The role of salicylic acid, L-ascorbic acid and oxalic acid in promoting the oxidation of alkenes with H$_2$O$_2$ catalysed by [Mn$^{IV}_2$(O)$_3$(tmtacn)$_2$]$^{2+}$†

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Received 30th May 2008, Accepted 12th August 2008
First published as an Advance Article on the web 10th October 2008
DOI: 10.1039/b809177c

The role played by the additives salicylic acid, L-ascorbic acid and oxalic acid in promoting the catalytic activity of [Mn$^{IV}_2$(O)$_3$(tmtacn)$_2$](PF$_6$)$_2$, where tmtacn = N,N',N″-trimethyl-1,4,7-triazacyclononane) in the epoxidation and cis-dihydroxylation of alkenes with H$_2$O$_2$ and in suppressing the catalysed decomposition of H$_2$O$_2$ is examined. Whereas aliphatic and aromatic carboxylic acids effect enhancement of the catalytic activity of 1 through the in situ formation dinuclear carboxylato bridged complexes of the type [Mn$^{III}$,(µ-O)(µ-RCO$_2$)(tmtacn)$_2$]$^{2+}$, for L-ascorbic acid and oxalic acid notable differences in reactivity are observed. Although for L-ascorbic acid key differences in the spectroscopic properties of the reaction mixtures are observed compared with carboxylic acids, the involvement of carboxylic acids formed in situ is apparent. For oxalic acid the situation is more complex with two distinct catalyst systems in operation; the first, which engages in epoxidation only, is dominant until the oxalic acid additive is consumed completely at which point carboxylic acids formed in situ take on the role of additives to form a second distinct catalyst system, i.e. that which was observed for alky1 and aromatic carboxylic acids, which yield both cis-diol and epoxide products.

Introduction

Manganese complexes based on the ligand tmtacn (where tmtacn = N,N',N″-trimethyl-1,4,7-triazacyclononane) have attracted considerable attention due to their catalytic activity, as structural models for dinuclear manganese containing proteins and their often rich magnetic spectroscopic and electrochemical properties.$^{1,2}$ Although initially developed as functional models for bioinorganic manganese systems, in particular, dinuclear manganese based catalase$^{3–5}$ enzymes and the water splitting component of photosystem II (PSII),$^6$ the ability of many of these complexes to engage in catalysing a wide range of oxidative transformations with H$_2$O$_2$ in both aqueous$^7$ and non-aqueous$^8$ media has generated considerable interest in their use for, e.g. textile stain bleaching,$^9$ benzyl alcohol oxidation,$^{10}$ C–H bond activation,$^{11}$ sulfoxidation$^{12}$ and cis-dihydroxylation and epoxidation of alkenes.$^{8,11}$

The oxidation of alkenes to cis-diol and epoxide products is a central oxidative transformation$^{12}$ employed in biological systems,$^5$ synthetic organic chemistry and the chemical industry.$^{13–15}$ Atom-efficient and environmentally friendly catalytic methods employing H$_2$O$_2$,$^{13}$ most notably in the use of Mn$^{II}$ salts$^{16}$ and complexes$^{17}$ and Fe$^{II}$ complexes$^{18}$ in the catalytic epoxidation of alkenes, have seen increasingly rapid progress. The potential of 1st row transition metals towards cis-dihydroxylation of alkenes has been demonstrated in the work of de Vos and coworkers using heterogenised Mn-tmtacn.$^{19}$ Que and coworkers with Fe$^{II}$ pyridylamine based complexes$^{18}$ and our own recent reports on the use of [Mn$^{IV}_2$(O)(tmtacn)$_2$]$^{2+}$ (1, Scheme 1), in the presence of carboxylic acids.$^{11}$

![Scheme 1](image-url)  
**Scheme 1** cis-Dihydroxylation and epoxidation of alkenes by 1.

Recently, we reported that 1 can engage in the atom efficient cis-dihydroxylation of alkenes with high turnover numbers when combined with electron deficient carboxylic acids (Scheme 1).$^{11}$ We demonstrated that carboxylic acids, at co-catalytic levels, are effective in suppressing the inherent catalase activity of 1$^{11}$ and allow for the tuning of the catalyst’s selectivity towards either cis-dihydroxylation or epoxidation. Electrochemical and spectroscopic investigations$^{11}$ demonstrated that control over the outcome of the reaction towards cis-dihydroxylation or epoxidation arises from the in situ formation of carboxylato bridged dinuclear complexes, e.g., complex 2 ($\{[Mn^{II}_{11},(µ-O)(µ-CCl_3CO_2)(tmtacn)]^{2+}\}$, during catalysis (Fig. 1), with the steric nature of the bridging carboxylato ligands being the primary factor controlling the selectivity of the catalyst.

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$^e$CCDC reference number 674966. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b809177c
Fig. 1 Complexes described in the text--complexes 1, 2, 3 and 4 have been characterized structurally. All complexes are PF$_6^-$ salts.

In our earlier reports, the structural and mechanistic features as well as the parameters that govern the activity and selectivity of the catalysis of this exceptionally H$_2$O$_2$ efficient catalytic system were described. The role of complexes such as 2 in the catalysis and the importance of the formation of the μ-carboxylato bridged Mn$^{III}_2$ complexes (in which the μ-oxo bridge is replaced by two labile hydroxido/aqua ligands) was addressed. We demonstrated that the predominant species present under catalytic conditions are Mn$^{III}_2$ bis-μ-carboxylato bridged complexes such as A and B (Scheme 2) and that the reaction of these complexes with H$_2$O and H$_2$O$_2$ is rate limiting.

Scheme 2 Proposed general mechanism for the oxidation of alkenes catalysed by 1/RCO$_2$H.

In addition, the outcome of the oxidation reactions catalysed by 1/RCO$_2$H was sensitive to bulk solvent conditions. It was found that when the reaction was carried out with the combination 1/carboxylic acid, a lag period is observed before the formation of Mn$^{III}_2$ bis-μ-carboxylato bridged complexes, e.g., 2 (Fig. 1), and the commencement of cis-dihydroxylation and epoxidation. This lag period was not observed when the Mn$^{III}_2$ bis-μ-carboxylato bridged complexes, e.g., 2 (Fig. 1), were employed as the catalyst and the H$_2$O content of the reaction mixture was sufficiently high.

