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# *Communications to the Editor*

## Photocatalytic Oxidation of Hydrocarbons by (5,10,15,20-Tetraphenylporphyrinato)manganese(III) Perchlorate and Periodate

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The photochemistry of metalloporphyrins is an active area of research.[1,2] The involvement of manganese in photosynthetic reaction centers[3] and the efficacy of manganese porphyrins for the catalytic photooxidation of hydroquinone to quinone[4] led us to investigate the photochemistry of simple manganese porphyrins. We report here the photocatalytic oxidation of hydrocarbons by (5,10,15,20-tetraphenylporphyrinato)manganese(III) ($MnTPP^+$) with $ClO_4^-$ and $IO_4^-$. This is the first photochemical activation of $ClO_4^-$ as a controlled oxidant.

The electronic absorption spectra of manganese porphyrins have been thoroughly examined.[5] Because of extensive metal $d\pi$–porphyrin $\pi$ orbital interaction, the $\pi \rightarrow \pi^*$ transitions of MnTPP(X) occur at much higher energy and intensity (for MnTPP($ClO_4$), 387 and 410 nm and shoulders at 430 and 456 nm), and the ligand-to-metal charge transfer (LMCT) band occurs at relatively lower energy (484 nm), as shown in Figure 1. It should be noted that there is substantial mixing of the excited states of these transitions.[5]

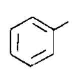
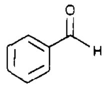
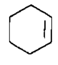
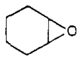
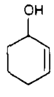
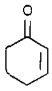
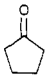
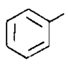
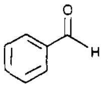
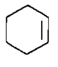
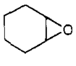
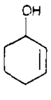
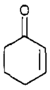
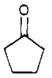
Irradiation of MnTPP($ClO_4$) into either its Soret or the LMCT bands cleanly produces Mn(TPP)Cl and the oxidation of various substrates (as given in Table I). The change in the electronic spectra as a function of irradiation time is shown in Figure 1. The quantitative conversion of Mn(TPP)$ClO_4$ to Mn(TPP)Cl on irradiation is clearly shown by the presence of isosbestic points at 612, 590, 482, 458, and 378 nm, which also demonstrates that there is no long-lived intermediates under these reaction conditions.

The photooxidation of substrates may be either stoichiometric (as in irradiation of MnTPP(X) where $X^- = ClO_4^-$ or $IO_4^-$) or catalytic (by the addition of $R_4N^+X^-$). For example, in the stoichiometric photooxidation of toluene by Mn(TPP)$ClO_4$, 4 mL of $2.95 \times 10^{-4}$ M Mn(TPP)$ClO_4$ was degassed and irradiated at 310–490 nm for 24 h. Products (benzaldehyde and MnTPP(Cl), only) were analyzed by GC and UV–vis, respectively: 1.94 equiv of benzaldehyde (97% of theoretical) and 0.92 equiv of MnTPP(Cl) were produced. Thus, the photochemical reaction's stoichiometry is cleanly established as shown.

$$\mathrm{Mn(TPP)ClO_4} + 2\mathrm{C_6H_5CH_3} \rightarrow \mathrm{MnTPP(Cl)} + 2\mathrm{C_6H_5CHO} + 2\mathrm{H_2O} \quad (1)$$

The quantum yield for the formation of Mn(TPP)Cl at this concentration was $2.7 \times 10^{-5}$. The stoichiometric photooxidation of cyclohexene under the same conditions gave 2.74 equiv of oxidized products (85% of theoretical, counting cyclohexanone for two oxidizing equivalents) and 1.00 equiv of MnTPP(Cl); for cyclopentane photooxidation, 1.67 equiv of cyclopentanone (84% of theoretical) and 0.99 equiv of MnTPP(Cl) were produced. The route by which $ClO_4^-$ is eventually converted to $Cl^-$ is not yet clear; the lower oxochloro species are, however, much less kinetically inert[6] than $ClO_4^-$.

**Table I.** Photocatalytic Oxidation of Hydrocarbons by MnTPP(X)[a]

| Mn complex | oxoanion | substrate | products | turnover no.[b] | rel % |
|---|---|---|---|---|---|
| MnTPP($ClO_4$) | $ClO_4^{-c}$ |  |  | 1.94 | 100 |
| MnTPP($ClO_4$) | $ClO_4^{-c}$ |  |  | 1.78 | 65 |
|  |  |  |  | 0.30 | 11 |
|  |  |  |  | 0.66 | 24 |
| MnTPP($ClO_4$) | $ClO_4^{-c}$ |  |  | 1.67 | 100 |
| MnTPP(OAc) | $IO_4^{-d}$ |  |  | 2.40 | 100 |
| MnTPP(OAc) | $IO_4^{-d}$ |  |  | 11.3 | 45 |
|  |  |  |  | 3.30 | 13 |
|  |  |  |  | 1.04 | 42 |
| MnTPP(OAc) | $IO_4^{-d}$ |  |  | 6.00 | 100 |

