PAPER

NJC
www.rsc.org/njc

Modulation of the catalytic activity of manganese(III) salen complexes in the epoxidation of styrene: influence of the oxygen source

Ana Rosa Silva, Cristina Freire* and Baltazar de Castro

REQUIMTE, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 4169-007, Porto, Portugal. E-mail: acfreire@fc.up.pt; Fax: +351 22 6082959; Tel: +351 22 6082890

Received* (in London, UK) *1st August 2003, Accepted 14th November 2003
First published as an Advance Article on the web 6th January 2004

Several achiral Mn(III) salen complexes with different groups in the diimine bridge and in the aldehyde fragment were synthesised and their catalytic activity in the epoxidation of styrene was studied at room temperature, using two oxygen sources, NaOCl or PhIO, and in two solvents, CH_3CN and CH_2Cl_2.

These manganese(III) salen complexes present high chemoselectivities as homogeneous catalysts in the epoxidation of styrene, using either iodosylbenzene or sodium hypochlorite as oxygen sources. In general, when iodosylbenzene is used as oxidant higher styrene epoxide yields and lower yields of by-products, other than benzaldehyde, are obtained than with aqueous sodium hypochlorite solutions. It was possible to tune the catalytic activities of "[Mn(salen)X]" complexes by introduction of substituents in the diimine bridge and in the aldehyde fragment. The presence of bulky substituents in the diimine bridge always increases the catalytic activity of these complexes, regardless of the oxidant, an indication of steric tuning. However, the electronic tuning of the catalytic activity by introducing substituents in the 5 and 3 positions of the aldehyde fragment has different effects depending on the oxygen source. For the one-phase system resulting from the use of PhIO, electron withdrawing groups increase (electron donating groups decrease) the catalytic activity of the complexes, which probably results from destabilisation (stabilisation) of [O=Mn(V)(salen)X], the identified active species making them more (less) reactive. However, when NaOCl is used, the observed behaviour is the opposite: electron donating groups make the complexes better catalysts. The apparent similarity between the solubility of the complexes in the organic solvent and their catalytic activity seems to suggest that solubility must play a key role in their activity.

Introduction

Epoxidation of alkenes is one of the most widely methods used in organic synthesis, as epoxides can be easily transformed into a large variety of compounds *via* highly regio- and stereoselective ring opening reactions,[1] and direct oxygen transfer to the alkene is the most common method of epoxide synthesis.[2]

Manganese(III) complexes with Schiff base and porphyrin ligands have been extensively used as models of a monooxidase, the heme containing citochrome P-450.[3] These complexes catalyse the transfer of oxygen atoms to organic substrates and are important in the study of bio-organic mechanisms and in the development of efficient catalysts in organic synthesis for laboratorial and industrial application.[4]

Epoxidation of alkenes catalysed by manganese(III) complexes with Schiff bases of N_2O_2 coordination sphere, commonly known in the literature as salen complexes, has been the object of numerous publications since Kochi *et al.* described in 1986 that they were highly effective, chemoselective and stereoselective catalysts.[5] At the beginning of the last decade, they were also found, independently by the Jacobsen and Katsuki groups, to be highly enantioselective catalysts when the Schiff base ligands have chiral centres in the diimine bridge, eventually also with bulky chiral groups near the metal centre.[3,6]

The synthetic accessibility of the manganese(III) Schiff base complexes from readily available and inexpensive precursors constitutes one of their vital and more attractive features. The salen ligand system is easily constructed in a convergent manner from diamines and salicylaldehyde derivatives, and optimal selectivities for a given substrate can be achieved by tunning the catalyst's steric and electronic properties.[3,6]

Thus, manganese(III) salen complexes have demonstrated to be useful laboratory and industrial homogeneous catalysts in the epoxidation of some unfunctionalised alkenes, using iodosylbenzene, sodium hypochlorite, hydrogen peroxide and alkyl hydroperoxides as oxygen sources.[3] The mechanism by which oxygen transfer takes place from the intermediate oxo-metallic species to the alkene, as well as the spin state of the intermediate oxo-metallic species, possibly in a higher oxidation state, is still a matter of debate.[1,2,6] Nevertheless, the [O=Mn(V)-salenCl] species was identified directly by mass spectrometry[7] and indirectly by nuclear magnetic resonance[8] when iodosylbenzene was used as the oxygen source. Recent reports have shown that the mechanism, and consequently the products, depend on several factors: alkene,[6] oxidant, counter-ion, structure of the salen ligands and added Lewis base.[2,9]

In contrast, with the structurally varied but extensively studied metalloporphyrins, the tuning of the catalytic activity of the manganese(III) salen complexes by the easy introduction of substituents on the structure remains a area of untapped potential,[10] since reports have been principally focused on the tuning of the asymmetric induction of the chiral counterparts.[3,6]

We have been interested in the covalent attachment of transition metal Schiff base complexes onto activated carbon,[11,12] especially of manganese(III) salen complexes[13] in order to prepare efficient heterogeneous catalysts making use of activated

DOI: 10.1039/b309125b

carbon as a support. However, due to the variety of experimental conditions reported for the epoxidation of alkenes, we chose to do an initial systematic study of their catalytic activity in homogeneous phase varying the oxidant and the solvent in order to apply to the heterogeneous case.

Herein we present a systematic study of the epoxidation of styrene catalysed by achiral manganese(III) salen complexes (Scheme 1) with different diimine bridges, using two common oxidants, sodium hypochlorite and iodosylbenzene, and two of the most commonly used solvents with these oxidants, dichloromethane and acetonitrile. Styrene was chosen as a model substrate because it is one of the most important pro-chiral alkenes.[14] Experimental conditions described by Jacobsen *et al.*[15] were chosen for the reaction with sodium hypochlorite as oxygen source, and adapted to the reactions with iodosylbenzene. Some conclusions concerning the effect of the groups in the diimine bridge and aldehyde fragment, the type oxygen source and solvent used are presented.

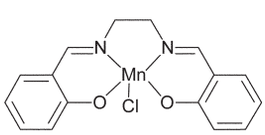
Experimental

Materials and solvents

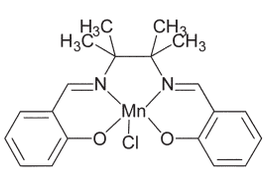
The reagents used in the synthesis of Schiff base ligands and their complexes were used as received, except for ethylenediamine and 1,2-diaminocyclohexane which were distilled prior to use. Ethylenediamine and 2-hydroxybenzaldehyde were from Merck; 1,2-diaminocyclohexane (mixture of *cis*/*trans* isomers), *meso*-1,2-diphenylethylenediamine, 2,3-dimethyl-2,3-dinitrobutane, tin (granulate), manganese(II) acetate tetrahydrate and iodobenzene diacetate from Aldrich; and manganese(II) chloride tetrahydrate from Sigma.

