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 centers3 and the efficacy of manganese porphyrins for the catalytic photooxidation of hydroquinone to quinone4 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$_4^-$, respectively. 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 dπ-porphyrin π orbital interaction, the π → π* 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 MnTPP(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 demonstrate 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$_4$N$^+$X$^-$). For example, in the stoichiometric photocatalytic oxidation of toluene by MnTPP(ClO$_4^-$), 4 mL of 2.95 × 10$^{-5}$ M MnTPP(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.

Mn(TPP)ClO$_4$ + 2C$_6$H$_5$CH$_3$ →
Mn(TPP)Cl + 2C$_6$H$_5$CHO + 2H$_2$O (1)

The quantum yield for the formation of Mn(TPP)Cl at this concentration was 2.7 × 10$^{-3}$. 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 Mn(TPP(Cl) for

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

<table>
<thead>
<tr>
<th>Mn complex</th>
<th>oxaon substrate</th>
<th>products</th>
<th>turnover no. $^a$</th>
<th>rel %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnTPP(ClO$_4^-$)</td>
<td>ClO$_4^-$</td>
<td>O</td>
<td>1.94</td>
<td>100</td>
</tr>
<tr>
<td>MnTPP(ClO$_4^-$)</td>
<td>ClO$_4^-$</td>
<td>O</td>
<td>1.78</td>
<td>63</td>
</tr>
<tr>
<td>MnTPP(ClO$_4^-$)</td>
<td>ClO$_4^-$</td>
<td>O</td>
<td>0.30</td>
<td>11</td>
</tr>
<tr>
<td>MnTPP(ClO$_4^-$)</td>
<td>ClO$_4^-$</td>
<td>O</td>
<td>0.66</td>
<td>24</td>
</tr>
<tr>
<td>MnTPP(OAc)</td>
<td>ClO$_4^-$</td>
<td>O</td>
<td>1.67</td>
<td>100</td>
</tr>
<tr>
<td>MnTPP(OAc)</td>
<td>ClO$_4^-$</td>
<td>O</td>
<td>2.40</td>
<td>100</td>
</tr>
<tr>
<td>MnTPP(OAc)</td>
<td>ClO$_4^-$</td>
<td>O</td>
<td>11.3</td>
<td>45</td>
</tr>
<tr>
<td>MnTPP(OAc)</td>
<td>ClO$_4^-$</td>
<td>O</td>
<td>33.0</td>
<td>13</td>
</tr>
<tr>
<td>MnTPP(OAc)</td>
<td>ClO$_4^-$</td>
<td>O</td>
<td>104</td>
<td>42</td>
</tr>
<tr>
<td>MnTPP(OAc)</td>
<td>ClO$_4^-$</td>
<td>O</td>
<td>6.00</td>
<td>100</td>
</tr>
</tbody>
</table>

*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.

Communications to the Editor

Photocatalytic Oxidation of Cyclopetanone

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Further work on the elucidation of the mechanism for these reactions is under way.

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

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In an earlier communication, 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 Chèbre, Felkin, and Prudent that asymmetric induction increases markedly in the series of compounds 1a-d as the size of R increases (eq 1) and also accommodates the observed dramatic increase in diastereofacial selectivity that is observed in Lewis acid mediated reactions of chiral aldehydes.

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. 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 have worked to extend the accuracy of these calculations by considering different nucleophiles and by including the counterion in the calculated model. However, except for a brief consideration in the work of Liotta, Burgess, and Eberhardt, there has been no theoretical investigation of nucleophilic attack on unsymmetrically substituted carbonyl compounds.

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

\[
\begin{align*}
(1) & \quad a: R = Me; \quad b: R = Et; \quad c: R = i-Pr; \quad d: R = Bu.
\end{align*}
\]

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]. Manganese porphyrins are known thermal catalysts for hydrocarbon oxidations with various strong oxidants. 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.

\[
\begin{align*}
\text{MnTPP(OAc)} + \text{IO}_4^- & \rightarrow \text{MnTPP(IO}_4^-) + \text{OAc}^- \\
\text{MnTPP(IO}_4^-) & \rightarrow \text{O}=\text{MnTPP}^+ + \text{IO}_4^- \\
\text{O}=\text{MnTPP}^+ + \text{R}_2\text{CH} & \rightarrow \text{MnTPP}^+ + \text{R}_2\text{COH etc.} \\
\end{align*}
\]

(2) Photochemical attack on ClO\(_4\) - or IO\(_4\) - has some precedent in the photocatalytic oxygen atom transfer by chromium porphyrins 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.

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 Mn(TPP)ClO\(_4\) as the source of 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.

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