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New ligands for manganese catalysed selective oxidation of sulfides to sulfoxides with hydrogen peroxide

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Abstract—In situ prepared manganese complexes with ligands 1–5 have been used in the catalytic oxidation of sulfides to sulfoxides using hydrogen peroxide at 0°C in acetone. Using ligand 4, methyl phenyl sulfoxide is obtained in 55% yield and turnover numbers up to 250, while the formation of sulfone is almost suppressed. © 2001 Elsevier Science Ltd. All rights reserved.

The selective catalytic oxidation of sulfides to sulfoxides has been a challenge for many years, owing to the importance of sulfoxides as intermediates in organic synthesis.¹ The use of H₂O₂ as an oxidant has been extensively studied. Compared to catalytic methods that require oxidants such as NaOCl and ammonium periodates, the use of aqueous H₂O₂ offers the advantage that it is a cheap, environmentally benign and a readily available reagent.² Since water is the only expected side product, catalytic oxidation methods using this reagent are undoubtedly appealing, providing efficient catalysis is accomplished. The undesired sulfone is a common by-product in sulfide oxidation with H₂O₂ and its formation has to be suppressed. Much effort has also been devoted to the development of catalytic methods for the preparation of optically active sulfoxides owing to their importance as chiral ligands,³ and bioactive products.⁴ Since the first reports of Kagan⁵ and Modena,⁶ who used diethyltartrate, Ti(Oi-Pr)₄ and hydroperoxides as oxidants yielding e.e.s higher than 90%, a number of publications related to this research followed.⁷ Hydrogen peroxide has been

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Figure 1.

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investigated as a terminal oxidant in the oxidation reactions with titanium derivatives supported on silica, but only low enantioselectivities (13%) were obtained.\textsuperscript{9}

The use of the Jacobsen (salen) Mn(III) complexes provided good chemical yields and enantiomeric excesses in the range of 34–68% with a reaction system consisting of hydrogen peroxide, acetonitrile as solvent and 2–3 mol% of the salen complex.\textsuperscript{10}

Considering that one could expect that a good epoxidation catalyst can also work as a promoter of the oxidation of thiethers, we report here the use of some preliminary results on the possibility of inducing enantioselectivity using the optically active Mn complex $\text{Mn(OAc)}_3$ (in acetonitrile) of sulfoxides with H\textsubscript{2}O\textsubscript{2}. Only 6% of methyl phenyl sulfoxide was converted to sulfoxide after 6 h in both solvents. When, under the same conditions, an excess (8 equiv.) of oxidant was used, 30% (in acetone) and 68% (in acetonitrile) of sulfide was converted.

Next the dinuclear manganese(IV) complex\textsuperscript{1} based on the $N,N',N''$-1,4,7-trimethyl-1,4,7-triazacyclononane (MeTACN) ligand\textsuperscript{13} (used as catalyst in the selective oxidation of sulfides to sulfones with periodic acid in pyridine\textsuperscript{14}) was used as catalyst for the oxidation of methyl phenyl sulfide with H\textsubscript{2}O\textsubscript{2}. Furthermore, the in situ-formed complexes with dinucleating ligands $N,N',N''$-tetrakis(2-pyridylmethyl)-1,3-propanediamine (2, TPTN) and $N,N',N''$-tetrakis(2-pyridylmethyl)-1,2-ethanediamine (3, TPEN) both featuring the three N-donor set for each Mn site, were used (Fig. 1). The ligands 2 and 3 contain a three- and two-carbon spacer, respectively, between the three N-donor sets.\textsuperscript{12}

Typical catalytic reactions were performed\textsuperscript{15} at 0°C under a nitrogen atmosphere using 1 equiv. of catalyst, 1000 equiv. of substrate and 8 equiv. of H\textsubscript{2}O\textsubscript{2} with respect to substrate. The complexes and in situ-formed catalysts turned out to be very active in sulfide oxidation. For instance, the dinuclear manganese complex based on 1 performs very efficiently in the oxidation of methyl phenyl sulfoxide and generally resulted in full conversion in 1 h (Table 2). Unfortunately, besides the desired sulfoxide, overoxidation to sulfone was observed. Manganese complexes based on TPTN-2 and TPEN-3 were also found to be very active. However, overoxidation was also found. Based on the oxidation results with complex 1 and Mn complexes derived from ligands 2 and 3 (all featuring three N-donor sets) and because of the successful Jacobsen salen oxidation catalysts containing two N-donor and two O-donor sets,\textsuperscript{10} we decided to use the new ligand 2-[[di(2-pyridyldimethyl)methyl][methyl]amino[methyl]phenol\textsuperscript{16} (4, Table 1. Oxidation of methyl phenyl sulfoxide with hydrogen peroxide (30% in water) in the presence of 0.2 mol% $\text{Mn(OAc)}_3$·2H\textsubscript{2}O at 0°C