For all of the alkanolic and benzoic acids examined, the formation of the Mn$^{III}_2$ bis-μ-carboxylato bridged complex was manifested by a disappearance of 1 (Mn$^{IV}_2$) from both the ESI-MS and UV-Vis absorption spectra and the appearance of the corresponding Mn$^{III}_2$ complex. However, there was one notable exception to this—salicylic acid. The reaction mixture, with the catalyst system 1/salicylic acid, exhibited distinct UV-Vis and ESI-MS spectroscopic differences, although, it otherwise behaved similarly to other carboxylic acids in terms of the catalytic oxidation of alkenes.

Furthermore, during the course of these studies, the question arose as to whether the additives used by others (Fig. 2), i.e., L-ascorbic acid (Berkessel et al.$^{39}$) and oxalate buffer (De Vos et al.$^{31}$), played a similar role as other alkanolic and aromatic carboxylic acids (Scheme 2). Making an accurate comparison between the carboxylic acid additives reported by our group, which allows 1 to engage in cis-dihydroxylation and epoxidation and the additives found to be effective for the epoxidation of alkenes by the groups of Berkessel and De Vos, i.e., L-ascorbic acid and oxalic acid, requires that these latter additives should be examined under conditions similar with that used for the 1/CCl$_3$CO$_2$H promoted reaction.

Fig. 2 Additives used in suppressing the catalase activity and enhancing the reactivity of 1.

In this contribution, the oxidation of alkenes catalysed by 1 in combination with a series of hydroxy-substituted benzoic acids, oxalic acid and L-ascorbic acid are examined, both in terms of the time dependence of the conversion of the substrate and product formation and the spectroscopic properties of the reaction mixture. The key question addressed is whether all of these systems behave in essentially the same manner or if there are fundamental mechanistic differences that may present opportunities with regard to providing further insight into controlling the reactivity and selectivity of the system 1/H$_2$O$_2$.

Experimental

All reagents are of commercial grade (Aldrich, Acros, Fluka) and used as received unless stated otherwise. H$_2$O$_2$ used: 50% w/w (Acros) or 30% v/v (Merck, medicinal grade) solution in water. H$_2^{18}$O (Icon Isotopes): 97 atom% $^{18}$O. The synthesis and characterisation of complexes 1, 2, 6 and 8 as their PF$_6^-$ salts were reported previously.
Complex 3 was prepared by modification of the general procedure reported by Hage et al.\textsuperscript{22} 1-Ascorbic acid (19 mg, 0.105 mmol) in 2 ml of H$_2$O was added to a solution of 1 (81 mg, 0.10 mmol) and benzoic acid (24 mg, 0.22 mmol) in 20 ml of H$_2$O with rapid stirring. The red-purple precipitate was isolated by filtration and recrystallized from acetonitrile in an ethylacetate bath. Yield 75\% (75 mg, 0.075 mmol). Mass spec. (calc. Mn$_2$C$_{32}$H$_{52}$N$_6$O$_5$ and recrystallized from acetonitrile in an ethylacetate bath. Yield rapid stirring. The red-purple precipitate was isolated by filtration

CCDC No. 674966: [C$_{32}$H$_{52}$Mn$_2$N$_6$O$_5$]$_2^+$

$\delta$ 71, 35, 21, 15, 13, 6, 0, –80, –94. Elemental analysis (calc. Mn$_2$C$_{32}$H$_{52}$N$_6$O$_5$P$_2$F$_{12}$) C 38.8\% (38.5\%), H 5.49\% (5.32\%), N 8.06\% (7.92\%).

Physical measurements

$^1$H NMR spectra (400.0 MHz) were recorded on a Varian Mercury Plus. Chemical shifts are denoted relative to the solvent residual peak ($^1$H NMR spectra CD$_3$CN: 1.94 ppm).\textsuperscript{23} Elemental analyses were performed with a Foss-Heraeus CHN-O-Rapid or a EuroVector Euro EA elemental analyzer. EPR spectra (X-band, 9.46 GHz) were recorded on a Bruker ECS106 instrument in liquid nitrogen (77 K). Samples for measurement were transferred from the reaction solution (250 \(\mu\)l) to an EPR tube, which was frozen to 77 K immediately. UV-Vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer or a JASCO 570 UV-Vis-NIR spectrometer using either 2 or 10 mm pathlength quartz cuvettes. Electro-spray ionization mass spectra were recorded on a Triple Quadrupole LC/MS/MS Mass spectrometer (API 3000, Perkin-Elmer Sciex Instruments). A sample (2 \(\mu\)l) was taken from the reaction mixture at the indicated times (vide infra) and was diluted in CH$_3$CN (1 ml) before injection in the mass spectrometer (via syringe pump). Mass spectra were measured in positive and negative mode and in the range of 100–1500 \(m/z\). Ion-spray voltage: 5200 V, orifice: 15 V, ring: 150 V, Q0: –10 V.

Procedures employed for catalysis studies

Procedure A. The alkene (10 mmol), 1,2-dichlorobenzene (internal standard, 735 mg, 5.0 mmol), 1 (8.1 mg, 10 \(\mu\)mol) and the respective acid (0.10 mmol) in acetonitrile (10 ml) were cooled to 6 °C. H$_2$O$_2$ (0.74 ml, 13 mmol) was added via syringe pump over 6 h (0.12 ml/h). The reaction mixture was stirred at 60 °C for 1 h after the addition of H$_2$O$_2$ was completed, prior to sampling by GC.

Procedure B. Catalyst pretreatment with H$_2$O$_2$. H$_2$O$_2$ (30 \(\mu\)l, 0.53 mmol) was added to a mixture of 1,2-dichlorobenzene (735 mg, 5.0 mmol), 1 (8.1 mg, 10 \(\mu\)mol) and the respective carboxylic acid (0.10 mmol) in acetonitrile (7 ml) at room temperature. The mixture was stirred for 20 min, after which the alkene (10 mmol) was added together with acetonitrile (3 ml) and the mixture was cooled to 0 °C. H$_2$O$_2$ (0.71 ml, 12.5 mmol) was added via syringe pump (0.12 ml h$^{-1}$). The reaction mixture was stirred at 0 °C for 1 h after the addition of H$_2$O$_2$ was completed, prior to sampling by GC.

GC analyses were performed on an Agilent 6890 Gas Chromatograph equipped with a HP-1 dimethyl polysiloxane column (30 m × 0.25 mm × 0.25 \(\mu\)m). Peak identification and calibration were performed using independent samples (either purchased from a commercial supplier or synthesized independently).\textsuperscript{11} Conversion and turnover numbers were determined in duplo employing 1,2-dichlorobenzene as internal standard. All values are ± 10\%.