Styrene, decane, chlorobenzene, sodium hypochlorite solution, benzaldehyde, styrene epoxide and iodobenzene used in the catalytic experiments were from Aldrich and used as received; dichloromethane and acetonitrile were of HPLC grade (Romil).

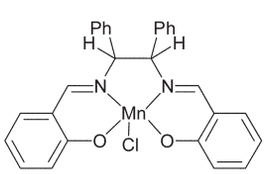
In the synthesis of H_2saltMe, 2,3-diamino-2,3-dimethylbutane was synthesised by reduction of 2,3-dimethyl-2,3-dinitrobutane with tin in acid media, using a procedure described in the literature.[16] Iodosylbenzene was synthesised using reported procedures,[17] by hydrolysis of iodobenzene diacetate with a solution of sodium hydroxide.



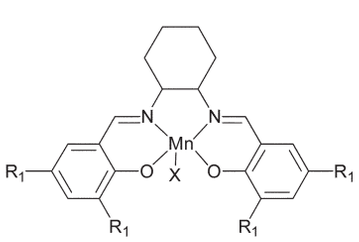
(**1**) [Mn(salen)Cl]



(**2**) [Mn(saltMe)Cl]



(**3**) [Mn(saldPh)Cl]



(**4**) [Mn(salhd)Cl]: R_1=H and X=Cl
(**5**) [Mn(3,5-dtButsalhd)Cl]: R_1=C$(CH_3)_3$and X=Cl
(**6**) [Mn(3,5-dClsalhd)CH_3COO]: R_1=Cl and X=CH_3COO

Scheme 1 Molecular formula of the Mn(III) salen complexes.

Synthesis of the manganese(III) complexes

The Schiff base ligands were prepared by the standard procedure of refluxing ethanolic solutions of the corresponding diamine and salicylaldehyde derivative in a 1 : 2 molar ratio.[18] Typically, 0.037 mol of the diamine were refluxed with 0.075 mol of the salicylaldehyde in 100 cm^3 of ethanol for 1–2 hours. The solutions were kept in the refrigerator overnight, and the precipitated solids were collected by filtration and dried under vacuum. Yields were in the range 75–90%. The following Schiff base ligands were prepared (Scheme 1): *N*,*N*′-bis(salicylidene)ethylenediamine, H_2salen; *N*,*N*′-bis(salicylidene)tetramethylethylenediamine, H_2saltMe; *N*,*N*′-bis(salicylidene)-1,2-diphenylethylenediamine, H_2saldPh; *N*,*N*′-bis(salicylidene)-1,2-cyclohexanediamine, H_2salhd; *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, H_2(3,5-dtButsalhd); and *N*,*N*′-bis(3,5-dichlorosalicylidene)-1,2-cyclohexanediamine, H_2(3,5-dClsalhd).

As the synthesis and characterisation of these ligands have already been reported in the literature,[19] their purity was only checked by ^{1}H NMR and infrared spectroscopy (FTIR).

The manganese(III) Schiff base complexes (Scheme 1), [Mn(salen)Cl] (**1**), [Mn(saltMe)Cl] (**2**), [Mn(saldPh)Cl] (**3**), [Mn(salhd)Cl] (**4**), [Mn(3,5-dtButsalhd)Cl] (**5**) and [Mn(3,5-dClsalhd)CH_3COO] (**6**), were prepared using procedures adapted from those described in the literature,[15] by refluxing equimolar quantities of an ethanolic solution of ligand and a methanolic solution of manganese(II) chloride tetrahydrate; in the synthesis of complex **6**, manganese(II) acetate tetrahydrate was used. Typically, 3.30 mmol of manganese(II) chloride tetrahydrate and 3.00 mmol of ligand in 100 cm^3 of ethanol were refluxed for 1–2 hours, during which the yellow-orange colour of the solution changed to dark brown. The solutions were concentrated by evaporation, yielding dark brown solids, which were re-crystalised from acetonitrile or ethanol, and dried under vacuum. Yields were in the range 30–75%.

[Mn(salen)Cl] (**1**), chloro-[*N*,*N*′-bis(salicylidene)ethylenediaminato]manganese(III): $MnC_{16}H_{14}N_2O_2Cl$. FAB-HRMS, *m*/*z*: calculated ($MnC_{16}H_{14}N_2O_2^+$) 321.0436, experimental 321.0438. UV–Vis, λ_{max}/nm: 230, ~293, ~329, 363, 417, ~500(sh), ~600(sh). FTIR, ν/cm^{-1}: 1624 vs, 1599 vs, 1541 s, 1468 m, 1444 s, 1386 m, 1332 m, 1325 m, 1292 vs, 1254 f, 1213 (sh), 1201 m, 1151 m, 1130 m, 1084 w, 1049 w, 1034 w, 978 w, 902 m, 866 w, 854 w, 825 w, 802 s, 773 s, 756 s, 688 w, 631 s, 594 m, 488 w, 467 s.

[Mn(saltMe)Cl] (**2**), chloro-[*N*,*N*′-bis(salicylidene)tetramethylethylenediaminato]manganese(III): $MnC_{20}H_{22}N_2O_2Cl$. EI-HRMS, *m*/*z*: calculated ($MnC_{20}H_{22}N_2O_2^+$) 377.1062, experimental 377.1060. UV–Vis, λ_{max}/nm: 277, 308, 352, 399, 480, ≈690 (sh). FTIR, ν/cm^{-1}: 2986 w, 2964 w, 1601 vs, 1539 m, 1466 w, 1443 m, 1396 m, 1380 vw, 1292 s, 1207 w, 1143 m, 1123 w, 1031 w, 905 w, 847 w, 798 w, 755 m, 740 w, 625 m, 534 m, 456 w, 427 w.

[Mn(saldPh)Cl] (**3**), chloro-[*N*,*N*′-bis(salicylidene)-1,2-diphenylethylenediaminato] manganese(III): $MnC_{28}H_{22}N_2O_2Cl$. EI-HRMS, *m*/*z*: calculated ($MnC_{28}H_{22}N_2O_2^+$) 473.1062, experimental 473.1047. UV–Vis, λ_{max}/nm: 231, 281, 308, ~343 (sh), 410, ~470 (sh), ~689 (sh). FTIR, ν/cm^{-1}: 1618 (sh), 1603 vs, 1537 s, 1495 w, 1468 m, 1441 s, 1383 m, 1338 w, 1308 s, 1300 s, 1280 m, 1248 w, 1221 (sh), 1207 m, 1149 m,

1126 m, 1101 w, 1074 w, 1045 w, 1032 w, 1016 vw, 995 m, 972 m, 945 w, 930 w, 908 m, 877 vw, 860 m, 831 vw, 816 m, 793 vw, 769 (sh), 760 s, 723 vw, 704 m, 660 mf, 644 m, 631 vw, 621 m, 590 w, 575 m, 559 vw, 530 m, 498 vw, 476 vw, 455 m.

