Spontaneous Formation of Reactive Oxometal Porphyrins by Oxygen Atom Transfer from Dioxirane

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Oxygen atom transfer to manganese(II) tetraphenylporphyrin (tpp) and iron(II) tetramesitylporphyrin (tmp) is readily effected at <-10 °C with dimethyldioxirane in anhydrous acetone to afford the labile oxometal species $O{=}Mn^{IV}$ (tpp) and $O{=}Fe^{IV}$ (tmp) in quantitative yields.

Current interest in the metal catalysis of organic oxidations has concentrated on the role of reactive oxometal species as critical intermediates.[1] Indeed the accompanying activity in the synthesis of various oxometallic species has centred on the use of such terminal oxidants as peroxides (peroxy acids, alkyl hydroperoxides, hydrogen peroxide *etc.*), iodosylarenes, hypochlorite, periodate, and different organic oxidants (amine oxides, oxaziridines *etc.*) as well as electrochemical methods to effect oxygen atom transer to metal complexes.[2] However, the search for new synthetic methodology, especially for *labile* oxometal species, continues in attempts to find an active yet selective reagent since each of the existing procedures has some inherent limitation. Thus, the recent availability of dioxiranes as terminal oxidants[3] has attracted our interest, owing to the potentially clean stoichiometric transfer of an oxygen atom, *i.e.* reaction (1), with the formation of an innocuous ketonic byproduct posing minimal complications for further involvement. In particular, the volatile dimethyl derivative ($R^1 = R^2 = Me$) allows the excellent solvent properties of acetone to be exploited for the oxygen transfer in eqn. 1 under homogeneous, nonaqueous conditions. As a test case, we have focused in this study on dimethyldioxirane (DMDO) for the efficient generation of the two prototypical (labile) oxometal species derived from manganese(II) and iron(II) porphyrins since they are currently among the most interesting catalytically active species.[4] Moreover, the thorough spectral characterization of oxomanganese(IV) tetraphenylporphyrin, O=Mn(tpp),[5] and oxoiron(IV) tetramesitylporphyrin, $O{=}Fe^{IV}(tmp)$,[6] in solution provides the requisite product identification for eqn. (1).

$$R^1R^2\overline{C\text{–}O\text{–}O} + ML_n \rightarrow O{=}ML_n + R_1COR_2 \qquad (1)$$

$$Mn^{II}(tpp) + Me_2\overline{C\text{–}O\text{–}O} \rightarrow O{=}Mn^{IV}(tpp) + Me_2CO \qquad (2)$$

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Table 1 Oxidation of manganese(III) porphyrins with dimethyldioxirane[a]

Manganese(III) porphyrin	λ/nm[b]	10^4[DMDO]/ mol dm^{-3}	10^2k_{ψ}[c]/s^{-1}	k_2/ dm^3 mol^{-1} s^{-1}
$ClMn^{III}(tpp)$	473	3.75	5.53	147
		2.10	3.11	148
		1.50	2.18	145
$(HO)Mn^{III}(tpp)$	476	2.10	3.3	157
$Mn^{III}(tpp)$ **II**	470	8.0[d]	1.4	18[f]
		8.0	1.8	22[f]
		8.0[e]	2.0	25[f]
$O[Mn^{III}(tpp)]_2$	470	3.0	0.45	15

[a] In anhydrous acetone at 0 °C, unless indicated otherwise. [b] Position (max.) of Soret band. [c] Pseudo first-order rate constant. [d] -10 °C. [e] 10 °C. [f] $\Delta H^{\ddagger} \approx 2$ kcal mol^{-1} (1 cal = 4.184 J).