$^{18}$O-labelling

Samples at $t$ = 60 min where analyzed by GC-MS. GC: HP 6890 equipped with a HP-5 column (30 m × 0.32 mm × 0.25 \(\mu\)m). MS: JMS-600H using chemical ionization (reaction gas: NH$_3$). The samples were analyzed by GC (HP-1 column, with FID) also as described above to determine t.o.n.\textsuperscript{11}$^{18}$O-labelling studies
where performed on cyclooctene on 1/20th scale of standard conditions, with the adjustment that a 2% H$_2$O$_2$ solution was used. Values corrected for H$_2$O$_2$/H$_2$O isotopic composition. For the system 1/oxalic acid, the isotopic labelling with H$_2$O was used for the second stage of the reaction (vide infra) was carried out as follows. The reaction was first performed using procedure A except that cis-2-heptene (250 μmol) was used as substrate in place of cyclooctene. H$_2$O$_2$ (50 w/w%, 4×30 μl, 2.1 mmol) was added every 15 min over 1 h. The reaction mixture was then left overnight and the presence of a Mn$^{III}$-bis(μ-carboxylato) complex was confirmed by UV-Vis spectroscopy. Part of this reaction mixture (500 μl) was taken and subjected to the procedure for $^{18}$O-labeling described above except that 250 μmol of cyclooctene were used in place of 500 μmol of cyclooctene.

**Definition of t.o.n. and mass balance.** Turnover number (t.o.n.): mol product/mol catalyst. Mass balance [%] = unreacted alkene [%] + (cis-diol and epoxide products [%]). Deviation from a mass balance of 100% indicates loss through further oxidation of the cis-diol formed initially and/or the occurrence of competing oxidation pathways other than cis-dihydroxylation and epoxidation.

**Preparation of suberic acid from cis-1,2-cyclooctanediol.** H$_2$O$_2$ (30 μl, 0.53 mmol) was added to a mixture of 1 (8.1 mg, 10 μmol) and 2,6-dichlorobenzoic acid (57.3 mg, 0.30 mmol) in CH$_3$CN (7 ml) at room temperature. The mixture was stirred for 20 min at room temperature followed by addition of cis-1,2-cyclooctanediol (0.72 g, 5 mmol) and CH$_3$CN (3 ml). The mixture was cooled at 0 °C. H$_2$O$_2$ (50% w/w, 1.13 ml, 20 mmol) was added via syringe pump (0.14 ml h$^{-1}$). The reaction mixture was stirred at 0 °C for 1 h after addition of H$_2$O$_2$ was completed. Water (10 ml) was added and the mixture was adjusted to pH 12 by addition of 2 M aq. NaOH. The basic aqueous layer was washed with Et$_2$O (3×15 ml) and subsequently acidified to pH 1 with 4 M aq. HCl. The acidic aqueous layer was extracted with Et$_2$O (5×15 ml) and the combined organic extracts were washed with brine (20 ml). After drying over anhydrous Na$_2$SO$_4$, the solvent was evaporated in vacuo yielding a colourless solid (367 mg, 42%). $^1$H NMR spectrum (400 MHz, acetone-d$_6$) δ 1.31–1.35 (m, 4H), 1.55–1.58 (m, 4H), 1.75–1.83 (m, 4H), 2.25 (t, J = 7.3 Hz, 4H). CI-MS m/z 192 [M + NH$_4$]$^+$. "

### Results

The synthesis and characterisation of complexes 1, 2, 6 and 8 are described elsewhere. Complexes 3 (Fig. 3), 5 and 7 were prepared by previously reported methods. The dinuclear complex [Mn$^{III}$,(μ-O)(μ-2-hydroxybenzoato)$_2$(tmtacn)]$_2$$^+$. 4 could be obtained in low yield by the general method employing l-ascorbic acid as reductant or in situ by reduction of 1 with hydrazine in CH$_3$CN in the presence of 2 equiv. of salicylic acid. However, even in dry CH$_3$CN this complex is unstable and converts readily to the more stable mononuclear complex [Mn$^{III}$(salicylato)(tmtacn)]$^+$. 8. (Fig. 4). Complexes 4 and 8 exhibit distinct UV-Vis absorption spectra (Fig. 5) with 4 showing the characteristic absorptions of a [Mn$^{III}$(μ-O)(μ-RCO$_2$)$_2$(tmtacn)]$^+$. complex. 1 ESI-MS of 4 in CH$_3$CN confirmed the presence of the dinuclear complex (m/z 371 [4]$^+$ and 887 [4·PF$_6$]$^+$), however, the mononuclear complex [8]$^+$ (m/z 362) was observed also.

![Fig. 3](image-url) Molecular structure of 3. PF$_6^-$ anions omitted for clarity.

![Fig. 4](image-url) Equilibrium between [Mn$^{III}$,(μ-O)(μ-2-hydroxybenzoato)$_2$(tmtacn)]$_2$$^+$ 4 and [Mn$^{III}$(salicylato)(tmtacn)]$^+$ 8.

![Fig. 5](image-url) UV-Vis spectra in CH$_3$CN of [Mn$^{III}$,(μ-O)(μ-hydroxybenzoato)$_2$(tmtacn)]$^{2+}$ 4 (1 mM) and [Mn$^{III}$(salicylato)(tmtacn)]$^+$ 8 (2 mM).

### Oxidation of cyclooctene catalysed by 1/salicylic acid

The influence of co-catalytic amounts of salicylic acid, l-ascorbic acid and oxalic acid on the oxidation of cyclooctene with H$_2$O$_2$ catalysed by 1 was investigated under the conditions employed in our earlier studies, i.e. 1/RCHO$_2$/H$_2$/cyclooctene/H$_2$O$_2$ in the ratio 1/10/1000/1300 in CH$_3$CN.

The changes in concentration of substrate and cis-diol and epoxide products over the course of the reaction where salicylic acid is present at 1 mol% w.r.t. cyclooctene (Fig. 6 and Table 1, entry 1), show that i) there is an initial lag period before conversion commences and ii) formation of both the cis-diol and epoxide products commences concomitantly, as observed previously for other carboxylic acids. The lag period is due primarily to the
delayed transformation of the \{Mn^{IV}\,(\mu-O)_{3}\} bridged complex 1 to a Mn^{III} \text{ bis(\mu-carboxylato)} complexes similar to 2 or B (Fig. 1 and Scheme 2, respectively).