[Mn(salhd)Cl] (**4**), chloro-*N*,*N*′-bis(salicylidene)-1,2-cyclohexanodiaminato]manganese(III): $MnC_{20}H_{20}N_2O_2Cl$. FAB-HRMS, *m*/*z*: calculated ($MnC_{20}H_{20}N_2O_2^+$) 375.0905, experimental 375.0920. UV–Vis, λ_{max}/nm: 212, ~276 (sh), 298, 352, 395, ~455 (sh), ~686 (sh). FTIR, ν/cm^{-1}: 2933 m, 2926 m, 2870 (sh), 2858 m, 1622 vs, 1599 vs, 1543 s, 1470 m, 1446 s, 1394 m, 1350 m, 1336 (sh), 1319 s, 1309 s, 1277 s, 1246 w, 1217 m, 1200 m, 1149 s, 1124 w, 1051 w, 1030 w, 1010 w, 906 m, 862 w, 848 w, 808 m, 750 s, 686 w, 623 m, 605 w, 569 m, 515 w, 459 w, 426 m.

[Mn(3,5-dtButsalhd)Cl] (**5**), chloro-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanodiaminato]manganese(III): $MnC_{36}H_{52}N_2O_2Cl$. FAB-HRMS, *m*/*z*: calculated ($[MnC_{36}H_{52}N_2O_2\text{-}Cl]^+$) 599.3409, experimental 599.3417. UV–Vis, λ_{max}/nm: 228, 282, 319, ~354(sh), 415, 510, ~642(sh). FTIR, ν/cm^{-1}: 2954 ff, 2906 m, 2867 m, 1612 vs, 1550 m, 1535 s, 1462 m, 1433 m, 1419 w, 1388 m, 1362 m, 1342 m, 1313 s, 1271 m, 1252 s, 1200 m, 1174 s, 1136 vw, 1092 vw, 1030 w, 987 vw, 972 vw, 953 vw, 930 vw, 895 vw, 870 vw, 839 m, 814 w, 781 m, 750 m, 640 vw, 567 m, 544 m, 515 vw, 486 w, 415 w.

[Mn(3,5-dClsalhd)CH_3COO] (**6**), carboxylate-*N*,*N*′-bis(3,5-di-chlorosalicylidene)-1,2-cyclohexanodiaminato]manganese(III): $MnC_{22}H_{19}N_2O_4Cl_4$. FAB-HRMS, *m*/*z*: calculated ($[MnC_{20}H_{16}N_2O_2Cl_4\text{–}CH_3COO]^+$) 512.9317, experimental 512.9320. UV–Vis, λ_{max}/nm: 227, ~273(sh), ~346(sh), 419, ~472(sh), ~612(sh). FTIR, ν/cm^{-1}: 1626 vs, 1589 w, 1529 s, 1439 s, 1410 m, 1385 m, 1342 w, 1317 m, 1286 w, 1223 w, 1209 w, 1180 m, 1107 vw, 1022 w, 966 vw, 922 vw, 870 w, 823 w, 769 m, 750 m, 723 vw, 667 vw, 654 vw, 611 vw, 582 vw, 548 m, 438 w.

Physical measurements

^{1}H NMR spectra were recorded with a Bruker AC 200 spectrometer at 397 K, using tetramethylsilane as internal reference. FTIR spectra were obtained as KBr pellets in a Biorad FTS 155 in the range 400–4000 cm^{-1}, and ultraviolet diffuse reflectance spectra on a Shimadzu UV-3101 PC in the range 1600–200 nm and using barium sulfate as reference.

FAB-HRMS and IE-HRMS were performed at 'Unidade de Espectometría de Masas', Universidade de Santiago de Compostela (Spain).

Gas chromatography experiments (GC) were performed with a Varian Star 3400CX chromatograph equipped with a TCD detector and using helium as carrier gas and a fused silica Varian Chrompack capillary column CP-Sil 8CB (30 m × 0.53 mm id; 1.50 μm film thickness). The chromatographic conditions were: 60 °C (3 min), 5 °C min^{-1}, 170 °C (2 min), 20 °C min^{-1}, 250 °C (10 min); injector temperature, 200 °C; detector temperature, 270 °C; filament temperature, 290 °C. Aliquots of 0.1 cm^3 were withdrawn from the reaction mixture with a hypodermic syringe, filtered through PP 0.22 μm syringe filters and injected directly into the injector using a 1 μl Hamilton syringe.

Catalysis experiments

The reactions were carried out in CH_2Cl_2 or CH_3CN, at room temperature with constant stirring, and the composition of the reaction medium was 2.50 mmol of styrene, 2.50 mmol of decane or chlorobenzene (internal standard), 0.10 mmol of Mn(III) salen complex (catalyst) and using 6.25 mmol of sodium hypochlorite or iodosylbenzene (oxidant), in 5.00 cm^3 of solvent. When the oxidant was sodium hypochlorite, the solution was buffered to pH 11 ($NaH_2PO_4 + NaHO$), to minimise formation of chlorinated products.[15] For each complex the reaction time for maximum epoxide yield was determined in CH_2Cl_2, by withdrawing periodically 0.1 cm^3 aliquots from the reaction mixture, and this time was used to monitor the efficiency of the catalyst, performing at least two independent experiments in each of the two solvents, CH_2Cl_2 and CH_3CN. The composition of reaction media was determined by GC with styrene, styrene epoxide and benzaldehyde being quantified by the internal standard method (decane in CH_2Cl_2 and chlorobenzene in CH_3CN). All other products detected by GC were designated as *others*. Blank experiments with each oxidant and using the same experimental conditions but without catalyst were also performed.

Results and discussion

Characterisation of the Mn(III) salen complexes

All manganese complexes synthesised are dark brown, as expected for manganese(III) Schiff base complexes,[20] but their solubility is strongly dependent on solvent polarity: complexes **2**, **3** and **5** (Scheme 1) are very soluble in CH_2Cl_2, CH_3CN, dmf and dmso, whereas complexes **1**, **4** and **6** are only moderately soluble in the less polar solvents, although very soluble in dmf and dmso.