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Oxidant equiv.</th>
<th>T.O.N.\textsuperscript{b} 2 h sulfoxide\textsuperscript{c} (sulfone\textsuperscript{c})</th>
<th>T.O.N.\textsuperscript{b} 4 h sulfoxide\textsuperscript{c} (sulfone\textsuperscript{c})</th>
<th>T.O.N.\textsuperscript{b} 6 h sulfoxide\textsuperscript{c} (sulfone\textsuperscript{c})</th>
<th>Sulfide not reacted (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetone</td>
<td>2</td>
<td>14 (0)</td>
<td>15 (0)</td>
<td>16 (0)</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>Acetone</td>
<td>8</td>
<td>56 (53)</td>
<td>61 (62)</td>
<td>73 (78)</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>Acetonitrile</td>
<td>2</td>
<td>20 (5)</td>
<td>20 (5)</td>
<td>20 (5)</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>Acetonitrile</td>
<td>8</td>
<td>98 (51)</td>
<td>115 (149)</td>
<td>126 (181)</td>
<td>32</td>
</tr>
<tr>
<td>5\textsuperscript{a}</td>
<td>Dichloromethane</td>
<td>8</td>
<td>21 (19)</td>
<td>27 (36)</td>
<td>35 (70)</td>
<td>75</td>
</tr>
</tbody>
</table>

\textsuperscript{a} H\textsubscript{2}O\textsubscript{2} with respect to substrate.

\textsuperscript{b} T.O.N. = turnover number = mol product/mol catalyst.

\textsuperscript{c} All products were identical to independent samples and identified by GC (HP 6890, column HP1 15×0.3 mm×2.65 μm, polydimethylsiloxane).

\textsuperscript{d} Room temperature.

Table 2. Oxidation of methyl phenyl sulfoxide with 8 equiv. of hydrogen peroxide (30% in water) in the presence of 0.2 mol% $\text{Mn(OAc)}_3$·2H\textsubscript{2}O and 0.2 mol% of ligand at 0°C

<table>
<thead>
<tr>
<th>Complex ligand\textsuperscript{a}</th>
<th>T.O.N.\textsuperscript{b} 2 h sulfoxide (sulfone)</th>
<th>T.O.N.\textsuperscript{b} 4 h sulfoxide (sulfone)</th>
<th>T.O.N.\textsuperscript{c} 6 h sulfoxide (sulfone)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>574 (395)\textsuperscript{c}</td>
<td>N.d.</td>
<td>N.d.</td>
</tr>
<tr>
<td>2</td>
<td>349 (222)</td>
<td>563 (342)</td>
<td>N.d.</td>
</tr>
<tr>
<td>3\textsuperscript{d}</td>
<td>330 (220)</td>
<td>342 (343)</td>
<td>357 (464)</td>
</tr>
<tr>
<td>4</td>
<td>247 (58)</td>
<td>248 (69)</td>
<td>255 (74)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} See Fig. 1.

\textsuperscript{b} T.O.N. = turnover number = mol product/ mol catalyst.

\textsuperscript{c} T.O.N. result after 1 h.

\textsuperscript{d} Room temperature.
Table 3. Oxidation of sulfides using Mn-catalysts based and (S)-5

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>R</th>
<th>Sulfoxide (%)</th>
<th>ee</th>
<th>Absolute configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>Me</td>
<td>55</td>
<td>18</td>
<td>R</td>
</tr>
<tr>
<td>2</td>
<td>p-MeC₆H₄</td>
<td>Me</td>
<td>50</td>
<td>8</td>
<td>R</td>
</tr>
<tr>
<td>3</td>
<td>p-MeOC₆H₄</td>
<td>Me</td>
<td>48</td>
<td>5</td>
<td>R</td>
</tr>
<tr>
<td>4</td>
<td>Ph</td>
<td>CH₂Ph</td>
<td>50</td>
<td>5</td>
<td>R</td>
</tr>
<tr>
<td>5</td>
<td>2-Naphthyl</td>
<td>Me</td>
<td>52</td>
<td>6</td>
<td>R</td>
</tr>
<tr>
<td>6</td>
<td>1-Naphthyl</td>
<td>Me</td>
<td>52</td>
<td>7</td>
<td>R</td>
</tr>
</tbody>
</table>

* Acetone, T=0°C under a N₂ atmosphere, reaction time 2 h, 8 equiv. of 30% H₂O₂ in water as oxidant.