[a] In a typical reaction, a benzene solution, 2 M in substrate and 2 mM in MnTPP(X), was photolyzed with filtered light, 310–490 nm. [b] Equivalents of product per equivalent of MnTPP. FID response factors of 0.75 were used for products relative to dodecane internal standard. [c] Stoichiometric reaction. [d] Catalytic reaction: ($n$-hexyl)$_4N^+IO_4^-$ added at ≈50 mM.

Photocatalytic oxidations have also been accomplished, simply by using an excess of the oxoanion, solubilized with $R_4N^+$ counterions. As shown in Table I, the reactions are catalytic in MnTPP(OAc), with more than 25 turnovers observed in one case. The kinetics of product formation have been examined in these systems: for MnTPP(OAc) + $R_4NIO_4$, the photocatalytic reactions are cleanly first order in [$IO_4^-$] and [Mn(III)TPP] and

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(4) (a) Harriman, A.; Porter, G.; Richoux, M. C. *J. Chem. Soc., Faraday Trans. 2* **1982**, *77*, 833. (b) Harriman, A. *Coord. Chem. Rev.* **1979**, *28*, 147. (c) Porter, G. *Proc. R. Soc. London, Ser. A* **1978**, *362*, 281. (d) Loach, P. A.; Calvin, M. *Biochemistry* **1963**, *2*, 361.

(5) Boucher, L. J. *Coord. Chem. Rev.* **1972**, *7*, 289.

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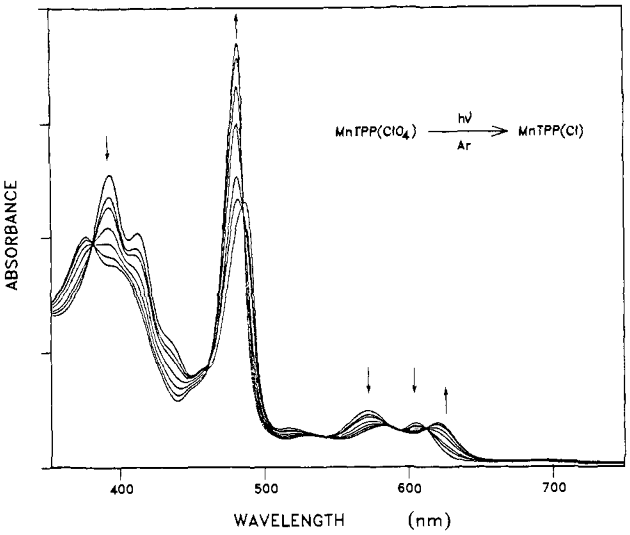

**Figure 1.** Photolytic conversion of MnTPP(ClO$_4$) to MnTPP(Cl). Arrows indicate the change in absorbance during irradiation. Irradiation of MnTPP(ClO$_4$) in toluene from 310 to 490 nm under Ar produces exclusively MnTPP(Cl) and benzaldehyde.

inverse first order in [OAc].[7] Manganese porphyrins are known *thermal* catalysts for hydrocarbon oxidations with various strong oxidants.[6,8,9] We have examined the product distributions for cyclohexene oxidation and find identical ratios of allylic oxidation to epoxidation for the thermal oxidation with iodosylbenzene and the photooxidations. This similarity strongly suggests that the active oxidizing species is the same in both cases: i.e., a putative O=MnTPP$^+$ complex. Secondary oxidation of initial products occurs in the photocatalytic systems, converting the initially formed alcohols to ketones or aldehydes. These results are consistent with the following partial mechanism.

$$\mathrm{MnTPP(OAc)} + \mathrm{IO_4^-} \rightleftharpoons \mathrm{MnTPP(IO_4^-)} + \mathrm{OAc^-} \quad (2)$$

$$\mathrm{MnTPP(IO_4^-)} \rightarrow \mathrm{O{=}MnTPP^+} + \mathrm{IO_3^-} \quad (3)$$

$$\mathrm{O{=}MnTPP^+} + \mathrm{R_3CH} \rightarrow \mathrm{MnTPP^+} + \mathrm{R_3COH}\ \text{etc.} \quad (4)$$

The photochemical O atom transfer from ClO$_4^-$ or IO$_4^-$ has some precedent in the photocatalytic oxygen atom transfer by chromium porphyrins[10] from *N*-oxides to 1-phenylethane-1,2-diol. In fact, the photolysis of CrTPP(ClO$_4$) produces the stable CrTPP(O) in quantitative yield.[11]

In summary, we have shown that Mn(TPP)ClO$_4$ can be photochemically converted cleanly to Mn(TPP)Cl, resulting in stoichiometric oxidation of organic substrates. This reaction can be extended to truly photocatalytic oxidations simply by using solubilized oxoanions. We believe that under these reaction conditions, higher oxidation state oxo-manganese species are formed, as has been demonstrated in the hydrocarbon oxidations by various active oxidants which manganese porphyrins catalyze. Further work on the elucidation of the mechanism for these reactions is under way.