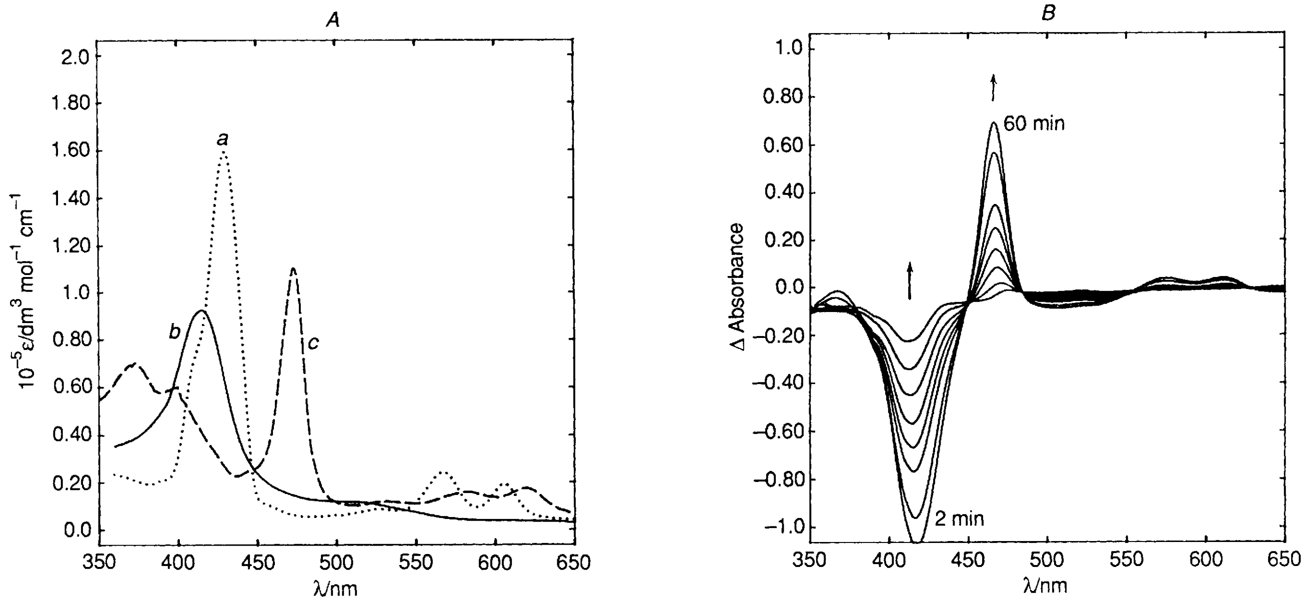

Fig. 1 (*A*) UV-VIS spectra of (*a*) $\mathrm{Mn^{II}(tpp)}$, (*b*) $\mathrm{O{=}Mn^{IV}(tpp)}$ and (*c*) $\mathrm{ClMn^{III}(tpp)}$ in acetone at −10 °C (*B*) Differential UV-VIS spectra of $\mathrm{O{=}Mn^{IV}(tpp)}$ (14×10^{-5} mol dm^{-3}) during decomposition at 25 °C to $\mathrm{Mn^{III}(tpp)}$; spectra are at 2, 5, 10, 15, 20, 30, 40 and 60 min

The oxidation of manganese(II) tetraphenylporphyrin was readily carried out with DMDO (excess) in anhydrous acetone simply by mixing at −50 °C and allowing the solution to warm to −20 °C. The quantitative conversion to $\mathrm{O{=}Mn^{IV}(tpp)}$ **I** is indicated in Fig. 1 by the hypsochromic shift of the Soret band of $\mathrm{Mn^{II}(tpp)}$ (λ_{max} 428 nm, ε 1.6×10^5 dm^3 mol^{-1} cm^{-1})[7] to the new Soret band at λ_{max} 416 nm (ε 9×10^4) in addition to the broad absorption of **I** at λ_{max} 518 nm (ε 1.1×10^4), in complete accord with the earlier spectral characterization.[6] When this red solution was allowed to warm to room temperature, it slowly turned green, and the spontaneous transformation of $\mathrm{O{=}Mn^{IV}(tpp)}$ into $\mathrm{Mn^{III}(tpp)}$ was observed with well defined isosbestic points, as shown by the family of difference spectra in Fig. 1*B*. Such a ready decomposition of **I** thwarted all attempts to isolate single crystals of $\mathrm{O{=}Mn^{IV}(tpp)}$ suitable for X-ray crystallography, and even the simple process of solvent (and DMDO) removal *in vacuo* at −50 °C afforded a violet-black solid of $\mathrm{O{=}Mn^{IV}(tpp)}$ that consistently contained a small amount of manganese(III) contaminant.† Careful spectral analysis of the oxygen atom transfer to $\mathrm{Mn^{II}(tpp)}$ in eqn. (2) revealed that it occurred in two discrete steps. Thus, upon mixing $\mathrm{Mn^{II}(tpp)}$ and DMDO at −50 °C the solution turned green and the Soret band at λ_{max} 428 nm was immediately shifted to 470 nm, diagnostic of a $\mathrm{Mn^{III}(tpp)}$ species **II**. This intermediate was then converted more slowly by the excess of DMDO to $\mathrm{O{=}Mn^{IV}(tpp)}$ with second-order kinetics (Table 1). Such a transformation was confirmed independently by the quantitative oxidation of the authentic manganese(III) porphyrins $\mathrm{ClMn^{III}(tpp)}$[8] and $\mathrm{(HO)Mn^{III}(tpp)}$[9] by DMDO at −10 °C to the same $\mathrm{O{=}Mn^{IV}(tpp)}$ with second-order rate constants k_2 (Table 1) that were both an order of magnitude faster than that for the oxidative conversion of **II**. The intermediate **II** is tentatively identified as the binuclear μ-oxo-manganese(III) species since the Soret band at λ_{max} 470 nm is the same as that of $\mathrm{(tpp)Mn^{III}OMn^{III}(tpp)}$ with λ_{max} 470 nm (ε 6×10^4) obtained immediately upon mixing equimolar solutions of $\mathrm{O{=}Mn^{IV}(tpp)}$ and $\mathrm{Mn^{II}(tpp)}$.[10] Furthermore, the second-order rate constant for the oxidative conversion of $\mathrm{(tpp)Mn^{III}OMn^{III}(tpp)}$ by DMDO to $\mathrm{O{=}Mn^{IV}(tpp)}$ occurs with k_2 = 15 dm^3 mol^{-1} s^{-1}, which is essentially the same as that for **II** (Table 1). Such an intermediate in eqn. 2 is most readily accommodated as in Scheme 1.