HRMS data indicate that the manganese(III) salen complexes have the expected stoichiometry (the diference between the experimental and calculated values are less than 5 ppm). These complexes ionise mainly as $[M - X]^+$, where M represents the manganese(III) salen complex without the axial anion coordinated to the metal centre, and X the axial anion. Low intensity peaks due to traces of dimeric species $[M + M - H]^+$ and $[M + M + X]^+$ are also observed. Formation of traces of these dimeric species in solution is common for manganese(III) salen complexes, and prevents the attainment of acceptable errors (<1%) for elemental analyses.[20,21]

When the energies of the C=N stretching vibration of the ligands are compared with those of their respective manganese(III) complexes, a shift of 4 to 26 cm^{-1} to lower energies is observed in all complexes (Table 1), a consequence of metal binding to the imine nitrogen atoms, sustaining the coordination of the metal to the Schiff base ligands.[21]

The electronic spectra of these compounds are dominated by intense bands in the 200–490 nm region due to: π* (C=N) ← d (charge transfer), π* (C=N) ← π and π* (phenolic oxygen) ← n (intraligand) transitions;[22] but show also several low intensity asymmetric bands (that may appear as shoulders) between 500 and 700 nm assigned to the three allowed *d*–*d* transitions expected for complexes with a square pyramidal geometry, ($d_{x^2-y^2} \leftarrow d_{xz}$), ($d_{yz}$, $d_{x^2-y^2} \leftarrow d_{xy}$) and ($d_{x^2-y^2} \leftarrow d_{z^2}$) (decreasing energy), which may or may not be resolved.[22]

Styrene epoxidation catalysed by Mn(III) salen complexes

The brown colour of solutions containing the Mn(III) salen complex and the substrate was intensified by addition of any oxidant, indicating the formation of oxo-metallic

Table 1 Energy of the C=N vibration of the manganese(III) salen complexes

Complex	ν/cm^{-1}	$\Delta\nu$/cm^{-1} [a]
[Mn(salen)Cl] (**1**)	1624	11
[Mn(saltMe)Cl] (**2**)	1601	26
[Mn(saldPh)Cl] (**3**)	1603	20
[Mn(salhd)Cl] (**4**)	1622	4
[Mn(3,5-dtButsalhd)Cl] (**5**)	1612	18
[Mn(3,5-dClsalhd)CH_3COO] (**6**)	1626	5

[a] Values refer to the difference in energy of the ligand and the respective complex.

intermediates of the catalyst.[6] After complete consumption of the alkene the solution regains its initial colour, suggesting that the catalyst was regenerated.

The reaction profiles at room temperature for the epoxidation of styrene catalysed by the several manganese(III) salen complexes were assessed in CH_2Cl_2, using NaOCl or PhIO as oxygen sources. For the reaction time at which the styrene epoxide yield reaches its maximum, at least duplicate experiments were subsequently performed in CH_2Cl_2 and CH_3CN.

The values of styrene conversion, and the selectivities in styrene epoxide, benzaldehyde, *others*, and styrene epoxide yields for each complex, both in CH_2Cl_2 and CH_3CN and for the reaction time that maximises the epoxide yield in CH_2Cl_2, are collected in Table 2 (NaOCl as oxidant) and in Table 3 (PhIO). Finally, it must be stressed that in all cases with no manganese(III) salen complexes in the reaction media (*blank* experiment), no styrene conversion was observed.

Epoxidation with sodium hypochlorite

Reaction profiles. The styrene epoxidation profiles in CH_2Cl_2 catalysed by the manganese(III) salen complexes and using NaOCl as oxidant are depicted in Fig. 1: (a) styrene conversion, (b) styrene epoxide selectivity, (c) styrene epoxide yield, (d) benzaldehyde selectivity, and (e) selectivity in *others*.

Analysis of Fig. 1 shows that under the conditions used only complexes **5** and **3** convert styrene efficiently. Nevertheless, all the catalysts are selective towards the formation of styrene epoxide, despite formation of by-products such as benzaldehyde and other reaction products (*others*), which have been identified by GC-MS as styrene epoxide derivatives: alcohols and chlorinated products. Formation of the latter deserves an explanation, because the reactions were carried out at pH 11, a value at which the quantity of chlorinated by-products is minimised;[15] these are formed because the oxygen transfer from the oxo-metallic active species to the alkene takes place at the inter-phase of CH_2Cl_2 (containing the organic substrate and the catalyst) with the aqueous NaOCl solution.[23]

With the exception of complexes **5** and **3**, all catalysts show a decrease in styrene epoxide selectivity with reaction time, and a concomitant increase in the amount of benzaldehyde and *others* formed. This behaviour has been attributed to catalyst deactivation[15] through formation of dimeric μ-oxo-Mn(IV) species,[24] which are inactive towards styrene epoxidation.[15,24] The decrease in styrene epoxide selectivity that is observed after a certain reaction time for the less efficient catalysts, **1**, **4**, **2** and **6**, must result from catalyst deactivation that makes the rate of styrene epoxidation smaller than the rate of the parallel reaction of degradation of styrene epoxide into alcohols and chlorinated products.

Catalytic activity. When the reactions are carried out in CH_2Cl_2, styrene conversions were of 91% and 100% using **3** and **5** as catalysts, respectively, whereas for the other complexes ranged between 9 and 38%. In CH_3CN, styrene conversion dropped to 62% for **3** and to 98% for **5**, whereas better conversions (34–45%) were generally obtained with the other complexes.

When the solvent is changed from CH_2Cl_2 to CH_3CN and for all catalysts the styrene epoxide selectivity drops and those of benzaldehyde and *other* by-products increase (Table 2 and

Table 2 Styrene epoxidation with NaOCl catalysed by manganese(III) salen complexes, in CH_2Cl_2 or CH_3CN (average of at least three experiments)

					Selectivity (%)		
Catalyst	Time/h	Solvent	Conversion (%)	Epoxide yield (%)	Epoxide	Benzaldehyde	*Other*
[Mn(salen)Cl] (**1**)	1.5	CH_2Cl_2	34.3 ± 1.0	26.4	77.0 ± 0.6	3.2 ± 0.2	19.8 ± 0.8
		CH_3CN	44.7 ± 0.7	22.5	50.3 ± 0.4	7.8 ± 0.0	41.9 ± 0.4
[Mn(saltMe)Cl] (**2**)	2	CH_2Cl_2	34.7 ± 0.6	32.3	93.1 ± 2.1	5.5 ± 0.3	1.4 ± 1.8
		CH_3CN	45.1 ± 0.2	40.6	90.1 ± 0.9	5.2 ± 0.8	4.7 ± 0.3
[Mn(saldPh)Cl] (**3**)	5	CH_2Cl_2	90.8 ± 0.3	83.9	92.4 ± 0.3	2.2 ± 0.3	5.3 ± 0.0
		CH_3CN	61.5 ± 5.3	51.5	83.8 ± 3.5	5.5 ± 1.1	10.7 ± 2.7
[Mn(salhd)Cl] (**4**)	3	CH_2Cl_2	37.5 ± 1.8	35.2	93.8 ± 1.9	3.3 ± 0.9	2.9 ± 1.2
		CH_3CN	34.2 ± 0.9	21.2	62.1 ± 3.4	15.9 ± 4.5	22.0 ± 6.8
[Mn(3,5-dtButsalhd)Cl] (**5**)	2	CH_2Cl_2	100.0 ± 0.0	95.7	95.7 ± 0.6	1.0 ± 0.4	3.0 ± 1.0
		CH_3CN	98.0 ± 0.9	85.7	87.4 ± 1.0	5.2 ± 1.0	7.2 ± 0.1
[Mn(3,5-dClsalhd)CH_3COO] (**6**)	5	CH_2Cl_2	9.1 ± 0.4	7.8	86.2 ± 0.3	8.3 ± 0.2	5.5 ± 0.1
	2	CH_3CN	37.7 ± 1.8	28.2	74.7 ± 2.1	7.1 ± 0.7	18.2 ± 1.4

