Manganese Oxidation Catalysts with 2-(2′-Hydroxyphenyl)oxazoline Ligands: Catalyst Intermediates and Degradation Products − Crystal Structure of Bis[{2-(2′-oxazolinyl)phenolato}bis(1-methylimidazole)manganese(III)] Perchlorate

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Manganese complexes with phox ligands [Hphox = 2-(2′-hydroxyphenyl)oxazoline] act as oxidation catalysts with dihydrogen peroxide. Their catalytic efficiency is strongly affected by the presence of a base, such as 1-methylimidazole (1-Meim). The crystal structure of an Mn–phox complex with two axial 1-Meim ligands, $[Mn(phox)_2(1\text{-}Meim)_2](ClO_4)$, is reported. The $[Mn(phox)_2]^+$ and $[Mn(phox)_2(1\text{-}Meim)]^+$ species have been detected in catalytic reaction mixtures by electrospray mass spectrometry. In the catalytic oxidation of styrene, turnover numbers of 428 and 456 have been obtained for styrene oxide in the presence of $[Mn(phox)_3]$ and of $[Mn(5'\text{-}NO_2phox)_3]$, respectively. During these reactions, catalyst degradation occurs, and is the main obstacle to obtaining higher turnover numbers. GC-MS analysis of the degradation products of $[Mn(5'\text{-}Clphox)_3]$ after catalytic reactions indicates that the oxazoline group is decomposed. The same decomposition products are also observed with electrospray mass spectrometry at higher ionisation potentials.

Introduction

Oxidations are versatile reactions for the synthesis of various fine chemicals and pharmaceuticals.[1] Traditionally, these reactions are performed with stoichiometric amounts of inorganic oxidants such as chromium or manganese oxides. However, the use of such reagents is environmentally unacceptable and there is an increasing demand for clean synthetic methods.[2,3] A very attractive method for oxidation reactions is the use of manganese catalysts with clean and cheap oxidants such as molecular oxygen or dihydrogen peroxide. Various manganese complexes with, for example, substituted tacn (1,4,7-triazacyclononane), porphyrin, salen [H_2salen = bis(salicylidene)ethylenediamine] or phox [Hphox = 2-(2′-hydroxyphenyl)oxazoline] ligands, have successfully been used in oxidation reactions and bleaching processes with dihydrogen peroxide.[4,5] In most reactions with these complexes, however, catalyst degradation results in loss of catalytic activity. Catalyst degradation is often a problem in oxidation catalysis,[6] and provision of increased stability in the manganese catalysts is therefore of great interest. A significant increase in stability has been accomplished by modification of the ligands. For instance, the introduction of halogen or nitro groups onto porphyrin catalysts results in a higher resistance towards oxidative degradation.[7] Similarly, the stability, and thus the catalytic efficiency, of Mn−salen complexes (or Jacobsen−Katsuki catalysts) has been reported to be improved by introduction of electron-withdrawing nitro substituents,[8] although in catalysed asymmetric epoxidation reactions this change results in significantly lower enantiomeric excesses (*ee*s) in the epoxides.[9] Alternatively, the addition of *N*-oxides[10] or, for reactions with dihydrogen peroxide,[11] of bases improves the catalytic efficiency without significantly reducing the *ee*s of the products. A base effect[12] and a substituent effect[13] have also been found for oxidations catalysed by the Mn−phox complexes. The didentate Hphox ligands, like the salen ligands, have a mixed N,O-donor set and are readily accessible. They are also known to be more stable to hydrolysis than the salen ligands.[14] However, the Mn−phox complexes also show a loss of catalytic activity over time during oxidation reactions.

The reactions causing the degradation of the complexes with the salen and similar phox ligands are not yet clearly understood. Dual-mode EPR spectroscopy has been used to gain insight into the mechanism of catalyst degradation of Mn−salen epoxidation catalysts.[15] This paper reports studies of the Mn−phox complexes during oxidation reac-

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tions, showing the effect of the reaction conditions on the catalytic efficiency, and the identification of various catalyst intermediates and degradation products.

Results and Discussion

Molecular Structure of $[Mn(phox)_2(1\text{-}Meim)_2](ClO_4)$

X-ray analysis of $[Mn(phox)_2(1\text{-}Meim)_2](ClO_4)$ (1-Meim = 1-methylimidazole) shows two similar independent molecules present in the unit cell, with $Z = 2$.