$$\mathrm{Mn^{II}(tpp) + Me_2\overline{C{-}O{-}O} \longrightarrow I + Me_2CO} \qquad (3)$$

$$\mathrm{I + Mn^{II}(tpp)} \xrightarrow{\text{fast}} \mathrm{II} \qquad (4)$$

$$\mathrm{II + Me_2CO_2 \longrightarrow 2I + Me_2CO} \qquad (5)$$

$$\mathrm{Fe^{II}(tmp) + Me_2\overline{C{-}O{-}O} \rightarrow O{=}Fe^{IV}(tmp) + Me_2CO} \qquad (6)$$

Scheme 1

Iron(II) tetramesitylporphyrin, $\mathrm{Fe^{II}(tmp)}$,[6] was similarly converted to $\mathrm{O{=}Fe^{IV}(tmp)}$ in quantitative yields upon mixing with DMDO at −10 °C, as indicated in Fig. 2 by the rapid bathochromic shift of the Q band from λ_{max} 538 (ε 3×10^4) to 552 nm (ε 1.3×10^4),[11] *i.e.* eqn. (6). [The formation of $\mathrm{O{=}Fe^{IV}(tmp)}$ in eqn. (6) was confirmed by its conversion to the pyridine (py) adduct, in which the Q band was further red-shifted and split into a pair of bands with λ_{max} 564 (ε 1.5×10^4) and 602 nm (ε 7.7×10^3).[6a,b]] When the solution of $\mathrm{O{=}Fe^{IV}(tmp)}$ was allowed to stand for 10 min at room temperature, the absorption band at 554 nm was converted completely to a new band at 510 nm characteristic of an iron(III) porphyrin.[6b,12] The same product was observed in all attempts to isolate crystalline $\mathrm{O{=}Fe^{IV}(tmp)}$ by solvent removal *in vacuo* at −78 °C. Iron(II) tetraphenylporphyrin, $\mathrm{Fe^{II}(tpp)}$,[6] also reacted with DMDO upon mixing the solutions at −10 °C, as indicated by the rapid disappearance of the Q band at λ 538 nm. However, the appearance of a pair of absorption bands at 570 and 608 nm was a diagnostic of the binuclear μ-oxo species $\mathrm{(tpp)Fe^{III}OFe^{III}(tpp)}$,[6b,11,12] which was probably formed by a process similar to that presented in Scheme 1. Unlike the behaviour of manganese porphyrins, however, the separate experiments with the μ-oxo-iron(III)

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† Although dissolution in acetone and retreatment with DMDO removed the adulterant, it always reappeared upon the reisolation of $\mathrm{O{=}Mn^{IV}(tpp)}$.