With increased concentrations of salicylic acid (5 and 10 mol%), it is apparent that epoxidation becomes favoured over \textit{cis}-dihydroxylation (Table 1, entries 1–3). A higher preference for epoxidation at increased carboxylic acid concentration was also observed previously for other carboxylic acids, such as CCl$_3$CO$_2$H. \textit{3-Hydroxybenzoic acid} and 5-bromosalicylic acid show similar product distributions (entries 6 and 8). \textit{4-Hydroxybenzoic acid} gives a substantially higher \textit{cis}-diol/epoxide ratio (Table 1, entry 7), comparable with the other \textit{para}-substituted benzoic acids. The mononuclear [Mn^{III}(salicylato)(tmtacn)]$^+$ complex 8 (\textit{vide infra}) (in combination with 1 mol\% of salicylic acid) shows essentially the same reactivity as the system 1/salicylic acid (entries 5 and 1, respectively), however the lag period is reduced from 2 h to 45 min, and as a consequence the conversion is somewhat higher (the \textit{cis}-diol/epoxide ratio is unaffected).

**Oxidation of cyclooctene and 1-octene catalysed by 1/L-ascorbic acid**

The use of L-ascorbic acid/sodium ascorbate as an effective additive in the epoxidation of two terminal alkenes (methyl acrylate and 1-octene) and the oxidation of both 2-pentanol (to 2-pentanone) and 1-butanol (to butanoic acid) catalysed by Mn(II)/tmtacn has been reported previously by Berkessel and coworkers.\textsuperscript{20} The oxidation of 1-octene in the presence of 1 mol\% of L-ascorbic acid under the conditions employed in the present study resulted in efficient epoxidation of 1-octene with only trace amounts of the \textit{cis}-diol product being formed (Table 2, entry 2), in agreement with the results of Berkessel et al.\textsuperscript{20} (entry 1). By contrast, oxidation of cyclooctene resulted in the formation of substantial amounts of the corresponding \textit{cis}-diol in addition to the epoxide product (entry 3).\textsuperscript{28} The conversion of cyclooctene to both the \textit{cis}-diol and epoxide products commenced at the same time and the ratio of both products remained constant over the entire course of the catalysed

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### Table 1 Oxidation of cyclooctene catalysed by 1/hydroxy- and methoxy-substituted benzoic acids\textsuperscript{a}

<table>
<thead>
<tr>
<th>Carboxylic acid</th>
<th>Conv. (%)</th>
<th>cis-Diol</th>
<th>Epoxide</th>
<th>cis-Diol/epoxide ratio</th>
<th>Mass bal. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Salicylic</td>
<td>64</td>
<td>225</td>
<td>320</td>
<td>0.7</td>
<td>90</td>
</tr>
<tr>
<td>2 Salicylic\textsuperscript{d}</td>
<td>74</td>
<td>132</td>
<td>510</td>
<td>0.25</td>
<td>90</td>
</tr>
<tr>
<td>3 Salicylic\textsuperscript{e}</td>
<td>61</td>
<td>102</td>
<td>431</td>
<td>0.24</td>
<td>92</td>
</tr>
<tr>
<td>4 Salicylic\textsuperscript{b}</td>
<td>75</td>
<td>30</td>
<td>590</td>
<td>0.05</td>
<td>87</td>
</tr>
<tr>
<td>5 Salicylic\textsuperscript{c}</td>
<td>75</td>
<td>249</td>
<td>371</td>
<td>0.7</td>
<td>87</td>
</tr>
<tr>
<td>6 3-Hydroxybenzoic</td>
<td>69</td>
<td>260</td>
<td>325</td>
<td>0.8</td>
<td>89</td>
</tr>
<tr>
<td>7 4-Hydroxybenzoic</td>
<td>46</td>
<td>219</td>
<td>170</td>
<td>1.3</td>
<td>93</td>
</tr>
<tr>
<td>8 5-Bromosalicylic</td>
<td>62</td>
<td>232</td>
<td>296</td>
<td>0.9</td>
<td>92</td>
</tr>
<tr>
<td>9 2-Methoxybenzoic</td>
<td>47</td>
<td>244</td>
<td>158</td>
<td>1.5</td>
<td>93</td>
</tr>
<tr>
<td>10 4-Methoxybenzoic</td>
<td>26</td>
<td>137</td>
<td>83</td>
<td>1.7</td>
<td>96</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Procedure A, 1 mol\% carboxylic acid. \textsuperscript{b} 1-Octene as substrate. \textsuperscript{c} Complex 8. \textsuperscript{d} 5 mol\%. \textsuperscript{e} 10 mol\%.

### Table 2 Oxidation of 1-octene and cyclooctene catalysed by 1 (0.1 mol\%) at 0 °C in the presence of L-ascorbic acid (1 mol\%)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Additive (mol%)</th>
<th>Conv. (%)</th>
<th>cis-Diol</th>
<th>Epoxide</th>
<th>Mass bal. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Octene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 L-Ascorbic acid/Na ascorbate\textsuperscript{a}</td>
<td>N.d.</td>
<td>0</td>
<td>1110 (max. 1333)</td>
<td>N.d.</td>
</tr>
<tr>
<td>2 L-Ascorbic acid (1)</td>
<td>89</td>
<td>36</td>
<td>672</td>
<td>82</td>
</tr>
<tr>
<td>Cylooctene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 L-Ascorbic acid (1)</td>
<td>83</td>
<td>275</td>
<td>384</td>
<td>83</td>
</tr>
<tr>
<td>4 Dehydroascorbic acid (1)</td>
<td>3</td>
<td>52</td>
<td>76</td>
<td>110</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Conditions: alkene (1000 mM), 1 (1 mM), L-ascorbic acid (10 mM), 1,2-dichlorobenzene (500 mM) in CH$_3$CN at 0 °C. H$_2$O$_2$ (50% aq., 1300 mM) was added by syringe pump addition over 6 h, t.o.n. and conversion reported after 7 h (general procedure A). \textsuperscript{b} From ref. 1, conditions: 1-octene:H$_2$O$_2$:Mn$^{II}$(OAc)$_2$:tmtacn:L-ascorbic acid:Na ascorbate 1333:3500:1:1.3:0.5:2.1 in CH$_3$CN/H$_2$O (6:4).
reaction (Fig. 7). In contrast to the system 1/CCl₃CO₂H, a lag period was not observed (vide infra). For the oxidised form of L-ascorbic acid, i.e. dehydroascorbic acid, only very low activity was observed.

