at m/z 1043 is depleted of the reactive fraction by admitting  $\beta$ -pinene into the ion path leading to the cell. The remaining ions, proven to be unreactive towards  $\beta$ pinene, are allowed to react with 2-fluoropyridine yielding the [(TPFPP-O)Mn<sup>III</sup>(2Fpy)]<sup>+</sup> adduct with a rate constant of  $(6.0 \pm 1.8) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup>s<sup>-1</sup>. It is useful to compare the similar value of  $(7.1 \pm 2.0) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup>s<sup>-1</sup> obtained for the rate constant of the reaction of **2** with 2-fluoropyridine yielding the [(TPFPP)Mn<sup>III</sup>(2Fpy)]<sup>+</sup> adduct. The agreement supports the similar features of the two reacting Mn<sup>III</sup>–porphyrin complexes.

As shown in Figure 2, when assayed by low-energy collision induced dissociation (CID), the  $[(TPFPP-O)Mn^{III}-(2Fpy)]^+$  adduct releases **3**, involving loss of unmodified 2Fpy and thus excluding the occurrence of an N–O coupling event.



Figure 2. ESI FT-ICR mass spectrum displaying the formation of  $[(TPFPP-O)Mn^{III}]^+$  ions at m/z 1043 when mass selected  $[(TPFPP-O)Mn^{III}(2Fpy)]^+$  ions at m/z 1140 are submitted to low-energy CID.

Only in the presence of the olefin,  $\beta$ -pinene and 2-fluoropyridine does the sum of ions at m/z 1043 react to completion. Figure 3 shows a kinetic plot in which the formation of **2** by OAT from **1** to  $\beta$ -pinene is followed by addition of 2Fpy to give the [(TPFPP)Mn<sup>III</sup>(2Fpy)]<sup>+</sup> adduct at m/z1124, while **3** yields the adduct [(TPFPP-O)Mn<sup>III</sup>(2Fpy)]<sup>+</sup>. Due to their different reactivity, the two neutral species are suited to discriminate the isomeric species comprising the ions at m/z 1043. Though depending on the procedure followed to prepare the solution to be submitted to ESI, the relative amount of **1** was never below 60% in the reported experiments.

However, an alternative hypothesis, that is, assigning the different reactivity of the isobaric ions to the presence of multiple electronic states of a single oxidant, may not be excluded. Indeed the critical role of different spin potential-

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Figure 3. Time dependence of the relative ion abundances (A, %) following the selection of ions at m/z 1043 in the presence of a gaseous mixture of 2-F-pyridine ( $6.5 \times 10^{-8}$  mbar) and  $\beta$ -pinene ( $5.0 \times 10^{-8}$  mbar) in the FT-ICR cell.

energy surfaces and of ensuing mixing has been proposed in several oxidation processes, including Mn-catalysed epoxidations.<sup>[3,13]</sup> In particular, recent detailed computational studies show that three possible spin states (singlet, triplet and quintet) are available to  $Mn^{V}$ -oxo-porphyrin complexes, separated by relatively narrow energy gaps.<sup>[6,7]</sup>

The bimolecular rate constants  $(k_{exp})$  along with the relative efficiencies  $(\Phi)$ , both listed in Table 1, indicate that ion 1 bearing no axial ligand is indeed an active oxidant toward olefins. Under the present experimental conditions, neither hydrogen-atom-transfer processes nor addition of L to ion 1 are ever observed. In contrast to the bare metal oxide

Table 1. Kinetic data for the reaction of  $[(TPFPP)Mn^VO]^+$  (1) with selected olefins in the gas-phase.<sup>[a]</sup>