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[7] Thermal oxidations with IO$_4^-$ were noted but in all cases were very much slower than the photocatalytic ones. Furthermore, in the case of cyclohexene oxidation, the thermal reaction gave almost exclusively allylic oxidation. Slow porphyrin oxidative degradation does occur under the thermal conditions, in the presence of IO$_4^-$. Control reactions run under Ar or O$_2$, in the absence of IO$_4^-$, with or without photolysis, gave no observable oxidation; controls run in the absence of MnTPP(OAc) gave no observable oxidation.

[8] (a) Suslick, K. S.; Cook, B. R.; Fox, M. M. *J. Chem. Soc., Chem. Commun.* **1985**, 580. (b) Cook, B. R.; Reinert, T. J.; Suslick, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 7281. (c) Suslick, K. S.; Cook, B. R. *J. Chem. Soc., Chem. Commun.*, **1987**, 200.

[9] (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073. (b) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3510 and references therein. (c) Hill, C. L.; Schardt, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6374. (d) Groves, J. T.; Kruper, W. J.; Haushalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375.

[10] Yuan, L.-C.; Caldewood, T. S.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 8273.

[11] Suslick, K. S.; Acholla, F. V., unpublished results.

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# On the Origin of Diastereofacial Selectivity in Additions to Chiral Aldehydes and Ketones: Trajectory Analysis[1]

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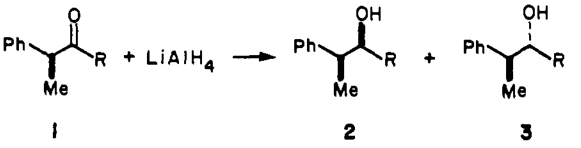
In an earlier communication,[2] we proposed that diastereofacial selectivity in nucleophilic additions to chiral aldehydes might be related to the trajectory of a nucleophile in its attack on the carbonyl group (Figure 1). This argument provides a tidy explanation of the observation by Chèrest, Felkin, and Prudent that asymmetric induction increases markedly in the series of compounds **1a–d** as the size of R increases (eq 1)[3] and also accommodates the observed dramatic increase in diastereofacial selectivity that is observed in Lewis acid mediated reactions of chiral aldehydes.[2]



**1** **2** **3** (1)

a: R = Me; b: R = Et; c: R = *i*-Pr; d: R = *t*-Bu.

The trajectory described by a nucleophile when it attacks a carbonyl, first deduced from a consideration of crystal structures of amino ketones, was confirmed theoretically by Bürgi, Dunitz, and co-workers.[4] These calculations, carried out on formaldehyde, showed that approach occurs on a plane perpendicular to the plane of the molecule, at an angle of approximately 107°, now known as the "Bürgi–Dunitz angle". Several research groups[5] have worked to extend the accuracy of these calculations by considering different nucleophiles and by including the counterion in the calculated model.[6] However, except for a brief consideration in the work of Liotta, Burgess, and Eberhardt,[7] there has been no theoretical investigation of nucleophilic attack on unsymmetric carbonyl compounds.

In order to evaluate the possible magnitude of steric effects such as that proposed[2] on nucleophilic trajectories, we have carried out

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[1] Part 39 in the series "Acyclic Stereoselection". For part 38, see: Oare, D. A.; Heathcock, C. H. *Tetrahedron Lett.* **1986**, *27*, 6169.

[2] Heathcock, C. H.; Flippin, L. A. *J. Am. Chem. Soc.* **1983**, *105*, 1667.

[3] In reductions of **1a–d** the **2**:**3** ratios are 2.8:1, 3.2:1, 5.0:1, and 49:1, respectively; Chèrest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199.

[4] (a) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065. (b) Bürgi, H. B.; Lehn, J. M.; Wipff, G. *J. Am. Chem. Soc.* **1974**, *96*, 1956. (c) Bürgi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563.

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[6] Kaufman, E.; Schleyer, P. v. R.; Houk, K. N.; Wu, Y.-D. *J. Am. Chem. Soc.* **1985**, *107*, 5560.

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