Oxidation of cyclooctene and 1-octene catalysed by 1 in the presence of oxalic acid

De Vos and coworkers reported the use of oxalate buffers in CH₃CN/H₂O in the epoxidation of several alkenes catalysed by Mn(II)/tmtacn.₂¹ Again, in order to make a direct comparison with the catalytic system 1/CCl₃CO₂H, reactions were performed at 0.1 mol% of 1 and 1 mol% of oxalic acid, Table 3, entry 2). In agreement with the results reported by De Vos et al. (entry 1), under the present conditions effective epoxidation of 1-octene was observed. However, with cyclooctene, substantial levels of cis-dihydroxylation are observed in addition to epoxidation (entry 3).

Whereas for the majority of carboxylic acids examined, a lag period followed by a rapid conversion of 1 to a Mn³⁺-μ-biscarboxylato complex and simultaneous commencement of both cis-dihydroxylation and epoxidation is observed, for the system 1/oxalic acid, oxidation of the alkene commences immediately upon addition of H₂O₂ and two distinct phases can be distinguished over the course of the reaction: (i) over the first 3 h (at 298 K)⁹ conversion of the alkene to the epoxide product is the only significant process observed; while (ii) from 3 h onwards both epoxidation and cis-dihydroxylation proceed with similar levels of conversion. This change in product distribution occurs at a time coincident with a pronounced change in the UV-Vis spectrum of the reaction mixture (Fig. 12c and d, vide infra). Over the first 3 h of the oxidation of cyclooctene catalysed by 1/oxalic acid, 7 t.o.n.s of cis-diol and 272 t.o.n.s of epoxide product are obtained, giving a cis-diol/epoxide ratio of 0.03. Between 3–5.5 h, however, 136 t.o.n.s for the cis-diol and 91 t.o.n.s of epoxide product are obtained, resulting in a cis-diol/epoxide ratio of 1.5 (within this 2 h period). The cis-diol/epoxide selectivity in the later stage of the reaction is similar to that found for alkanoic acids (ca. 2–3:1)¹¹ and that reported for 1/gmha₈ (cis-diol/epoxide 1.2).

If, after 2.5 h, a second 1 mol% of oxalic acid is added to the reaction mixture, the formation of the cis-diol product (from 3 h onwards) is suppressed in favour of continued epoxide formation (Fig. 8). This suggests that the oxalic acid inhibits formation of the catalytically active species present in the later stage of the reaction. The observation of two distinct stages in the oxidation of cyclooctene catalysed by 1/oxalic acid is intriguing and raises

![Fig. 7](image_url) Oxidation of 1-octene (upper) and cyclooctene (lower) catalysed by 1 (1 mM)/L-ascorbic acid (10 mM) in CH₃CN at 0 °C.

### Table 3  Catalysed oxidation of alkenes by 1 (0.1 mol%) at 0 °C in the presence of oxalic acid (1 mol%)²

<table>
<thead>
<tr>
<th>Additive (mol%)</th>
<th>Conv. (%)</th>
<th>T.o.n.</th>
<th>Epoxide</th>
<th>Mass bal. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cis-Diol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Hexene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Oxalic acid/Na oxalate (0.2/0.2)⁶</td>
<td>&gt;99</td>
<td>0</td>
<td>660</td>
<td>&gt;98</td>
</tr>
<tr>
<td>1-Octene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Oxalic acid (1)</td>
<td>86</td>
<td>0</td>
<td>724</td>
<td>86</td>
</tr>
<tr>
<td>Cyclooctene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Oxalic acid (1)</td>
<td>92</td>
<td>169</td>
<td>599</td>
<td>85</td>
</tr>
<tr>
<td>4-Oxalic acid (1)</td>
<td>97</td>
<td>154</td>
<td>622</td>
<td>81</td>
</tr>
<tr>
<td>5-Oxalic acid (1)</td>
<td>99</td>
<td>14</td>
<td>860</td>
<td>89</td>
</tr>
<tr>
<td>6-Oxalic acid (1)</td>
<td>94</td>
<td>176</td>
<td>564</td>
<td>80</td>
</tr>
<tr>
<td>7-Oxalic acid (1)</td>
<td>99</td>
<td>15</td>
<td>838</td>
<td>87</td>
</tr>
</tbody>
</table>

* Procedure A. ⁶ From ref. [21], conditions: 1-hexene:H₂O₂:oxalate:Mn 666:1000:3:1 in CH₃CN:H₂O (3.5:1). ¹ H₂O₂ and H₂O pre-treatment. ⁷ An extra 1 mol% of oxalic acid added at t = 3.5 h. ⁸ Performed at r.t. ⁹ An extra 1 mol% of oxalic acid added at t = 2.5 h.
the possibility that two distinct catalysts or catalytic pathways are operating in each of these two stages.

$^{18}$O labelling of both $\text{H}_2\text{O}$ and $\text{H}_2\text{O}$ has proven to be a valuable probe in elucidating the source of oxygen in the products of oxidation reactions.\cite{15,16,17} However its use in probing the oxalic acid promoted oxidation of cyclooctene catalyzed by 1 is complicated by the fact that there are two distinct mechanisms operating during the 1st and 2nd half of the reaction. These two distinct catalyst systems require examination of the two stages independently; otherwise only an ‘average’ result will be obtained. Probing the present system through $^{18}$O labelling as performed previously\cite{17} is therefore non-trivial. In the present study $^{18}$O labelled water was employed as a probe.

For the epoxide product the incorporation of oxygen atoms from water in the first part of the reaction is minor (2%). Indeed it is significantly lower than the level of $^{18}$O incorporation reported by Gilbert et al. (7%) in the epoxidation of cinnamic acid catalysed by Mn-tmtacn/oxalic acid.\cite{15} However, it should be noted that the substrate employed in that example (i.e. cinnamic acid) contains a free carboxylic acid group. Indeed the level $^{18}$O incorporation from water in the 2nd stage of the reaction (9%) in the present study is in agreement with that observed by Gilbert et al.\cite{15} This suggests that in both the present study and in the report of Gilbert et al. carboxylic acids other than oxalic acid may play the role of ligand to the catalyst.

