Homogeneous cis-dihydroxylation and epoxidation of olefins with high H$_2$O$_2$ efficiency by mixed manganese/activated carbonyl catalyst system

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Received 18 January 2002; accepted 8 February 2002

Abstract—The use of [Mn$_2$O$_3$(tmtacn)$_2$](PF$_6$)$_2$ (tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) in combination with glyoxylic acid methylester methyl hemiacetal (GMHA) results in a highly active and hydrogen peroxide efficient catalyst for the epoxidation of olefins as well as the first homogeneous catalytic cis-dihydroxylation system with H$_2$O$_2$ and with turnover numbers up to 420.

For economic and environmental reasons catalytic olefin oxidations based on O$_2$ or H$_2$O$_2$ are preferred over traditional stoichiometric oxidations, e.g. epoxidation with peracids and cis-dihydroxylation with permanganate. Several methods are available for catalytic epoxidation with aqueous H$_2$O$_2$ (notably Re-, W-, and Mn-based catalysts), but high turnovers for cis-dihydroxylation are only achieved using Os. However, the high cost and toxicity of Os hamper large scale application and provide a strong incentive to develop benign Fe- or Mn-based cis-dihydroxylation catalysts. Que et al. recently reported the first cis-dihydroxylation with H$_2$O$_2$ catalysed by a non-heme iron complex. Although this system shows good cis-diol selectivities, turnover numbers (t.o.n.) are rather low (up until 22 t.o.n.). Recently Mn complexes based on tmtacn were found to be highly active in catalytic oxidation, but apart from high turnover, it is essential to develop catalytic systems that employ H$_2$O$_2$ very efficiently, as many Mn or Fe catalysts are known to be particularly effective in decomposition of H$_2$O$_2$. This can be suppressed by working in acetone; however, this solvent is not acceptable for large-scale applications because of the risk of formation of explosive cyclic peroxides. H$_2$O$_2$ decomposition by Mn–tacn complexes can be suppressed by addition of oxalate or ascorbic acid as co-catalysts, or by anchoring the tacn ligand to a solid support. Significant amounts of cis-diols besides epoxides are formed during alkene oxidation with this heterogenised Mn catalyst.

Herein, we report efficient alkene oxidations with H$_2$O$_2$, catalysed by Mn–tmtacn in the presence of GMHA in acetone. Surprisingly, the latter not only strongly suppresses H$_2$O$_2$ decomposition by the Mn catalyst, but also imparts the first homogeneous catalytic cis-dihydroxylation activity to a Mn catalyst. Catalytic oxidations were performed by adding aqueous, 50% hydrogen peroxide (1.3 equiv. with respect to the sub-
strate) in 6 h to a mixture of alkene, Mn–tmtacn catalyst (0.1 mol%), and GMHA (25 mol%) in MeCN at 0°C. Under these reaction conditions, the presence of GMHA as the co-catalyst enables high conversions with only a 30% excess of oxidant with respect to substrate (Table 1) and the H₂O₂ efficiency is drastically improved compared to previous Mn systems using excess of H₂O₂. In most cases the conversions were also significantly higher than those obtained with oxalate as co-catalyst and 1.3 equiv. of H₂O₂ (for similar experiments with a larger excess of H₂O₂, see Ref. 8a).

In particular, styrene afforded a high yield of styrene oxide in the presence of GMHA, whereas the use of oxalate resulted in only modest conversion of styrene. When a mixture of GMHA (25 mol%) and oxalate (0.3 mol%) was used as the co-catalyst system, the epoxide yields even surpassed those obtained with the Mn/GMHA catalytic system, and high epoxide yields at complete conversion were obtained for the non-stereically hindered alkenes (Table 1, entries 1–3, 6, 8).

Unexpectedly, substantial amounts of cis-diols were formed besides epoxides when only GMHA was present as the co-catalyst. The epoxide/cis-diol ratio depends strongly on the alkene structure. The highest amount of cis-diol was found for cyclooctene (entry 3), which afforded the cis-diol as the main product (42%, 420 t.o.n.) besides the epoxide (36%, 360 t.o.n.). Minor amounts of 2-hydroxycyclooctanone were also found due to overoxidation of the diol. The ring size of cycloalkenes has a profound influence on the epoxide/cis-diol ratio (entries 1–4). For these cyclic olefins, almost no trans-diol could be detected (ratio cis-diol/trans-diol >99.5/0.5). cis-Diol formation is also observed for aliphatic acyclic alkenes. Yields of diol are significantly lower for trans-2-hexene than from cis-2-hexene, but the epoxide/cis-diol ratio was similar for both substrates. The aryl-substituted alkenes (entries 7, 8) yield epoxide nearly exclusively under these conditions. Limited cis/trans isomerisation is observed in the epoxide formation of cis-2-hexene. The cis/trans isomerisation points to epoxidation via a Mn oxo species, with formation of epoxides from C-centred radical intermediates with a lifetime sufficient for some C–C bond rotation prior to reaction to the epoxide. In line with this mechanism, olefins that form a relatively long-lived radical intermediate, such as cis-stilbene, show substantial loss of configuration in epoxide. No diols were formed on replacing the substrate by epoxides (Table 1).

