The dinuclear manganese complex Mn2O(OAc)(2)(TPTN) as a catalyst for epoxidations with hydrogen peroxide
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Published in:
Chemical Communications

DOI:
10.1039/a910232i

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2000

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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In acetonitrile and at ambient temperature, the dinuclear manganese complex of TPTN is able to catalyse the oxidation of several alkenes to the corresponding epoxides with high turnovers numbers (up to 900) using \( \text{H}_2\text{O}_2 \) as oxidant.

Selective oxidation of alcohols to aldehydes and the formation of epoxides from olefins are among the key reactions in organic chemistry. In the ongoing pursuit to develop environmentally benign synthetic methodologies there is currently great interest in new and more efficient catalytic versions of these oxidations. Compared to catalytic methods that require oxidants like NaOCl and ammonium periodates the use of \( \text{H}_2\text{O}_2 \) offers the advantage that it is a cheap, environmentally friendly and a readily available reagent. Since water is the only expected byproduct, synthetic applications of this reagent are undoubtedly appealing provided efficient catalysis is accomplished.

Recently a number of metal complexes have been found to be suitable catalysts for selective epoxidation reactions with \( \text{H}_2\text{O}_2 \) as oxidant.\(^1\) Noyori and coworkers reported a catalytic system based on \( \text{Na}_4\text{WO}_4 \) dihydrate for the epoxidation of terminal olefins and turnovers numbers (TON) were found in the range 150–200 per W atom by using 150 mol% \( \text{H}_2\text{O}_2 \) and 0.2–2 mol% of the catalyst.\(^1\) Methyltrioxorhenium (MTO) is also emerging as a highly suitable epoxidation catalyst.\(^2\) A remarkable acceleration effect on the epoxidation rate was found by Sharpless and coworkers by using pyridine and pyridine derivatives for the MTO catalysed epoxidation of terminal and internal olefins.\(^3\) The Jacobsen catalysts\(^4\) and the related Katsuki catalysts\(^5\) are commonly applied for asymmetric epoxidation reactions of cis-olefins. However, with a few exceptions\(^6\)-\(^8\) NaOCl is used as oxidant for which TON values in the range of 35–40 were found. Recently it was found that a manganese(IV) complex based on the \( N,N'N''A,N''A,N''A \) tris(dimethylamino)acetylene (MeTACN) ligand is a highly active oxidation catalyst.\(^4\)

This dinuclear manganese complex \(1\) is capable of the epoxidation of alkenes with TON usually below 100\(^6\)-\(^9\) but in some cases up to 1000 have been reported using \( \text{H}_2\text{O}_2 \) as oxidant.\(^10\) This complex was also shown by us to be a highly active and selective catalyst for the oxidation of benzyl alcohols to benzaldehydes (TON up to 1000).\(^10\) Synthesis and modifications of the MeTACN ligand are, however, not easily accomplished due to lengthy and tedious preparation whereas the sensitivity of the corresponding metal complexes to changes in the MeTACN structure often leads to completely inactive Mn-complexes. Therefore a challenge is the design of novel dinucleating ligands featuring the three N-donor set for each Mn-site and retaining the high oxidation activity. We present here, high catalytic epoxidation activity for the manganese complex \(2\) based on the ligand TPTN\(^†\) using \( \text{H}_2\text{O}_2 \) as oxidant.

Advantages of this type of ligands are the accessibility and the possibility for ligand modification. The ligands and manganese complexes examined here were synthesised following literature procedures and complexes \(2\) (and \(3\)) have been reported as mimics for the photosystem II (PS II)\(^12\)-\(^15\). Preliminary screening in a number of different catalytic epoxidations showed that complex \(3\) based on TPEN,\(^†\) featuring a two-carbon spacer between the three N-donor sets in the ligand, was unreactive in epoxidation reactions.\(§\) In sharp contrast, complex \(2\), based on TPTN with a three-carbon spacer, is able to catalyse the oxidation of various alkenes to the corresponding epoxides, with \( \text{H}_2\text{O}_2 \) as oxidant in acetone and at ambient temperature (Scheme 1).