The structure of these molecules consists of a C_i-symmetric manganese(III) ion with two phox ligands *trans*-coordinated in the equatorial plane and two monodentate axial 1-Meim ligands (Figure 1), together with a noncoordinating perchlorate anion. Selected bond lengths and angles are given in Table 1.

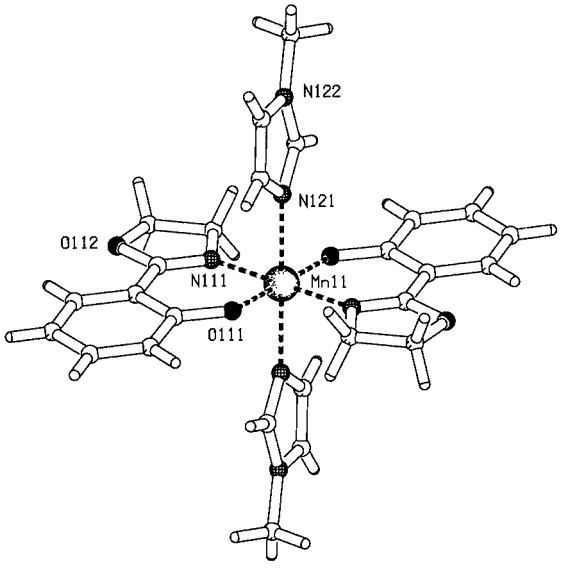

Figure 1. PLATON projection of the structure of one of the $[Mn(phox)_2(1\text{-}MeIm)_2]^+$ ions

Table 1. Selected bond lengths [Å] and angles [°] of one of the molecules of $[Mn(phox)_2(1\text{-}MeIm)_2](ClO_4)_2$; symmetry operation: $'$: $-x, -y, 1 - z$

Mn11−O111	1.867(2)	Mn11−N121	2.235(3)
Mn11−N111	2.045(3)		
O111−Mn11−N111	90.59(11)	O111−Mn11−N121′	89.88(10)
O111−Mn11−N111′	89.41(11)	N111−Mn11−N121	89.40(10)
O111−Mn11−N121	90.12(10)	N111−Mn11−N121′	90.60(10)

The differences in the ligand-to-metal bond lengths between the independent units are within 0.03 Å, while the differences in the bond angles are within 0.06°. The axial bonds of 2.235(3) (Mn1−N121) and 2.261(3) Å (Mn2−N221) are longer than the coordination bonds between the manganese ion and the phox ligands, as is to be expected for a Jahn−Teller-distorted d^4 ion. The Mn1−O111 and Mn−O211 bond lengths are similar to the bond lengths found in the $[Mn(phox)_2(MeOH)_2]^+$ units of the other Mn−phox complexes,[16] while the bonds of the manganese ion to the oxazoline nitrogen atoms are slightly longer.

Manganese(III) complexes with similar N_4O_2 coordination have been characterised for various Mn−salen complexes with pyridine molecules as axial ligands.[17] The main differences are the longer axial coordination bonds (between 2.30[18] and 2.48 Å[19]) for these complexes, as compared to $[Mn(phox)_2(1\text{-}Meim)_2](ClO_4)$. A manganese(III) complex with two axially coordinated imidazole groups from 1,4-di(1-imidazolyl)butane has been synthesised; in this case the two imidazole groups of one ligand coordinate to different manganese atoms, resulting in a network structure.[20] The bond lengths of the Mn−N bonds in this complex (2.28 and 2.29 Å) are only slightly longer than those in $[Mn(phox)_2(1\text{-}Meim)_2](ClO_4)$.

Catalysis

The solvent employed has a large effect on $[Mn(phox)_3]$-catalysed oxidation reactions;[13] the most interesting solvents were found to be methanol and acetone. The catalytic efficiency in the reactions in acetone (similarly to that in the reactions in methanol[12]) is increased by the addition of a base such as 1-Meim. In acetone, however, much higher turnover numbers have been obtained. It has been proposed that an acetone adduct of dihydrogen peroxide would be formed under these conditions, and that this would slowly release dihydrogen peroxide during the reaction,[21] although the adduct itself might also act as the actual oxidant. Gas evolution due to dihydrogen peroxide decomposition is visible during the reactions in acetone, and hydrogen peroxide decomposition is the limiting factor for these reactions. In methanol, ligand degradation limits the cumulative turnover numbers; after 15 min, hydrogen peroxide is still present and activity can be restored by addition of fresh quantities of the ligand. The amounts of dihydrogen peroxide used were varied to study the result on the turnover numbers, as well as the efficiency, relative to the oxidant (Table 2).