Attempts to probe $^{18}$O incorporation into the cis-diol and epoxide substrate is hampered by the uncertainty in the $^{18}$O level of the $\text{H}_2\text{O}$ present in the reaction mixture at this stage (as water is both added with the $\text{H}_2\text{O}_2$ and is released stoichiometrically from $\text{H}_2\text{O}_2$ following epoxidation). The absence of significant levels of cis-dihydroxylation during the first stage of the reaction can allow for the approximation that the single incorporation into the cis-diol (55%, $^{18}$O/$^{16}$O using $\text{H}_2\text{O}_2$/($\text{H}_2\text{O})$ product is representative of the 2nd stage of the reaction.\cite{18}

Electronic and EPR spectroscopy

Hydroxybenzoic acids. For the majority of carboxylic acids examined, with the exception of salicylic acid, the formation of Mn$^{\text{III}}$, bis($\mu$-carboxylato) species from 1 at the end of the lag period (Fig. 6) was confirmed earlier\cite{19} by the appearance of characteristic features in the UV-Vis absorption spectra of the reaction mixture. For 1/salicylic acid, a considerable increase in absorption in both the UV and visible regions was observed at the end of the lag period also.\cite{20} However, the increase was larger and the final spectrum atypical of a Mn$^{\text{III}}$, bis($\mu$-carboxylato) complex (Fig. 9). The differences in the absorption spectra of the reaction mixture with 1/salicylic acid compared with those of the other carboxylic acids can be assigned, tentatively, to the presence of a ring-opened dinuclear complex (i.e. B, Scheme 2).\cite{21}

When 8 ([Mn$^{\text{III}}$(salicylato)(tmtacn)]$^+$) is used in place of 1, the UV-Vis spectrum of the reaction mixture after the lag period is identical to that observed for the reaction catalysed by 1/salicylic acid. This is in agreement with the observation that the 1/salicylic acid and 8/salicylic acid systems provide essentially the same product distributions (Table 1).

ESI-MS of the reaction mixture at several stages of the catalysis did not reveal the appearance of a Mn$^{\text{III}}$, bis($\mu$-carboxylato) dimer (i.e. 4) and instead only the mononuclear complex [Mn$^{\text{III}}$(salicylato)(tmtacn)]$^+$ has been observed. However, it should be noted that even the ESI mass spectrum of the Mn$^{\text{III}}$, bis($\mu$-salicylato) complex 4 in dry CH$_3$CN solution shows the signal assigned to the mononuclear complex 8 in addition to the dinuclear Mn$^{\text{III}}$, bis($\mu$-carboxylato) complex 4.\cite{22} EPR spectra (77 K) of the reaction mixture at all stages of the oxidation of cyclooctene catalysed by 1/salicylic acid showed no signals as was the case for the reaction catalysed by 1/CCl$_3$CO$_2$H.\cite{23} This precludes the presence of complexes in oxidation states which are EPR active such as a Mn$^{\text{III}}$ monomer and Mn$^{\text{IV}}$, and Mn$^{\text{III,IV}}$, dimer. Mn$^{\text{III}}$, dimers such as 2–7 are EPR silent at 77 K.

1-Ascorbic acid. The oxidation of cyclooctene catalysed by 1/ascorbic acid was monitored by UV-Vis spectroscopy. Addition of 1-ascorbic acid (10 mM, 1 mol%) to the mixture of 1 (1 mM) and cyclooctene (1.0 M) in CH$_3$CN, results in a decrease in the absorbance due to 1 (395 and 495 nm) over several minutes. EPR spectroscopy after addition of 1-ascorbic acid shows the appearance of a 16-line spectrum (at = 69 G, Fig. 11a(i)). This 16-line species is indicative of a mixed valent Mn$^{\text{III,IV}}$, species,\cite{24} most probably {Mn$^{\text{III,IV}}$(µ-O)$_3$}, with an a-value identical to that

![Graph](image-url)
Addition of H$_2$O$_2$ (50 equiv.) resulted in an increase in the absorbance in both the UV and visible regions of the spectrum, which then decreased in intensity over time, and eventually, at low concentrations of H$_2$O$_2$ (i.e. after consumption of the H$_2$O$_2$ during the oxidation of cyclooctene), a spectrum typical for a $\{\text{Mn}^{III}_2(\mu-O)(\mu-carboxylato)_2\}$ species was observed (Fig. 10a, dotted line).

![Fig. 9](image1)

Fig. 9 (a) UV-Vis spectra of the reaction mixture during the catalytic oxidation of cyclooctene (1 M) in CH$_3$CN at 0 °C with 1 (1 mM) and salicylic acid (10 mM) (at 10 min intervals between 0–2 h) from ref. 11a, SI. (b) UV-Vis spectra in CH$_3$CN (1 mM) of complexes 4, 5 and 6.

reported by Hage et al.$^{22}$ for the one electron reduction of 1 by Co(Cp)$_2$ in CH$_3$CN (see Scheme 3).

![Scheme 3](image2)

Scheme 3 Summary of species present during the oxidation of alkenes catalysed by 1/L-ascorbic acid.

![Fig. 10](image3)

Fig. 10 UV-Vis spectra of the reaction mixture of the oxidation of cyclooctene (1 M) by H$_2$O$_2$ catalysed by 1 (1 mM) and L-ascorbic acid (10 mM) in CH$_3$CN. L-Ascorbic acid is added in one batch at $t = 0$, addition of H$_2$O$_2$ begins at $t = 10$ min. (a) Immediately after each addition of H$_2$O$_2$ (53 mM, every 15 min) an intense featureless spectrum is observed (dashed line), while at low H$_2$O$_2$ concentrations (14 min after addition of each batch of H$_2$O$_2$) a spectrum characteristic of a Mn$^{III}_2$ bis(carboxylato) complex is observed (dotted lines). (b) Absorbance changes, over time, monitored at 400, 480 and 520 nm (addition of H$_2$O$_2$ is indicated by arrows).

The EPR spectrum after addition of H$_2$O$_2$ shows a 16-line spectrum also, but with an increased $a$-value of 76 G (Fig. 11a ii–iv). As for the absorption spectrum the intensity of this latter 16-line signal decreases with time. A subsequent addition of H$_2$O$_2$ results in the recovery of the same intense featureless UV-Vis absorption spectrum (Fig. 10b) and in the intensity of the 16 line
EPR signal (Fig. 11b), both of which decrease again as the H₂O₂ concentration decreases.