Table 3 Styrene epoxidation with PhIO catalysed by manganese(III) salen complexes, in CH_2Cl_2 or CH_3CN (average of at least three experiments)

					Selectivity (%)		
Catalyst	Time/h	Solvent	Conversion (%)	Epoxide yield (%)	Epoxide	Benzaldehyde	*Other*
[Mn(salen)Cl] (**1**)	3	CH_2Cl_2	91.9 ± 0.2	85.7	93.3 ± 0.1	5.1 ± 0.2	1.6 ± 0.1
		CH_3CN	77.9 ± 0.9	71.2	91.4 ± 0.6	7.7 ± 0.4	0.8 ± 0.2
[Mn(saltMe)Cl] (**2**)	2	CH_2Cl_2	100.0 ± 0.0	85.7	85.7 ± 0.5	1.2 ± 0.1	12.9 ± 0.4
		CH_3CN	100.0 ± 0.0	98.3	98.3 ± 1.1	0.1 ± 0.1	1.7 ± 1.0
[Mn(saldPh)Cl] (**3**)	2	CH_2Cl_2	99.3 ± 0.2	87.5	88.1 ± 0.5	3.4 ± 0.1	8.5 ± 0.5
		CH_3CN	100.0 ± 0.0	98.2	98.2 ± 0.3	1.7 ± 0.1	0.2 ± 0.2
[Mn(salhd)Cl] (**4**)	3	CH_2Cl_2	100.0 ± 0.0	86.9	86.9 ± 0.4	2.5 ± 0.0	10.4 ± 0.4
		CH_3CN	93.6 ± 0.2	88.5	94.6 ± 0.1	5.4 ± 0.1	0.0 ± 0.0
[Mn(3,5-dtButsalhd)Cl] (**5**)	2	CH_2Cl_2	61.3 ± 1.1	60.0	97.9 ± 0.8	1.4 ± 0.1	1.3 ± 0.7
		CH_3CN	81.5 ± 2.7	77.3	94.9 ± 0.1	5.1 ± 0.1	0.0 ± 0.0
[Mn(3,5-dClsalhd)CH_3COO] (**6**)	2	CH_2Cl_2	100.0 ± 0.0	95.5	95.5 ± 0.0	2.9 ± 0.2	1.6 ± 0.3
		CH_3CN	98.3 ± 0.1	94.7	96.3 ± 0.0	3.1 ± 0.6	0.6 ± 0.6

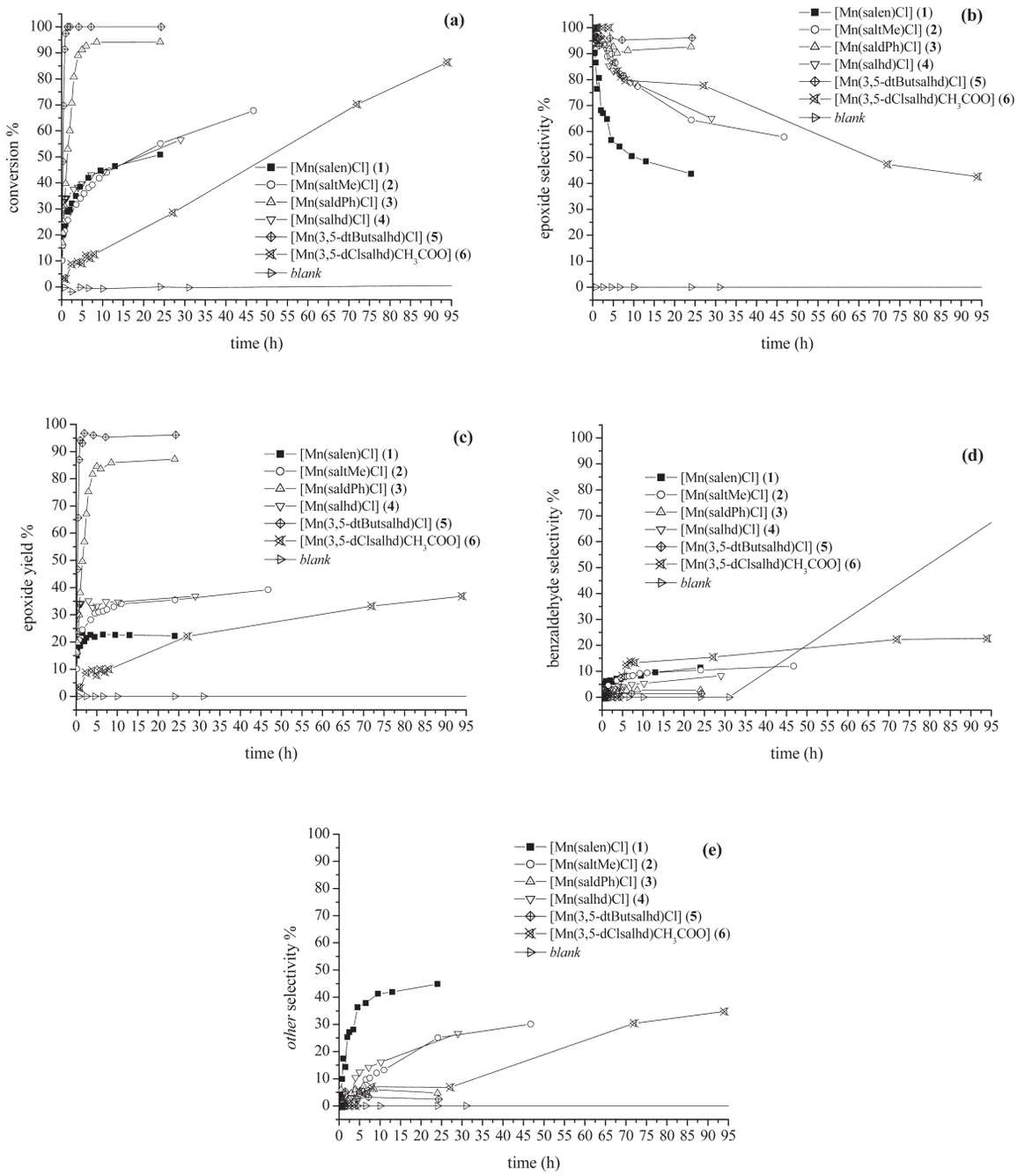


Fig. 1 Reaction profiles of the styrene epoxidation with NaOCl catalysed by Mn(III) salen complexes in CH_2Cl_2, at room temperature: (a) styrene conversion, (b) styrene epoxide selectivity, (c) styrene epoxide yield, (d) benzaldehyde selectivity and (e) *others* selectivity.