The results in Table 2 clearly show that the use of only 2.1 mmol of dihydrogen peroxide (10% of the standard amount) already results in a turnover number of 22 in methanol, an efficiency of 14.7% relative to dihydrogen peroxide. With larger amounts of dihydrogen peroxide, the turnover numbers level off, with a concomitant decrease in the efficiency based on the oxidant. This efficiency and the turnover number can be slightly increased by slow addition of the oxidant (five times 4.2 mmol in 15 min), resulting in a turnover number of 40 towards styrene oxide (efficiency of 2.7% based on H_2O_2) and of 4 towards benzaldehyde.

In acetone, contrary to the situation in methanol, an increase in the amount of oxidant from 5.3 mmol to 21 mmol results in a significant increase in the turnover numbers. The highest efficiency (15.8%) towards the oxidant is obtained on addition of 15.8 mmol of dihydrogen peroxide. At higher amounts of the oxidant, added at once, the turnover

Table 2. Effect of the amount of 1-Meim and dihydrogen peroxide on the turnover numbers and efficiency towards H_2O_2 in the [Mn(phox)$_3$]-catalysed oxidation of styrene

1-Meim Amount [mmol]	H_2O_2 Amount [mmol]	Turnover numbers towards styrene oxide[a] Methanol	Acetone	Yield of styrene oxide based on H_2O_2 (%) Methanol	Acetone
0.0	21.0	4	9	0.3	0.6
2.0	2.1	22	3	14.7	2.0
2.0	5.3	33	16	8.7	4.2
2.0	10.5	33	104	4.4	13.9
2.0	15.8	34	178	3.0	15.8
2.0	21.0	34	220	2.3	14.7
2.0	21.0[b]	40	n.d.	2.7	n.d.
2.0	4 × 21.0[c]	34	428	0.6	7.1

[a] Reactions in methanol were carried out with stirring by dissolving [Mn(phox)$_3$] (14 μmol) in methanol (20 mL) at room temperature; subsequently, the substrate (14 mmol), 1-MeIm (2.0 mmol) and the indicated amount of dihydrogen peroxide were added (t = 0); turnover numbers are the total turnover numbers at t = 15 min; reactions in acetone were carried out by stirring acetone (10 mL) and the indicated amount of dihydrogen peroxide at 0 °C for 30 min; subsequently, the substrate (14 mmol), 1-MeIm (2.0 mmol) and [Mn(phox)$_3$] (14 μmol) were added (t = 0); turnover numbers are the total turnover numbers at t = 15 min. [b] Slow addition of the oxidant (five times 4.2 mmol in 15 min); n.d. = not determined. [c] 21.0 mmol was added before the reaction; additional amounts of 21.0 mmol of the oxidant, dissolved in 5 mL of acetone, were added, at t = 15, 30 and 45 min.

numbers appear to reach a maximum. It may be that a maximum activity is found at a certain dihydrogen peroxide concentration, or it may indicate that by this time most of the extra dihydrogen peroxide added is decomposed into water and dioxygen. In contrast to the reactions in methanol,[12] the catalytic activity could not be restored by addition of fresh Hphox ligand. Subsequent addition of extra dihydrogen peroxide instead of the ligand, however, results in an increase in the total turnover number. After three consecutive additions of quantities of 21 mmol of dihydrogen peroxide in 5 mL of acetone at t = 15, 30, and 45 min (by which time the solution had turned colourless), a turnover number of up to 428 was obtained. The addition of even more dihydrogen peroxide did not result in any further increase in the turnover number, but gas evolution still continued. To regain catalytic epoxidation activity at this point, addition of fresh Hphox ligand appeared to be necessary, indicating that the catalyst had been degraded by this time.

Higher turnover numbers have been obtained with the more stable [Mn(5′-NO_2phox)$_3$] catalyst, similarly to the case of the reactions in methanol.[13] For [Mn(5′-NO_2phox)$_3$], the obtained turnover number of 456 towards styrene oxide obtained for the reaction in acetone (4×21 mmol H_2O_2) corresponds to a yield of 46% relative to styrene. The addition of extra dihydrogen peroxide increases the turnover numbers, but lowers the efficiency relative to the oxidant to 7.1% (reaction with [Mn(phox)$_3$]) and 7.6% (reaction with [Mn(5′-NO_2phox)$_3$]).