Olefin (IE) <sup>[b]</sup>	$k_{\mathrm{exp}}^{\mathrm{[c,d]}}$	$arPsi^{[e]}$
propene (9.73)	0.0020	0.021
3,3-dimethyl-1-butene (9.45)	0.041	0.43
( <i>E</i> )-2-butene (9.10)	0.072	0.78
(Z)-2-butene (9.11)	0.75	8.1
allylbenzene (7.8-8.7)	0.070	0.76
styrene (8.46)	0.63	6.8
cyclohexene (8.95)	0.75	7.7
1,4-cyclohexadiene (8.8)	0.69	7.8
1-propene, 2-methoxy (8.64) <sup>[f]</sup>	1.7	16
1,3,5-cycloheptatriene (8.30)	1.9	21
(+)-camphene ( $\leq 8.86$ )	2.6	28
indene (8.14) <sup>[g]</sup>	1.2	12
$(1S)-(-)-\alpha$ -pinene (8.07)	9.0	100
β-pinene (n.a.)	9.3	100
(R)-(+)-limonene (8.3)	9.2	100

[a] In all cases, only the [(TPFPP)Mn<sup>III</sup>]<sup>+</sup> product ion of the OAT channel is observed, unless stated otherwise. [b] Ionisation energies (IE [eV]) given in parentheses are from reference [19]; n.a. stands for not available. [c] Second-order rate constants  $(k_{exp})$  in units of  $10^{-10}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>, at the temperature of the FT-ICR cell of 300 K. The estimated error is  $\pm 30\%$ ; the internal consistency of the data is within  $\pm 10\%$ . [d] The following reactants failed to react with 1: CO; ethylene; cyclohexane; benzene. [e] Reaction efficiency,  $\Phi = k_{exp}/k_{coll} \times 100$ . Collision rate constants  $(k_{coll})$  evaluated with the parameterised trajectory theory. [f] The reaction of this olefin with [(TPP)Mn<sup>V</sup>O]<sup>+</sup> (TPP=5,10,15,20-tetraphenylporphinato dianion) is characterised by  $k_{exp} = 0.091 \times 10^{-10}$  cm<sup>3</sup>molecule<sup>-1</sup> s<sup>-1</sup> and  $\Phi = 0.85$ . [g] Electron transfer yielding L<sup>+</sup> is also observed, accounting for 40% of the product ions.

cation MnO<sup>+</sup>,<sup>[14]</sup> complex **1** does not react at an appreciable rate with ethylene under ICR conditions ( $k_{exp} < 10^{-12}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>). Undoubtedly, the presence of the porphyrin ligand in **1** moderates its reactivity and the onset of the olefin epoxidation is only reached with propene. Also the electron demand by the porphyrin macrocycle clearly plays a role in the gas phase as well as in solution.<sup>[8,15,16]</sup> In fact the OAT reactivity towards 2-methoxypropene is about twenty times higher for **1** than with [(TPP)Mn<sup>V</sup>O]<sup>+</sup>, devoid of fluorine atoms on the phenyl rings (see footnote [f] in Table 1).

The kinetic data summarised in Table 1 display a wide range of efficiencies, which span from 0.02% for a terminal olefin like propene, to 100% for electron-rich monoterpenes. The OAT reactivity increases as the ionisation energy (IE) of the olefin decreases. In the case of indene, the OAT process is accompanied by an electron-transfer reaction, which sets a lower limit of 8.1 eV for the IE value of gaseous [(TPFPP)Mn<sup>IV</sup>O]. Another issue from the kinetic data reported in Table 1 regards the reactivity of naked 1 towards E/Z isomers. The performance of manganese complexes in stereoselective epoxidations is of high synthetic value, although the nature of the reactive intermediate is still under debate. The gas-phase reaction of complex 1 with (Z)-2butene is ten times faster than the one with (E)-2-butene. This inherent selectivity may provide a valuable reference to account for the stereoelectronic factors affecting the interaction between an olefin and a Mn<sup>V</sup>-oxo complex.<sup>[17]</sup>

Facing the considerable OAT reactivity of **1** towards olefins, the question arises whether the corresponding *trans*-dioxomanganese(V) ( $Mn^VO_2^-$ ) species can be generated in the gas phase and tested for reaction with the same substrates. Operating in negative ESI, complex **4** at m/z 1059, formally corresponding to [(TPFPP) $Mn^VO_2$ ]<sup>-</sup>, is observed. When the ion is isolated in the FT-ICR cell in the presence of selected neutrals, no reaction is found to occur [Eq. (3)]. Not only electron-rich olefins, but also compounds prone to oxidation, such as sulfides, appear remarkably inert.