(a)

(b)

Fig. 11 EPR spectra of samples taken from the reaction mixture of the oxidation of cyclooctene (1 M) in CH₃CN catalysed by 1 (1 mM) and l-ascorbic acid (10 mM): (i) after stirring for 15 min prior to addition of H₂O₂ (lower solid line, y-axis offset for clarity), (ii) 15 min after 1st addition of H₂O₂ (solid line), (iii) 15 min after 2nd addition of H₂O₂ (dashed line); (iv) 1 min after 3rd addition of H₂O₂ (dotted) (9.47 G, attenuation/power 10 dB/20.1 mW, conversion time 81.9 ms) (b) Signal intensity just before (solid squares) and immediately after (open circles) addition of H₂O₂ (50 equiv. w.r.t. Mn). The 16-line EPR signal observed after addition of H₂O₂ is assigned to a mixed valent Mn III,IV species. However, the change in hyperfine coupling constant from 69 to 76 G indicates a change in the nature of the bridging ligand(s) as the a-value is very similar to that observed for complexes such as 1, 2 bis(μ-carboxylato)2+ species observed by UV-Vis spectroscopy) by ESI-MS were unsuccessful: i.e. although 1 was converted completely within 30 min of the start of the reaction and a series of weak signals were observed, conclusive assignments could not be made. However, as suberic acid, which can form through further oxidation of the cis-diol product, hydrolysis of the γ-lactone of l-ascorbic acid or dehydroascorbic acid or an oxidation product of either compound (e.g., C-C bond cleavage between the ketone functional groups of dehydroascorbic acid or oxidation of the primary alcohol) are all potential sources of the carboxylato ligands, the formation of charge neutral species is possible and would preclude detection by ESI-MS.

**Oxalic acid.** For the oxidation of cyclooctene catalysed by I/oxalic acid changes in the UV-Vis absorption spectrum of the reaction mixture, and hence 1, are observed as the reaction proceeds, however as for salicylic acid, EPR signals are not observed at any stage. Surprisingly, when the reaction mixture is allowed to stand at r.t. overnight, the UV-Vis spectrum becomes that typical of a [MnIII,(μ-O)(μ-carboxylato)₂(tmtacn)]²⁺ complex (Fig. 12b). The presence of carboxylato ligands in the ESI-MS spectra is deprotonation of the non-coordinated carboxylic acid group, resulting in the formation of charge neutral species, which are not detectable by ESI-MS.

Nevertheless, the evolution of the UV-Vis absorption spectrum with time shows that complex 1 undergoes conversion to a catalytically active species immediately upon addition of H₂O₂. The increase in molar absorptivity and the absence of any EPR signals suggests that the active catalyst is in the MnIII or MnIII,IV state rather than a MnII, MnII, or MnIII,IV, state. Remarkably, after ca. 3 h a sudden decrease in absorptivity is observed and the spectrum changes to that reminiscent of the [MnIII,(μ-OH)₂(μ-CO₂)₂(tmtacn)]²⁺ “open” complex (i.e. B, see Scheme 2). On standing overnight the spectrum of the reaction mixture changes further to that typical of a [MnIII,(μ-O)(μ-CO₂)₂(tmtacn)]²⁺ complex.

**Discussion**

**Hydroxybenzoic acid promoted oxidation of alkenes by I**

Although it is tempting to consider the involvement of the proximal –OH group of salicylic acid in ligation to the manganese ions, or as proton donor/acceptor group in rationalising the selectivity towards epoxidation over cis-dihydroxylation for the system I/salicylic acid, it should be noted that the selectivity achieved with 3-hydroxybenzoic acid is essentially the same as with salicylic acid (Table 1, entry 1 and 6). UV-Vis spectroscopy shows that the mononuclear complex 8 is not present during the catalytic oxidation of cyclooctene by I/salicylic acid, in contrast to ESI-MS studies. However, it should be noted that for the MnIII₂ bis(μ-carboxylato) complex 4 generated in CH₃CN solution from I/salicylic acid by reduction with H₂NNH₂, the mononuclear complex 8 was present as a major signal in its mass spectrum. Furthermore, ¹⁸O-labeling results show similar incorporation of the oxygens in the cis-diol and epoxide products for the reaction catalysed by I/salicylic acid as was found for...
other carboxylic acids. Thus, for the catalytic system 1/salicylic acid the results suggest that the mechanism is essentially the same as that described for 1/CCl₃CO₂H, and that the differences in spectroscopic features of the reaction mixture observed are due to the involvement of the hydroxyl group in the electronic structure of the complex.

Hence, although the mononuclear complex 8 was isolated, UV-Vis spectroscopy demonstrates that this mononuclear species is not present during the catalytic oxidation reaction by the system 1/salicylic acid. Instead, just like for all other (substituted) benzoic acids, tentatively, a ‘open’ dinuclear Mn III₂ bis(carboxylato) complex (i.e. B, Scheme 2), which does not bear a μ-oxido bridge is present (cf. A, Scheme 2).

**L-Ascorbic acid promoted oxidation of alkenes by 1**

Berkessel and coworkers reported the epoxidation of terminal alkenes by the combination of Mn-tmtacn and L-ascorbic acid. In the present study these results were confirmed, however, especially when cyclooctene is used as substrate with L-ascorbic acid as additive, substantial cis-dihydroxylation is observed in addition to epoxidation. That the system 1/L-ascorbic acid shows higher levels of cis-dihydroxylation for cyclooctene than for terminal alkenes, is in agreement with the trends observed for the substrate scope of the 1/carboxylic acid promoted catalytic oxidation of alkenes, where the highest selectivities towards cis-dihydroxylation were observed with electron rich cis-alkenes.

The absence of a lag period for the system 1/L-ascorbic acid can be attributed to the reducing power of L-ascorbic acid. Whereas for other carboxylic acid promoted systems the reduction of 1 by H₂O₂ is facilitated by protonation of 1 by the carboxylic acid, from both EPR and UV-Vis spectroscopy it is clear that L-ascorbic acid is a sufficiently powerful reductant to reduce 1 directly to lower oxidation states which can engage in ligand exchange to form active species. From UV-Vis spectroscopic data it is clear that a Mn III₂ bis(μ-carboxylato) complex is present when the concentration of H₂O₂ is low. However, the observation of a Mn IIIIV₂ bis(carboxylato) species by EPR and UV-Vis spectroscopy may be misleading in terms of the direct involvement of such a species in the catalysis. The propensity of manganese carboxylate complexes to engage in disproportionation and self-exchange reactions should not be overlooked. Indeed, the one-electron
Oxaldehyde acid promoted oxidation of alkenes by 1

The catalyst system 1/oxalic acid was found to provide the selective epoxidation of a terminal alkene (i.e. 1-octene), in agreement with the report of De Vos and coworkers. From the time course of the reaction it is clear that a lag period, which is normally observed for the combination 1/carboxylic acid, is not present. As for L-ascorbic acid, it is possible that oxalic acid facilitates the reduction of 1 and thereby activates the catalyst towards ligand exchange to form the active state.