Catalyst Degradation

The major obstacle to the obtainment of higher turnover numbers in the Mn−phox-catalysed oxidation reactions is catalyst degradation. It has been reported that the decrease in catalytic activity during the reactions in methanol coincides with a change in the original green colour of the solution to pale yellow or colourless and the appearance of a manganese(II) EPR signal, while the addition of fresh free ligand results in regeneration both of the green solution and of the catalytic activity, indicating that the ligand decomposes during the catalytic reactions.[12] Similarly, the appearance of the manganese(II) EPR signal and decolouration of the solution also occur for the reactions in acetone, although loss of the catalytic activity due to catalyst degradation and the related decolouration of the solution both proceed less quickly (45 min) than in methanol (15 min, see above).

ES-MS studies were performed during the oxidation of styrene with [Mn(phox)$_3$] and [Mn(5′-NO_2phox)$_3$] in methanol and in acetone. In the absence of the oxidant, the main fragments detected for the [Mn(phox)$_3$] and [Mn(5′-NO_2phox)$_3$] complexes (both in the methanol and in the acetone solutions) are the $[MnL_2]^+$ and the $[MnL_2(1\text{-Meim})]^+$ ions. These two fragments may originate from species of the type $[MnL_3]$ or $[MnL_2L'_xL''_y]^+$ (with L′ and L″ being, for instance, 1-methylimidazole or solvent molecules) after dissociation of one or two coordinating groups. After addition of dihydrogen peroxide, the $[MnL_2]^+$ and $[MnL_2(1\text{-Meim})]^+$ fragments are still the most important species observed in

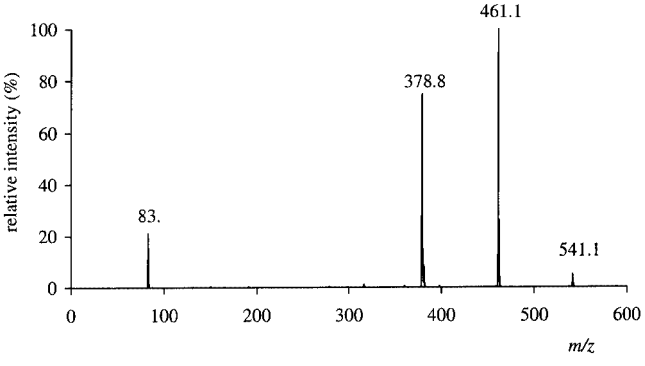

Figure 2. Electrospray mass spectrum at the start (t = 1 min) of the oxidation of styrene with [Mn(phox)$_3$] and dihydrogen peroxide in methanol: m/z = 83.0 [1-MeIm + H^+], 378.8 $[Mn(phox)_2]^+$, 461.1 $[Mn(phox)_2(1\text{-MeIm})]^+$, 541.1 $[Mn(phox)_3]^+$

both solvents during the first minutes of the reaction (Figure 2).

A few minutes after the start of the reaction, the ES-MS spectra of all reaction mixtures show decreases in the intensities of the $[MnL_2]^+$ and $[MnL_2(1\text{-Meim})]^+$ peaks. In these spectra, the parent peak originates from the [1-Meim + H^+] fragment, while various other peaks of low intensity are also present; these could not be clearly assigned. In mass spectra of reaction mixtures taken towards the end of all reactions, only various small peaks are observed. Apart from the peaks already assigned, no other peaks that could be clearly assigned to a manganese-containing species or a ligand degradation product have been observed.

In order to try to identify the ligand degradation products, catalysis experiments were performed. During these, an excess of fresh ligand (2×30 equiv. with respect to Mn) was added. GC-MS analysis of the oxidation products of H-5′-Clphox in an ethanol/methanol solution showed nearly quantitative conversion of the ligand. The main product appeared to be 5-chlorosalicylic acid; the secondary products methyl 5-chlorosalicylate and ethyl 5-chlorosalicylate, which are due to the acidic alcoholic conditions used for GC-MS, are also observed. The formation of these products indicates degradation of the catalyst at the oxazoline moiety. No traces of derivatives of the $-NCH_2CH_2-$ part of the oxazoline group were found.