### Table 1. Oxidation of selected olefins by H₂O₂ with catalyst 1¹¹

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Conversion (%)</th>
<th>Product</th>
<th>Turnover number (t.o.n.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Additive:</td>
<td>Additive:</td>
<td>Additive:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GMHA⁺ (2)</td>
<td>2 + oxalate</td>
<td>oxalate</td>
</tr>
<tr>
<td>1</td>
<td>Cyclopentene</td>
<td>97</td>
<td>100</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexene</td>
<td>88</td>
<td>100</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
<td>Cyclooctene</td>
<td>90</td>
<td>100</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>Norbornylene</td>
<td>95</td>
<td>88</td>
<td>59</td>
</tr>
<tr>
<td>5</td>
<td>trans-2-Hexene</td>
<td>77</td>
<td>93</td>
<td>37</td>
</tr>
<tr>
<td>6</td>
<td>cis-2-Hexene</td>
<td>93</td>
<td>100</td>
<td>80†</td>
</tr>
<tr>
<td>7</td>
<td>cis-Stilbene</td>
<td>82</td>
<td>77</td>
<td>32</td>
</tr>
<tr>
<td>8</td>
<td>Styrene</td>
<td>97</td>
<td>100</td>
<td>44</td>
</tr>
</tbody>
</table>

*a Co-catalyst GMHA (25 mol%).
*b Co-catalyst mixture of GMHA (25 mol%) and oxalate (0.3 mol%).
*c Co-catalyst oxalate (0.3 mol%), for similar experiments with a larger excess of H₂O₂, see Ref. 8a.
*d All products were identical to independent samples and identified by GC and ¹H NMR.
*e Determined by GC.
*f 32 mmol scale
ide, thus excluding epoxide hydrolysis. This conclusion is further supported by the time course profile of the 1/GMHA-catalysed oxidation of cyclooctene, which shows that both epoxide and diol increase progressively with time (Fig. 2).

Attempts to increase the cis-diol selectivity by addition of acid or base resulted in a dramatic decrease of conversion. Besides GMHA, a few other carbonyl compounds were tested as co-catalyst (25 mol%) for the oxidation of cyclooctene with $\text{H}_2\text{O}_2$ (1.3 equiv.). In the presence of glyoxylic acid hydrate, the epoxide was formed in 840 t.o.n. and cis-diol formation was almost completely suppressed. Modest cis-diol yields (<250 t.o.n.) and predominant formation of the epoxide were seen with diethyl ketomalonate or 2-ketoglutaric acid as the co-catalysts. However, cis-diol formation (370 t.o.n.) predominated over epoxide (310 t.o.n.) formation in the presence of chloral hydrate. Thus, a variety of carbonyl compounds with an adjacent electron withdrawing group are able to reduce $\text{H}_2\text{O}_2$ decomposition by 1 and to impose cis-dihydroxylation activity on manganese catalyst 1, albeit with variable cis-diol/epoxide ratios.

Since cis-diol formation through Mn-catalysed epoxide hydrolysis can be excluded (vide supra), we propose that the cis-diol is formed by reaction of the alkene with an Mn oxo-hydroxo species. As in the case of oxalate, hydrated activated carbonyl compounds might break down the catalase active binuclear Mn complex 1 into a mononuclear Mn species via complexation to the Mn centre. cis-Diol formation from an Mn oxo-hydroxo species with a coordinated hydrated carbonyl ligand could be induced through a hydrogen bonded six-membered ring transition state (concerted pathway, Scheme 1). Reoxidation of the Mn centre with $\text{H}_2\text{O}_2$, release of the diol from Mn, and hydration of the carbonyl compound closes the catalytic cycle. In conclusion, use of activated carbonyl compounds in combination with Mn–tmtacn results in a highly active (up to 860 t.o.n.) and $\text{H}_2\text{O}_2$ efficient epoxidation system. Besides epoxidation this new catalytic system also provides, to the best of our knowledge, the most active Os-free homogeneous catalyst for cis-dihydroxylation (up to 420 t.o.n.). Compared with the anchored Mn–tacn catalyst, the present homogeneous 1/activated carbonyl compound system is much more accessible, since both 1 and many activated carbonyl compounds have large scale applications. Efforts to enhance diol selectivity and to elucidate the cis-dihydroxylation mechanism are in progress.

Acknowledgements

We thank Dr. D. Schipper (DSM Food Specialities) for NMR experiments on the GMHA/50% aq. $\text{H}_2\text{O}_2$ system and DSM Fine Chemicals Austria for supply of GMHA.
References


11. Typical oxidation procedure with Mn–tmtacn/GMHA system: H2O2 (50% aq., 52 mmol) was added in 6 h at 0°C to a solution of Mn2O3(tmtacn)2(PF6)2 (1, 0.04 mmol), GMHA (10 mmol), substrate (40 mmol) and internal standard (1.2-dichlorobenzene, 20 mmol) in acetone (40 mL). Samples for GC (HP 6890, column HPL 15×0.3 mm×2.65 μm, polyethylsiloxane) analysis were taken 1 h after complete addition of oxidant.

12. Jacobsen, E. N.; Deng, L.; Furukawa, Y.; Martinez, L. E. Tetrahedron 1994, 50, 4323–4334. With the combined epoxidation/cis-dihydroxylation by a heterogenised Mn–tmtacn complex also limited cis/trans isomerisation was observed (see Ref. 9).


14. ’GMHA is an equilibrium mixture, which also contains some hydrated methyl glyoxylate. NMR experiments showed that formation of peroxhydrate from GMHA and aqueous H2O2 is very slow.