With cyclooctene as substrate, cis-dihydroxylation was observed in addition to epoxidation. However, substantial amounts of the cis-diol are formed only after 3 h at room temperature (and after ca. 4–5 h at 0 °C), indicating that two distinct catalytic systems are operating. Furthermore, an abrupt change in the UV-Vis spectrum of the reaction mixture coincides with the onset of cis-dihydroxylation activity. Importantly, if a second batch of oxalic acid (1 mol%) is added after 2.5 h, the occurrence of this second phase is suppressed, i.e. cis-dihydroxylation is not observed at any stage and only epoxidation takes place.

While the nature of the catalytically active species during the first 3 h of the reaction remains elusive, during the latter period of the reaction, the oxalic acid system bears close resemblance to that of other alkanolic and benzoic carboxylic acids. UV-Vis spectroscopy indicates the presence of a dinuclear MnIII oxidation bis(μ-carboxylato) complex. However, the identity of the bridging carboxylato ligand(s) is as yet unclear. A possible candidate is suberic acid (formed from cyclooctene by C=C cleavage).

Summary

For salicylic acid it is apparent that although the proximal hydroxyl group has a profound influence on the coordination chemistry and spectroscopy of the MnIII oxidation bis(μ-carboxylato) complex it forms upon reduction of 1, the mechanism by which salicylic acid enhances the activity of 1 in the oxidation of alkenes is essentially the same as that of other carboxylic acid co-catalysts.

The effectiveness of L-ascorbic acid and oxalic acid in suppressing the catalase activity of Mn-tmtacn in order to attain effective epoxidation of alkenes was reported by the groups of Berkessel and De Vos, respectively. In our hands, and under somewhat modified conditions these additives give effective epoxidation of (terminal) alkenes also. However, when cyclooctene was used as substrate, the combination of 1 and L-ascorbic acid or oxalic acid resulted in a catalytic system capable of cis-dihydroxylation in addition to epoxidation, as for the other carboxylic acid additives we examined earlier.

For the substrate 1-octene the system 1/salicylic acid yields primarily the epoxide product (Table 1, entry 4). Both oxaldehyde acid and L-ascorbic acid additives give slightly higher conversion then salicylic acid (Table 2 and 3, respectively), however, for all three additives the epoxide is the main product in agreement with earlier reports.

Several key differences between the systems 1/L-ascorbic acid, 1/oxalic acid and 1/RCO2H, are notable and demonstrate clearly that more than one possible mechanism for enhancing the reactivity of the Mn-tmtacn system may be available.

For the systems 1/L-ascorbic acid and 1/oxalic acid, the conversion of cyclooctene was seen to proceed immediately upon addition of H2O2. This is in stark contrast to the 0.5–3 h lag-period observed for the system 1/RCO2H which we demonstrated was due to the delayed reduction of 1 and subsequent formation of catalytically active MnIII oxidation-bis(μ-carboxylato) complexes. This difference in behaviour can, however, be rationalised on the basis of the inherent ability of both L-ascorbic and oxalic acid to act as reductants. For L-ascorbic acid this ability is manifested in the reduction of 1 observed by UV-Vis and EPR spectroscopy prior to addition of H2O2. For oxalic acid, although reduction is not observed prior to addition of H2O2, 1 is reduced quickly upon addition of H2O2 to the reaction mixture, in contrast to the system 1/RCO2H. Indeed, for dehydroascorbic acid very low activity was observed over the entire course reaction, primarily due to its inability to reduce 1 and the absence of a proton source to enable H2O2 to engage in reduction of H1+ either.

Oxalic acid behaves somewhat differently compared to all other carboxylic acids examined. Although 1 undergoes reduction and presumably ligand exchange reactions in the very early stages of the catalysis (observed as a rapid change in the UV-Vis spectrum), only epoxidation is observed during the first 3 h of the reaction and not until a sudden change in the UV-Vis spectrum of the reaction mixture (during the second phase of the 1/oxalic acid promoted reaction) are substantial amounts of cis-diol formed in addition to the epoxide product. In contrast, for all other carboxylic acids examined, cis-dihydroxylation and epoxidation commenced and proceeded simultaneously. The sudden change in selectivity accompanied with a sudden change in the UV-Vis spectrum of the reaction mixture of the catalytic system indicates the sudden formation of a different active species. The change in reactivity is very much likely to be due to the decomposition of oxalic acid as addition of a second equivalent of oxalic acid after 2 1/2 h results in a near complete suppression of this change in selectivity (i.e. cis-dihydroxylation is suppressed).

It is clear that at least the possibility of formation of dinuclear MnIII oxidation-bis(μ-carboxylato) species either early (L-ascorbic acid) or later in the reaction (oxalic acid) is indicated in the present study. However, when L-ascorbic acid is used as additive, a mixed-valent MnIII oxidationIV species is observed at high H2O2 concentration also. The hyperfine splitting constant indicates that this mixed-valent species contains different bridging ligands than present in 1 (which contains three μ-oxo bridges), possibly two carboxylato bridges.

Conclusions

Additives such as oxalic acid have been proposed to induce the formation of mononuclear species which can engage in the catalysed oxidation of alkenes. However, from the data presented here, it is clear that definitely for salicylic acid and very likely for L-ascorbic acid and oxalic acid (that is, during the second phase...
of the reaction) dinuclear MnIII, βι(μ-carboxylato) complexes are present and are likely to be involved in the catalysed cis-dihydroxylation and epoxidation of cyclooctene. Unfortunately, the exact nature of the bridging carboxylato ligands in the case of the dihydroxylation and epoxidation of cyclooctene. Unfortunately, a representation and like ytob be involved in the catalysed

We thank Prof. J. Reedijk and Dr J. G. Roelfes for discussions and financial support. We thank Prof. J. Reedijk and Dr J. G. Roelfes for discussions and financial support.

Notes and references


24 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
28 Cyclooctene was not employed by Berkessel and Sklorz (ref. 20) in their study of this catalytic system.
29 The same phases and processes are observed at 0°C, however at slightly longer times. To enable direct comparison with spectroscopic data, the reactions discussed in this section were performed at r.t.
30 *i.e.* while conversion proceeds at a constant rate, before substantial overoxidation occurs.
32 However, for the cis-diol product the low conversion and the uncertainty in the exact H$_2$O content of the reaction precludes interpretation of the results beyond confirming that at least some of the oxygen of the cis-diol product originates from the water present in the reaction mixture.
33 It should be noted that, as shown previously in ref. 11b, the propensity of these types of complexes to undergo rearrangements in their coordination sphere and be reduced in the ESI-MS requires that the data obtained are interpreted with caution. In the present example the observation of a mononuclear complex by ESI-MS does not necessarily mean that the same species is actually present in solution to a significant degree.