Further indications that the oxazoline group is the part of the ligand most susceptible towards degradation are obtained by analysis of the ES-MS spectra of the pure $[Mn(5'\text{-Clphox})_3]$, $[Mn(phox)_3]$ and $[Mn(phox)_2(MeOH)_2]$-$[Mn(phox)_2(ClO_4)_2](H_2O)_2$ complexes. With a +70 V nozzle ionisation potential, the main fragments observed are the $[MnL_2]^+$ and the $[HL + H]^+$ fragments. Additional information can be obtained by use of other ionisation potentials. For $[Mn(5'\text{-Clphox})_3]$, $[Mn(phox)_3]$ and $[Mn(phox)_2(MeOH)_2][Mn(phox)_2(ClO_4)_2](H_2O)_2$, the application of a +170 V nozzle ionisation potential results in mass spectra showing fragments that might be related to catalyst degradation products. In the mass spectra of $[Mn(phox)_3]$ and $[Mn(phox)_2(MeOH)_2][Mn(phox)_2(ClO_4)_2](H_2O)_2$ (Figure 3), the $[Mn(phox)_2]^+$ fragments can be observed at m/z = 379.0. The mass difference of m/z = 42.2 between this signal and the signal at m/z = 336.8 corresponds to the loss of an $-NCH_2CH_2-$ fragment. A small signal at m/z = 121.0, corresponding to the $(Ar-C=O)^+$ fragment (see Figure 4) of a decomposed ligand, can also be observed.

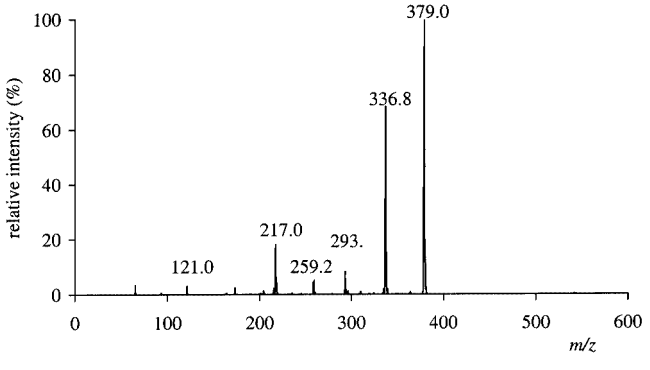

Figure 3. Ligand degradation observed in the electrospray mass spectrum of $[Mn(phox)_2(MeOH)_2][Mn(phox)_2(ClO_4)_2](H_2O)_2$ at a 170 V nozzle ionisation potential: m/z = 121.0 $[Ar\text{-}C=O]^+$, 217.0 $[Mn(phox)]^+$, 259, 293 unidentified, 336.8 $[Mn(phox)(Ar-C=O)]^+$, 379.0 $[Mn(phox)_2]^+$

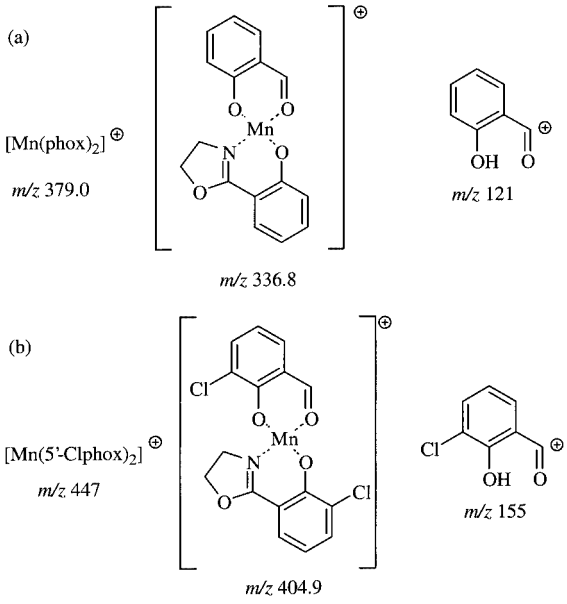

Figure 4. Schematic overview of degradation products (with m/z) observed in the ES-MS spectra of: (a) $[Mn(phox)_3]$, (b) $[Mn(5'\text{-Clphox})_3]$

A similar complex degradation pattern is found in the mass spectrum of $[Mn(5'\text{-Clphox})_3]$. The degradation of the $[MnL_2]^+$ fragment (m/z = 447.0) results in the $[Mn(5'\text{-Clphox})(Ar-C=O)]^+$ ion, which is clearly observed at m/z = 404.9. The isotope pattern of the latter fragment confirms the presence of two chlorine atoms. The $(Ar-C=O)^+$ fragment in this mass spectrum is observed at m/z = 155 (Figure 4). The reaction of the $(Ar-C=O)^+$ fragment, found in the ES-MS measurements, with water or an alcohol results in salicylic acid or one of its esters, which are the ligand decomposition products identified after the oxidation reaction with $[Mn(5'\text{-Clphox})_3]$ and excess of the H-5′-Clphox ligand (see above). Fragments containing the $-NCH_2CH_2-$ part of the oxazoline group were not identified.