* Isolated yield after column chromatography (SiO₂, EtOAc).

* Determined by HPLC on a Daicel Chiralcel OB-H column.

* Determined by Daicel Chiralcel OJ column; determined by comparison with literature values. 7b

Fig. 1), featuring a three N-donor and one O-donor ligand. Using the complex formed in situ from ligand 4 (with Mn(OAc)₃·2H₂O and methyl phenyl sulfoxide as a test compound, high selectivity was observed, while only slight overoxidation was found. After 4 h, 248 turnover numbers to sulfoxide and only 69 turnover numbers to sulfone were detected (Table 2). After column chromatography a 55% isolated yield of pure sulfoxide was obtained.

Even in the case of slow oxidant addition (over a 1 h period), only a negligible effect in increasing the conversion was found. Using Mn(ClO₄)₂·6H₂O instead of Mn(OAc)₃·2H₂O caused an increase in overoxidation to sulfone, whereas switching from acetone to acetonitrile or dichloromethane as solvent resulted in a dramatic decrease in conversion. It turned out that the best conditions for ligand 4 are acetone as the solvent, and performing the oxidation at 0°C and 8 equiv. of hydrogen peroxide. In summary, the Mn complex with ligand 4 is a promising catalyst in the selective oxidation of methyl phenyl sulfoxide using hydrogen peroxide: with a very low amount of catalyst (0.2 mol%) we obtained the corresponding sulfoxide with 55% chemical yield, without formation of sulfone. We decided to test ligand (S)-5, a chiral version of ligand 4, reasoning that we should obtain sulfoxides with conversion comparable with those obtained using ligand 4, but in optically active form. The results of oxidation of several substrates using this new ligand are presented in Table 3.

Employing the catalyst formed in situ by reacting the enantiopure ligand (S)-5 (Fig. 1) with manganese acetate, sulfoxides are obtained in good yields ranging from 48 to 55%. It seems that the structure of the substrate does not affect the chemical yield of the reaction. An important feature is that only minor amounts of by-products resulting form overoxidation were found. Using (S)-5 we always obtained sulfoxides with (R)-configuration and e.e.s up to 18% (methyl phenyl sulfoxide). Increasing the amount of catalyst from 0.2 to 2 mol% did not improve the enantioselectivity.

In conclusion, the Mn complex based on ligands 4 and 5 is a highly selective and active system for catalytic oxidation of sulfides to sulfoxides using aqueous hydrogen peroxide as a terminal oxidant. Studies to enhance the enantioselectivity in this new catalytic system are in progress.

Acknowledgements

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References


15. Catalytic reactions with complex 1 (Fig. 1) were started by mixing 1.0 ml of a 1.2 μM stock solution of the manganese complex in acetone and 1.0 ml of a stock solution of 1.2 mM of substrate and 0.5 mM of bromobenzene (internal standard) at 0°C under a nitrogen atmosphere. After stirring for 2 min, an excess of hydrogen peroxide (1.0 ml of 30% aq. H2O2, 9.8 mM, 8 equiv. with respect to substrate) was added. The progress of the reaction was monitored by GC by taking a small sample of the reaction mixture and filtering over a short column of silica. To establish the identity of the sulfoxides unequivocally, the retention times and spectral data were compared to those of commercially available and independently synthesised compounds. The same procedure as described for the catalytic reactions of complex 1 was followed with ligands 2–5, except that the reactions were started by mixing 1.0 ml of a 2.4 μM stock solution of Mn(OAc)3·2H2O and 1 ml of a 1.2 μM stock solution of ligand 2 (or 3). In the case of ligands 4 and 5 a 2.4 μM stock solution was used. After stirring for 15 min the substrate was added at 0°C under a nitrogen atmosphere. After stirring for 2 min an excess of hydrogen peroxide (1.0 ml of 30% aq. H2O2, 9.8 mM, 8 equiv. with respect to substrate) was added. The progress of the reaction was monitored by GC.