Fig. 2). These results may be attributed to the larger miscibility between CH_3CN and the sodium hypochlorite aqueous solution, leading to more extensive hydrolysis of the styrene epoxide and formation of chlorinated by-products. In summary, the use of NaOCl as oxygen source in CH_2Cl_2 led to lower yields of by-products and, for the better catalysts, to larger styrene conversions than in CH_3CN.

Epoxidation with iodosylbenzene

Reaction profiles. Analysis of the styrene epoxidation profiles in CH_2Cl_2 catalysed by the manganese(III) salen complexes when PhIO is the oxidant (Fig. 3) show that in contrast with the results obtained with NaOCl as oxidant, all complexes are very efficient catalysts in the conversion of styrene and present very high selectivities in styrene epoxide.

Despite the high styrene epoxide selectivities obtained with PhIO, which do not decrease so drastically with reaction time as when NaOCl is used as the oxygen source, formation of benzaldehyde and of other by-products, although different from those of the reaction with NaOCl, is also observed.

Kochi *et al.* have shown that the by-products of alkene epoxidation with PhIO are mostly formed during the course of epoxidation and are not due to subsequent rearrangements of the styrene epoxide.[5] In fact, these authors noted that addition of PhIO to a solution of complex **1** in CH_2Cl_2 with *no* alkene present led to an increase of intensity of the brown colour of the solution, taken as an indication of formation of oxometallic species, and to catalytic conversion of iodosylbenzene to iodobenzene;[5] the other reaction products formed must thus be degradation products from PhIO. These observations imply that in the present study neither benzaldehyde nor the other by-products originate from reactions of styrene epoxide, but from degradation reactions of PhIO that take place in parallel to styrene epoxidation. Furthermore, in blank experiments (no catalyst) no iodobenzene was detected in the reaction media.

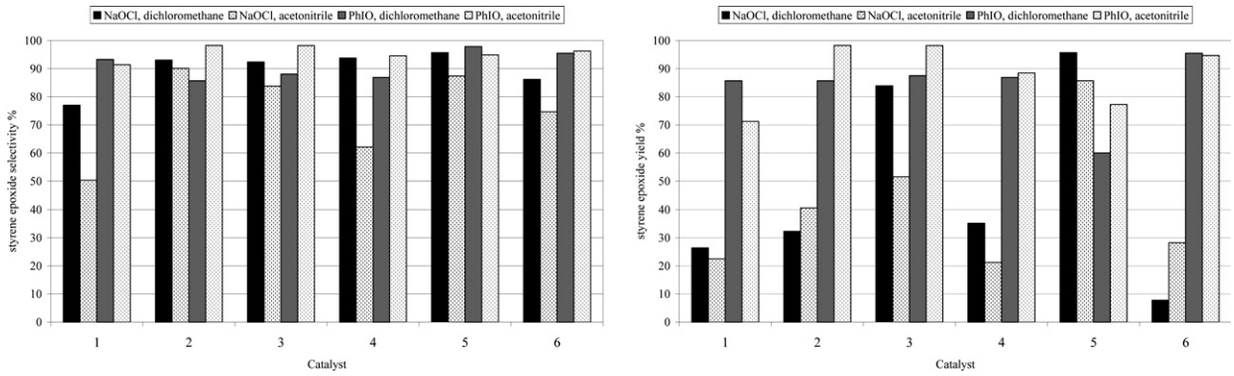


Fig. 2 Styrene epoxide selectivity and % yield with NaOCl or PhIO of the Mn(III) salen catalysts in CH_2Cl_2 or CH_3CN.