The $\{[MnL_2]^+ - 42\}$ fragment is present with higher relative intensities in the mass spectra of $[Mn(phox)_2(MeOH)_2][Mn(phox)_2(ClO_4)_2](H_2O)_2$ and $[Mn(phox)_3]$ than in the spectra of $[Mn(5'\text{-Clphox})_3]$. In the mass spectrum of $[Mn(5'\text{-}NO_2phox)_3]$, no such signal is observed at all. In the reactions in methanol, $[Mn(5'\text{-}NO_2phox)_3]$ remains active for a longer time than the other catalysts.[12] This indicates that the complexes containing Hphox ligands with electron-withdrawing substituents are more resistant towards oxidative degradation, which is similar to the trend found for manganese complexes with porphyrin[7] and Mn−salen[8] ligands.

Conclusion

The most important reactions occurring during oxidation catalysis with the Mn−phox complexes are substrate oxidation, dihydrogen peroxide decomposition and catalyst degradation. The choice of the catalyst and the reaction conditions have considerable influence on all these reactions and therefore also on the catalyst efficiency. For instance, the addition of a base such as 1-Meim to the reaction mixtures is required to improve the catalytic efficiency. 1-Meim can coordinate to the manganese complex, as shown by the crystal structure of $[Mn(phox)_2(1\text{-}Meim)_2](ClO_4)$. The presence of $[Mn(phox)_2(1\text{-}Meim)]^+$ species during the catalytic reactions has been observed with ES-MS. Furthermore, coordination of 1-Meim significantly influences the electrochemical properties of the complexes containing the $Mn(phox)_2$ unit, as indicated by the changes in the cyclic voltammograms.[16] Therefore, the higher catalytic efficiency observed in the presence of 1-Meim is likely to be caused by coordination of 1-Meim to manganese atoms, thus resulting in a more active or stable catalyst.

In the reactions in acetone, oxygen evolution caused by dihydrogen peroxide decomposition is visible. Upon addition of extra dihydrogen peroxide, higher turnover numbers can be obtained in styrene oxidation, but the efficiency relative to dihydrogen peroxide is decreased. Despite the addition of extra dihydrogen peroxide, the reactions finally cease completely because of catalyst degradation, and the maximum turnover numbers obtained are 428 with $[Mn(phox)_3]$ and 456 with $[Mn(5'\text{-}NO_2phox)_3]$ as catalysts.

Changes in the solvent used or the addition of a base notwithstanding, the catalytic reactions cease in the end due to ligand degradation, which is the main obstacle to obtaining high turnover numbers. The decolouration of the reaction solution, and the appearance of an Mn^{II} EPR signal coincide with decreasing catalytic activity.[12] In methanol, the activity could easily be regenerated by addition of fresh Hphox ligand, which simultaneously restored the green colour of the solution. ES-MS measurements and analysis of the oxidation products of H-5′-Clphox indicate that the oxazoline group is the part of the Mn−phox catalysts most susceptible towards oxidative degradation. The introduction of a nitro substituent resulted in a more stable catalyst, as shown by the catalytic experiments and the ES-MS studies. The higher catalytic efficiency and the prolonged catalytic activity of $[Mn(5'\text{-}NO_2phox)_3]$ in styrene oxidation in methanol[13] directly reflects higher stability of the catalyst, as shown by electrochemistry (the irreversible oxidation of $[Mn(5'\text{-}NO_2phox)_3]^+$ occurs at the highest potentials)[13] and ES-MS, which is in accordance with the disappearance of the green colour being slower than in the reactions with the other catalysts. These results indicate that the introduction of strongly electron-withdrawing substituents decreases the susceptibility of the oxazoline group towards degradation. The first step of ligand degradation is presumably an oxidation reaction. In the literature, decomposition of oxazoline groups has been reported in reactions with the oxidants *m*-chloroperbenzoic acid (*m*-CPBA)[22] and sodium hypochlorite.[23] The oxidation products may be the oxaziridine and the oxazoline *N*-oxide,[22] with the ring still intact, as well as ring-opening products such as various esters,[22,23] which have also been found after oxidation of the excess H-5′-Clphox, indicating that similar oxazoline degradation reactions occur.