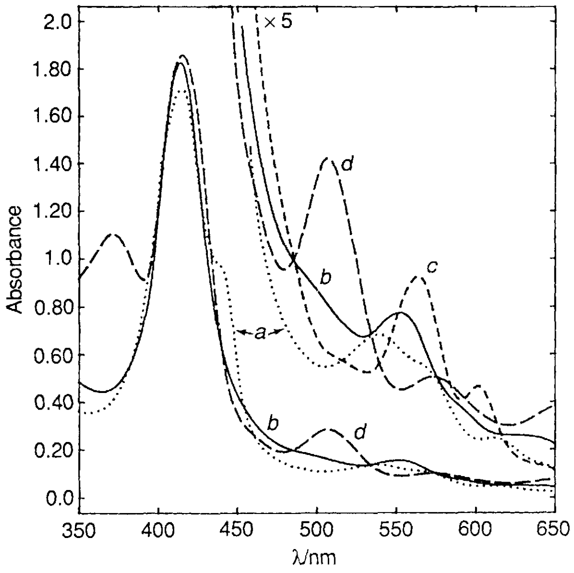

Fig. 2 UV-VIS spectra of (*a*) Fe^{II}(tmp) (4×10^{-4} mol dm^{-3}) and (*b*) $O{=}Fe^{IV}$(tmp) (1.3×10^{-5} mol dm^{-3}); (*c*) $O{=}Fe^{IV}$(tmp) (py) and (*d*) $ClFe^{III}$(tmp) in acetone at 25 °C. Inset shows the enlargement (×5) of the low energy Q band region.

tetraphenylporphyrin with excess of DMDO (*cf.* eqn. 5) provided no evidence for the route to a persistent O=Fe(TPP).

Preliminary experiments with other square-planar, coordinatively unsaturated derivatives of tetraphenylporphyrin with chromium(II), cobalt(II) and nickel(II)[13] exhibited similar reactivity with DMDO, but the product stoichiometries await definitive structural characterization.

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References

1 R. H. Holm, *Chem. Rev.*, 1987, **87**, 1401; K. A. Jørgensen, *Chem. Rev.*, 1989, **89**, 431.

2 R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.

3 R. W. Murray, *Chem. Rev.*, 1989, **89**, 1187; W. Adam, R. Curci and J. O. Edwards, *Acc. Chem. Res.*, 1989, **22**, 205; R. Mello, M. Fiorentino, C. Fusco and R. Curci, *J. Am. Chem. Soc.*, 1989, **111**, 6799.

4 O. Bortolini, M. Ricci, B. Meunier, P. Friant, I. Ascone and J. Goulon, *New J. Chem.*, 1986, **10**, 39; J. T. Groves and M. K. Stern, *J. Am. Chem. Soc.*, 1987, **109**, 3812; 1988, **110**, 8628; T. G. Traylor and A. R. Miksztal, *J. Am. Chem. Soc.*, 1989, **111**, 7443 and references therein.

5 K. R. Rodgers and H. M. Goff, *J. Am Chem. Soc.*, 1988, **110**, 7049; I. Willner, J. W. Otvos and M. Calvin, *J. Chem. Soc., Chem. Commun.*, 1980, 964.

6 (*a*) A. Gold, K. Jayaraj, P. Doppelt, R.. Weiss, G. Chottard, E. Bill, X. Ding and A. X. Trautwein, *J. Am. Chem. Soc.*, 1988, **110**, 5756; (*b*) A. L. Balch, Y. W. Chan, R.-J. Cheng, G. N. LaMar, L. Latos-Grazynski and M. W. Renner, *J. Am. Chem. Soc.*, 1984, **106**, 7779; (*c*) J. T. Groves and J. A. Gilbert, *Inorg. Chem.*, 1986, **25**, 123.

7 R. D. Jones, D. A. Summerville and F. Basolo, *J. Am. Chem. Soc.*, 1978, **100**, 4416.

8 L. J. Boucher, *J. Am. Chem. Soc.*, 1970, **92**, 2725; M. M Williamson and C. L. Hill, *Inorg. Chem*, 1986, **25**, 4668.

9 W. R. Scheidt, Y. J. Lee, W. Luangdilok, K. J. Haller, K. Anzai and K. Hatano, *Inorg. Chem.*., 1983, **22**, 1516.

10 See A. L. Balch *et al.* in ref. 6*b* for the iron analogy.

11 D.-H. Chin, J. Del Gaudio, G. N. LaMar and A. L. Balch, *J. Chem. Soc.*, 1977, **99**, 5486.

12 E. B. Fleisher and T. S. Srivastava, *J. Am. Chem. Soc.*, 1969, **91**, 2403.

13 See W. R. Scheidt and Y. J. Lee, *Struct. Bonding*, 1987, **64**, 1.