Catalytic reactions were performed under a nitrogen atmosphere using 1 equiv. of complex \(2\), 1000 equiv. substrate and \( \text{H}_2\text{O}_2 \) was used as oxidant (1 ml of 30% aqueous \( \text{H}_2\text{O}_2 \), 9.8 mM, 8 equiv. with respect to substrate).\(¶\) During the oxidation reaction in acetone at room temperature gas bubbles developed rapidly when the excess of oxidant was added. As for the reactions using 1\(^\text{st}\)–\(^{11}\) part of the \( \text{H}_2\text{O}_2 \) disproportionates to \( \text{O}_2 \). An increase of the catalyst TON was obtained by performing the

[Diagram of the manganese complex]

**Scheme 1.**
catalytic reactions in aceton at 0 °C suppressing H2O2 decomposition. For the selected olefins generally up to 300 TONs were found. Addition of a further 1 ml of H2O2 (30% aqueous solution in water, 9.8 mmol, 8 equiv. with respect to substrate) resulted in a considerable increase in epoxide yield after 4 h (total TON up to 900, for cyclohexene). These results indicate that the catalyst is very robust under the conditions used. High selectivity is observed and it should be emphasized that in the epoxidation reaction of cyclic alkenes (especially for cyclohexene), besides the epoxides, no allylic oxidation products were found. In control experiments replacing Mn(OAc)3(TPTN) 2 with Mn(OAc)3·3H2O, strong peroxide decomposition and no epoxide formation was found. Data for the conversion of various alkenes to the corresponding epoxides are compiled in Table 1. Styrene epoxidation is accompanied by the formation of a small amount of benzoic in water, 8 equiv. with respect to substrate) resulted in a considerable increase in epoxide yield after 4 h (total TON up to 900, for cyclohexene). These results indicate that the catalyst is very robust under the conditions used. High selectivity is observed and it should be emphasized that in the epoxidation reaction of cyclic alkenes (especially for cyclohexene), besides the epoxides, no allylic oxidation products were found. In control experiments replacing Mn(OAc)3(TPTN) 2 with Mn(OAc)3·3H2O, strong peroxide decomposition and no epoxide formation was found. Data for the conversion of various alkenes to the corresponding epoxides are compiled in Table 1. Styrene epoxidation is accompanied by the formation of a small amount of benzoic

Table 1 Oxidation of selected olefins with Mn2O(OAc)2(TPTN) complex

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Producta</th>
<th>TONb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Styrene</td>
<td>Styrene oxide</td>
<td>157  208  176  271</td>
</tr>
<tr>
<td></td>
<td>Cyclohexene</td>
<td>Cyclohexene oxide</td>
<td>247  352  286</td>
</tr>
<tr>
<td>2</td>
<td>Cyclooctene</td>
<td>Cyclooctene</td>
<td>193  262  575</td>
</tr>
<tr>
<td>3</td>
<td>Benzaldehyde</td>
<td>Benzaldehyde</td>
<td>49  61  48</td>
</tr>
<tr>
<td>4</td>
<td>Cinnamyl alcohol</td>
<td>Cinnamyl oxide</td>
<td>208  219  321</td>
</tr>
<tr>
<td>5</td>
<td>trans-2-Octene</td>
<td>trans-Oct-2-ene</td>
<td>118  178  248</td>
</tr>
<tr>
<td>6</td>
<td>trans-4-Octene</td>
<td>trans-Oct-2-ene</td>
<td>97  153  210</td>
</tr>
<tr>
<td>7</td>
<td>1-Decene</td>
<td>1-Decene oxide</td>
<td>28  80  97</td>
</tr>
<tr>
<td>8</td>
<td>cis-β-Methyl-styrene</td>
<td>cis-oxide</td>
<td>19  23  115</td>
</tr>
</tbody>
</table>

a Experimental conditions, see text. b All products were identical to independent samples and identified by GC (HP 6890, column HP1 15 × 0.3 mm × 2.65 μm, polydimethylsiloxane) and 1H NMR. c Turnover number = mol product per mol catalyst, 8 equiv. H2O2 with respect to substrate. d 16 equiv. H2O2 with respect to substrate.

Main advantages of the new catalytic system are the facile synthesis and possibility for ligand modification. In acetone and at ambient temperature the manganese complex of TPTN is able to catalyse the selective oxidation of various alkenes to the corresponding epoxides, with H2O2 as oxidant. Further studies towards the elucidation of the mechanism and introduction of chirality in the ligand are in progress.

Notes and references


Communication a910252i