As shown in this study, Mn−phox- and Mn−salen-catalysed oxidation reactions with hydrogen peroxide have similar characteristics. Examples are the decolouration of the reaction solutions, the beneficial effect of the addition of bases on the catalytic efficiency and the increased stability upon introduction of electron-withdrawing substituents. Two oxidative conversions of Mn−salen complexes have been reported. Treatment of an Mn−salen complex in pyridine with dioxygen resulted in the oxidation of one imine group to an amide,[24] while complex degradation by visible light photolysis resulted in 2-(2′-hydroxyphenyl)benzimidazole, salicylaldehyde and a manganese(II) ion.[25] The products formed in the latter reaction, salicylaldehyde and manganese(II), are similar to the observed Mn−phox degradation products after the oxidation reactions. These results emphasise that for the Mn−phox complexes, the oxazoline group is the most oxidation-sensitive, while it is indicated that the imine group is the most sensitive position of the Mn−salen catalysts. Replacement of these groups should therefore be required to enhance the catalyst stability and indeed, for a similar catalyst system, the replacement of an imine by a tertiary amine group has resulted in a significantly more stable catalyst.[26] Given the potential of the Mn−salen complexes as asymmetric (ep)oxidation catalysts, further studies of stabilisation of these complexes are of paramount importance.

Experimental Section

General Remarks: All manganese complexes were synthesised by published procedures.[12,13,16] Solvents were used as technical grade, p.a. grade or, for acetonitrile, as HPLC grade (Rathburn) and, unless noted otherwise, were used as received. All p.a. grade solvents were purchased from Baker, except for acetone (Acros). Dihydrogen peroxide (35% in water) and styrene were supplied by Merck, all other chemicals used were obtained from Acros.

Equipment: A Varian Star 3400CX gas chromatograph with a J&W Scientific/Fisons DB-1701 (14% cyanopropylphenyl-methylpolysiloxane) column was used for analysis of the oxidation experiments. UV/Vis/NIR measurements were performed with a Perkin−Elmer Lambda 900 UV/Vis/NIR spectrometer. EPR measurements were performed at 77 K with a Jeol Esprit RE-2X spectrometer with a Jeol Esprit 330 ESRE data system. EPR *g* values were determined relative to DPPH as an external "*g*-mark" (g = 2.0037). GC-MS analysis of the ligand degradation products was recorded with a Finnigan MAT ITD 700 (EI mode) coupled with a Hewlett−Packard 438a GC. Electrospray mass spectra at higher ionisation potentials and before and during the oxidation reactions were performed at the Pharmacy department of the University of Groningen and were recorded with a NERMAG R 3010 triple quadrupole mass spectrometer equipped with an in-house atmospheric pressure ionisation source and ion spray interface.[27,28] The

PE-Sciex API 3 data system with an in-house and digital interface was used for data acquisition and data processing.

Catalysis: The catalytic reactions were carried out in methanol and in acetone, usually with a catalyst/substrate/oxidant ratio of 1:1000:1500. All flasks and stirrer bars used were thoroughly cleaned with acid to remove traces of metal, after which they were washed with an aqueous sodium carbonate solution. The turnover numbers given are the total turnover numbers per manganese ion after the indicated period of time. All reactions were performed at least in duplicate. ***Caution!*** The combination of acetone and dihydrogen peroxide is potentially explosive, especially under acidic conditions.[29] However, it can be handled safely by performing reactions on a small scale at 0 °C under slightly alkaline conditions, as used in the experiments described below.

In Methanol: The catalyst (14 μmol) was dissolved with stirring in 20 mL of methanol at room temperature. Styrene (14 mmol), chlorobenzene (5.0 mmol) and 1-methylimidazole (1-Meim, 2.0 mmol) were added to the resulting green solution, followed (at $t = 0$ min) by dihydrogen peroxide (35% in water, 21 mmol). Except for the reaction mixture with [Mn(5′-NO_2phox)], which slowly started to turn pale yellow after $t = 10$ min, the colours of the reaction mixtures changed to slightly yellow to colourless within the first few minutes of the reactions. At $t = 15$ min, a sample was taken and analysed by gas chromatography, with chlorobenzene as the internal standard.

In Acetone: Dihydrogen peroxide (35% in water, 21 mmol) and acetone (10 mL) were stirred for 30 min at 0 °C. Next, styrene (14 mmol), chlorobenzene (5.0 mmol) and 1-Meim (2.0 mmol) were added, followed by the powdered catalyst (14 μmol, $t = 0$). The green solution became slightly red-brown within the first few minutes of the reactions. After 10 min, the solution slowly turned pale green-yellow. At $t = 15$ min, a sample was taken and analysed by gas chromatography, with chlorobenzene as the internal standard.