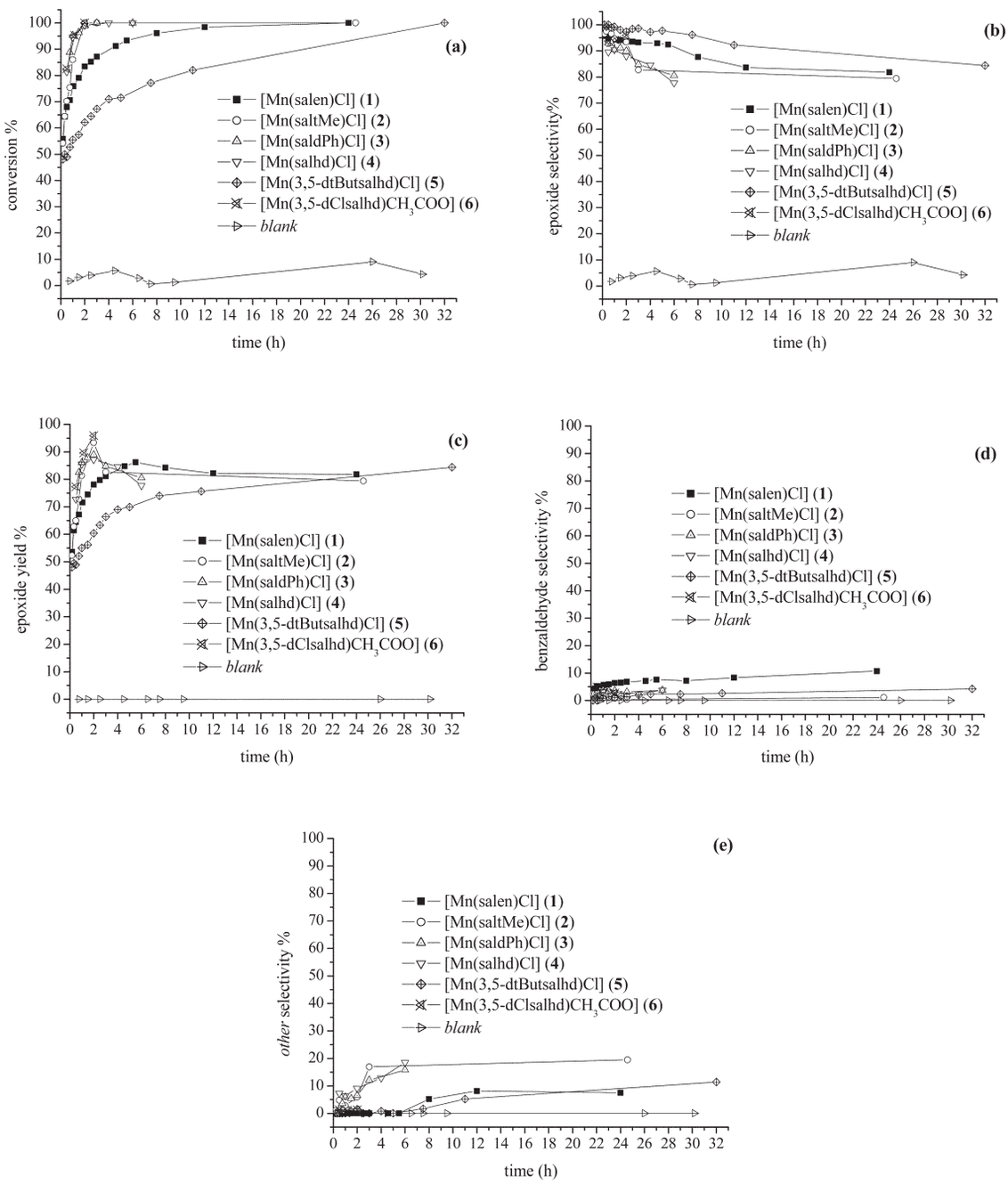


Fig. 3 Reaction profiles of the styrene epoxidation with PhIO catalysed by Mn(III) salen complexes in CH_2Cl_2, at room temperature: (a) styrene conversion, (b) styrene epoxide selectivity, (c) styrene epoxide yield, (d) benzaldehyde selectivity and (e) *others* selectivity.

The catalytic activity of the manganese(III) salen complexes in the decomposition of iodosylbenzene to iodobenzene, and despite of the rate of oxygen transfer from the oxo-metallic intermediate species to the alkene being higher than the rate of homolytic degradation of the oxidant, requires the use of excess PhIO to obtain 100% conversion of styrene.[12]

Catalytic activity. From Table 3 it can be gathered that in CH_2Cl_2, with the sole exception of complex **5**, which converts 61% of styrene, the other catalysts exhibit styrene conversions between 92 and 100% after 2–3 hours of reaction; in CH_3CN conversions range between 78 and 100% (Table 3).

The selectivity in styrene epoxide is high both in CH_2Cl_2 and in CH_3CN, with a general tendency to be larger in CH_3CN (Table 3 and Fig. 3). The selectivity in *others* is lower than those obtained when the oxygen source is NaOCl, and is smaller in CH_3CN, in contrast to what is observed using NaOCl as oxidant.

As can be seen from Fig. 2, with the exception of **5**, larger styrene epoxide yields and selectivities are obtained using PhIO as oxidant than with NaOCl, which may be correlated with the facile deactivation of the manganese(III) salen complexes using the sodium hypochlorite aqueous solutions as oxidant. Moreover, the use of PhIO as oxidant lowers the quantities of other by-products, mainly because no styrene epoxide degradation products are observed (*i.e.* alcohols and chlorinated products).

Effect of the diimine bridge substituents

Next the catalytic activities of the manganese(III) salen complexes derived from the same aldehyde fragment but with different diimine bridges are going to be compared. Using NaOCl, the styrene epoxide yield for the manganese(III) salen complexes increases in following order: in CH_2Cl_2, $\mathbf{1} < \mathbf{2} < \mathbf{4} < < \mathbf{3}$; in acetonitrile, $\mathbf{1} \sim \mathbf{4} < \mathbf{2} < \mathbf{3}$.

With PhIO, the yields in styrene epoxide for the manganese(III) salen complexes in CH_2Cl_2 are insensitive to the presence of substituents in the diimine bridge, whereas in CH_3CN they increase in following order: $\mathbf{1} < \mathbf{4} < \mathbf{2} \sim \mathbf{3}$.

Under all experimental conditions used, **3** is always one of the most efficient catalyst in the epoxidation of styrene and **1** is among the less efficient. With the exception of using PhIO in CH_2Cl_2, the introduction of methyl or other bulky groups in the diimine bridge improves epoxide yield (Scheme 1, Fig. 2), implying that steric modulation may be involved in the activity of the manganese catalysts, as has been claimed in the literature.[5] This observation deserves further elaboration, as the accepted mechanism for the catalytic role of the "[Mn(salen)Cl]" complexes involves the formation of an adduct with the oxidant and the presence of bulky substituents would pose a steric barrier to its formation. However, the conclusions of a recent computational study on oxomanganese(V)-salen complexes suggest that a side-on approach of the olefin might more favourably occur from the salicylaldehyde ring than from the imine portion.[25] The existence of bulky groups on the ethylene bridge would force the M=O bond to bend away from the bridge, thus easing the approach of the olefin in the proposed pathway. Nevertheless, a possible role of bulky groups in diimine bridge in stabilising the manganese(III) salen complexes cannot be ruled out, as it would reduce catalyst desactivation, and thus result in higher catalyst efficiency.

Effect of substituents in the aldehyde fragment

The effect of substituents in the aldehyde moiety can be judged by comparing the catalytic behaviour of the complexes that share the same diimine bridge.

Using PhIO as oxygen source, the styrene epoxide yields for the different "[Mn(salhd)X]" type complexes used as catalysts follow the order: $\mathbf{5} < \mathbf{4} < \mathbf{6}$, either in CH_2Cl_2 or in CH_3CN (Fig. 3 and Table 3). The introduction of electron withdrawing groups (chloro) in the 3 and 5 positions of the aldehyde fragment of the Schiff base (Scheme 1) increases always the styrene epoxide yield, while the introduction of electron donating substituents (*tert*-butyl) decreases this yield. These results are in agreement with the studies of the epoxidation of alkenes with PhIO catalysed by manganese(III) salen complexes reported by Kochi *et al.*, in which they concluded that the introduction of electron withdrawing groups (chloro and nitro) in the 5 positions of the aldehyde fragment of the Schiff base makes the corresponding manganese(III) salen complexes more efficient catalysts.[5] In this system [O=Mn(V)salenCl] was identified directly by mass spectrometry[7] and indirectly by nuclear magnetic resonance[8] as being the active oxidant species of the catalyst. The introduction of electron withdrawing groups in position 5 of the aldehyde fragment destabilises the [O=Mn(V)salenCl] species, making it more reactive, hence increasing the catalytic activity of the complex.