$$[(TPFPP)Mn^{V}O_{2}]^{-} + L \rightarrow unreactive$$
(3)

In conclusion, the gas-phase ion chemistry of  $Mn^{V}$ -oxoporphyrin complexes has provided direct evidence that a  $Mn^{V}$ -oxo-porphyrin cation such as [(TPFPP)Mn^{V}O]<sup>+</sup> (1), generated as a naked five-coordinate species, performs as an efficient oxygen-atom donor to olefins. In contrast, the dioxo species **4**, [(TPFPP)Mn^{V}O\_2]<sup>-</sup>, a gas-phase counterpart of the *trans* dioxo-Mn<sup>V</sup>-porphyrins identified by Spiro, Groves and their co-workers in the condensed phase,<sup>[5]</sup> has proven unreactive.

#### **Experimental Section**

The experiments were run on a Bruker BioApex 4.7 T Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with an Apollo I electrospray (ESI) ionisation source. Ions were driven into a

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cylindrical "infinity" cell within a 4.7 T superconducting magnet. Neutral compounds were leaked through needle valves up to constant pressures in the range of  $1.0-15 \times 10^{-8}$  mbar. The pressure was measured with a cold cathode sensor (IKR Pfeiffer Balzers S.p.A., Milan, Italy), calibrated by using the rate constant  $k = 1.1 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}$  for the reference reaction  $CH_4^{+}+CH_4 \rightarrow CH_5^{+}+CH_3^{-}$ , and corrected for different response factors. Pseudo-first-order- rate constants were obtained from the slope of semilog decrease of the reactant ion abundance versus time and divided by the substrate concentration to evaluate the bimolecular rate constants  $(k_{exp})$ . Reactions were run at least in triplicate at the temperature of the FT-ICR cell of 300 K and averaged results are presented. The  $k_{exp}$  values and product ion distributions were found to be invariant with respect to the pressure of the neutral and of an added inert bath gas (Ar). The reaction efficiencies ( $\Phi$ ) are percentages of the collision rate constant ( $k_{coll}$ ) calculated by the parametrised trajectory theory.[18] Whereas the reproducibility of  $k_{\rm exp}$  was good, the estimated error in their absolute values  $(\pm 30\%)$  is mainly due to uncertainty in pressure measurements.

Collision-induced dissociation (CID) experiments were performed by accelerating the mass-selected ion in the FT-ICR cell and allowing collisions with a pulse of argon (peak pressure ca  $4 \times 10^{-6}$  mbar) for 1 s.

The solution to be delivered to the electrospray ionisation (ESI) source by means of a syringe pump was prepared as follows. {5,10,15,20-Tetrakis(pentafluorophenyl)porphynato}manganese(III) chloride ([(TPFPP)Mn<sup>III</sup>]Cl, 2-Cl; ca. 5 μм) was dissolved in methanol at -20°C together with iodosylbenzene (ca. 0.5 mM). The solution develops a deep orange colour and is stable for a few days at -20°C. The ESI-FT-ICR mass analysis shows two prominent clusters, characterised by the same isotopic pattern, namely the species of interest ion 1, [(TPFPP)Mn<sup>V</sup>=O]<sup>+</sup>, centred at m/z 1043, and the resting form 2, [(TPFPP)Mn<sup>III</sup>]<sup>+</sup>, centred at m/z 1027. However, as described in the discussion, the ion population at m/z 1043 was not only composed of 1, characterised by its ability to oxygenate selected olefins. The remaining fraction is unreactive as an oxygen-atom donor and likely corresponds to an isobaric [(TPFPP-O)Mn<sup>III</sup>]<sup>+</sup> ion oxidised on a pyrrolic nitrogen. This fraction was evaluated by its quantitative addition reaction to 2-F-pyridine.

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**Keywords:** epoxidation • kinetics • mass spectrometry • manganese • oxido ligands • porphyrinoids

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