Addition of Extra Dihydrogen Peroxide to the Oxidation of Styrene with [Mn(phox)$_3$] and [Mn(5′-NO_2phox)$_3$]: Dihydrogen peroxide (35% in water, 21 mmol) and acetone (10 mL) were stirred for 30 min at 0 °C. Styrene (14 mmol) and 1-Meim (2.0 mmol) were then added, followed by [Mn(phox)$_3$] (14 μmol, $t = 0$ min). At $t = 15$ min, a sample was taken from the pale green-yellow solution and analysed by gas chromatography, with chlorobenzene as the internal standard. Subsequently, 5 mL of a solution of dihydrogen peroxide (42 mmol) in acetone (20 mL), which had been stirring for 30 min at 0 °C, was added. At $t = 30$ and 45 min, a sample was taken for analysis, after which an additional 5 mL of the dihydrogen peroxide solution was added. At this time, the solution had turned almost colourless to pale yellow. A final sample was taken at $t = 60$ min.

Oxidation of the H-5′-Clphox Ligand: [Mn(5′-Clphox)$_3$] (14 μmol) was dissolved at room temperature, with stirring, in a mixture of methanol (10 mL) and ethanol (10 mL). Styrene (1.4 mmol) was added to this green solution, followed by dihydrogen peroxide (35% in water, 21 mmol). After 15 min, during which the solution turned from green to colourless, a sample was taken and analysed by gas chromatography, with chlorobenzene as the internal standard. Next, H-5′-Clphox (0.42 mmol) was added, resulting in the regeneration of the green color of the reaction solution. Samples were taken each 15 min and were analysed by gas chromatography, with chlorobenzene as the internal standard. The H-5′-Clphox peak could be clearly detected. The reaction was monitored over time by gas chromatography until the solution had become almost colourless and most of the ligand had disappeared. Further H-5′-Clphox (0.42 mmol) and dihydrogen peroxide (21 mmol) were added. After disappearance of most of the ligand, a sample was taken and analysed by GC-MS.

Electrospray Mass Spectrometry: Electrospray mass spectra of [Mn(phox)$_3$], [Mn(5′-phox)$_3$], [Mn(5′-NO_2phox)$_3$] and [Mn(phox)$_2$-(MeOH)$_2$][Mn(phox)$_2$(ClO_4)$_2$](H_2O)$_2$ were recorded in methanol and acetone, both in the absence and in the presence of water and/or 1-Meim. Mass spectra were also recorded on samples taken during the oxidation of styrene with [Mn(phox)$_3$] or [Mn(5′-NO_2-phox)$_3$] and dihydrogen peroxide. For these reactions, the standard conditions in methanol and acetone were used, with exception of the use of 10.5 mmol of dihydrogen peroxide instead of 21 mmol.

X-ray Data Collection and Structure Determination of [Mn(phox)$_2$(1-Meim)$_2$](ClO_4): The data were collected with an Enraf−Nonius Kappa CCD area detector on a rotating anode, with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The crystallographic data of the complex are presented in Table 3. The unit cell parameters were checked for the presence of lattice symmetry.[30] The structures were solved by automated direct methods (SHELXS-86).[31] Refinement on F^2 was carried out by full-matrix, least squares (SHELXL-97-2).[32] Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography.[33] Geometrical calculations and illustrations were performed with PLATON.[34] All calculations were performed with a DEC Alpha 255. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms. CCDC-181805 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystallographic data for [Mn(phox)$_2$(1-MeIm)$_2$](ClO_4)

Empirical formula	$C_{26}H_{28}ClMnN_6O_8$
Formula mass	642.93
Crystal dimensions [mm]	0.06 × 0.20 × 0.30
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
a [Å]	8.5401(10)
b [Å]	9.6127(15)
c [Å]	19.153(3)
α [°]	83.522(7)
β [°]	89.034(8)
γ [°]	65.008(7)
Cell volume [Å^3]	1415.2(4)
Z	2
F(000)	664
$D_{calcd.}$ [g·cm^{-3}]	1.5088(4)
μ(Mo-K_α) [mm^{-1}]	0.62
T [K]	150
No. of measured reflections	17005
No. of independent reflections	5013
R_{int}	0.060
R	0.053 {for 4302 [$F_o > 4\sigma(F_o)$]}
wR_2	0.138
S	1.08
No residual density outside [e·Å^{-3}]	−0.52, 0.89 (near Mn)

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