When NaOCl is used as oxygen source, and in contrast with what is observed with PhIO as oxidant, the order of styrene epoxide yield obtained with the "[Mn(salhd)X]" catalysts is solvent dependent; in CH_2Cl_2 the order is $\mathbf{6} < \mathbf{4} \ll \mathbf{5}$, whereas in CH_3CN is $\mathbf{4} < \mathbf{6} \ll \mathbf{5}$ (Fig. 1 and Table 2). But more striking is the observation that the introduction of electron donating groups (*tert*-butyl) in the 3 and 5 positions of the aldehyde fragment of the Schiff base increases in both solvents significantly the yield in styrene epoxide (Scheme 1). On the other hand, the introduction of electron withdrawing groups (chloro) decreases this yield, although only in CH_2Cl_2.

It has been demonstrated that the introduction of substituents in the 3 and 5 positions of the aldehyde fragment (Scheme 1) might have direct interactions in the electronic properties of the manganese(III) salen complexes, although the 3 position has been reported to be associated with stereochemical effects.[6,26] Electrochemical studies of the Mn(II)/Mn(III) process of manganese(III) salen complexes have shown that the oxidised species are stabilised by the introduction of electron donating substituents in the 5 position of the aldehyde fragment (Scheme 1), and destabilised by electron withdrawing groups in the same position, and the same effects have been assumed to be operative in the reactive intermediate species.[6,27] These observations may be used to support the results obtained in the present study with the PhIO, but fails to explain the results obtained with NaOCl.

Adam *et al.*[2] in an elegant study have proposed recently, based on the *cis*/*trans* ratios obtained for the epoxidation of *cis*-stilbene, that the mechanism by which epoxidation of alkenes catalysed by manganese(III) salen complexes takes place might involve two different active intermediate species: (i) an active [L–O–Mn(III)salenCl] species, where L represents the leaving group of the oxidant, that transfers the oxygen to the alkene by a concerted step, and that was found to be mainly associated with sodium hypochlorite as oxygen source; and (ii) and active [O=Mn(V)salenCl] species, that transfers the oxygen to the alkene by a stepwise radical mechanism, and that was observed with iodosylbenzene.

Data in Fig. 1 suggest that electron donating groups accelerate the reaction when the oxidant is NaOCl, what may be taken as indirect evidence to support the concerted mechanism involving [L–O–Mn(III)salenCl], as these groups would ease the cleavage of the O–L bond (L is cleaved as an anion). The opposite behaviour is observed in CH_2Cl_2 when electron withdrawing groups are present, as the O–L bond would be more difficult to cleave. However, in CH_3CN the presence of electron withdrawing groups does not make the complex a worse catalyst.

Nevertheless, our data seem to suggest the existence of the two mechanisms outlined above: a concerted mechanism (i) with NaOCl, and a stepwise radical mechanism (ii) with PhIO. The anomalous behaviour in CH_3CN when NaOCl is the

oxidant may reside in the simplification of picture outlined above, since the concerted mechanism requires simultaneous O–C bond formation, which can make the prediction of electronic effects a difficult task but, on the other hand, may also be related to the solubility of the complexes.

In fact, we recall that the oxygen transfer takes place at the water/organic solvent interphase,[23] and that the catalyst must exist in the latter. By noting that complex **5** is completely soluble in CH_2Cl_2 and in CH_3CN, whereas complexes **4** and **6** are only partially soluble (at least for the concentrations used in this study), and that the latter is roughly ten times less soluble than **4**, it is also possible to correlate epoxide yield with solubility in CH_2Cl_2. The lack of such a correlation in CH_3CN results probably from a subtle balance between solubility, electronic effects and counter-ion. The large solubility, and the presence of electron donating groups in conjunction with a concerted mechanism, may explain why the Jacobsen catalyst is so effective with NaOCl.

Conclusions

The manganese(III) salen complexes studied present high chemoselectivities as homogeneous catalysts in the epoxidation of styrene at room temperature, whether using iodosylbenzene or sodium hypochlorite as oxygen sources. The styrene epoxide chemoselectivities decrease with reaction time due to the deactivation of the manganese(III) complexes, which is more evident when sodium hypochlorite is used as oxidant. With the latter, significant quantities of styrene epoxide degradation by-products are obtained due to the aqueous–organic biphasic system. This degradation can also account for the larger styrene epoxide yields that are obtained with iodosylbenzene as oxygen source (60–98%) than with sodium hypochlorite (8–96%).

It was possible to tune the catalytic activities of "[Mn(salen)X]" complexes by introduction of substituents in the diimine bridge and in the aldehyde fragment. The presence of bulky substituents in the diimine bridge always increases the catalytic activity of these complexes, regardless of the oxidant, thus suggesting steric tuning. However, the electronic tuning of the catalytic activity by introducing substituents in the 5 and 3 positions of the aldehyde fragment (Scheme 1) has different effects depending on the oxygen source. For the one-phase system resulting from the use of PhIO, electron withdrawing groups increase (and electron donating groups decrease) the catalytic activity of the complexes, which probably results from destabilisation (stabilisation) of [O=Mn(V)(salen)X], the identified active species,[7,8] making them more (less) reactive.

However, when NaOCl is used the observed behaviour is the opposite: electron donating groups make the complexes better catalysts. This may support the concerted mechanism proposed by Adam *et al.*[2] in which the existence electron donating groups in the active [L–O–Mn(III)salenCl] species would make the release of the L group easier. On the other hand, the apparent similarity between the solubility of the complexes in the organic solvent and their catalytic activity seems to suggest that their solubility may also play an important role in their activity. Since the structure of the manganese(III) salen complexes can be easily tuned, we are pursuing their study in order to gain further insights on the relation between the effects of different substituents in the aldehyde moieties of manganese(III) salen complexes on catalytic efficiency and on their solubility (when NaOCl is the oxygen source).

Acknowledgements

ARS thanks the Fundação para a Ciência e Tecnologia (Lisboa) and the European Social Fund for a fellowship. This work was financed by FCT and FEDER through Proj. no. POCTI/QUI/42931/2001.

References

1 C. T. Dalton, K. M. Ryan, V. M. Wall, C. Bousquet and D. G. Gilheany, *Top. Catal.*, 1998, **5**, 75.
2 W. Adam, K. J. Roschmann, C. R. Saha-Möller and D. Seebach, *J. Am. Chem. Soc.*, 2002, **124**, 5068.
3 T. Katsuki, *J. Mol. Catal. A: Chem.*, 1996, **113**, 87; T. Katsuki, *Coord. Chem. Rev.*, 1995, **140**, 189.
4 H. Yoon, T. R. Wagler, K. J. O'Connor and C. J. Burrows, *J. Am. Chem. Soc.*, 1990, **112**, 4568.
5 K. Srinivasan, P. Michaud and J. K. Kochi, *J. Am. Chem. Soc.*, 1986, **108**, 2309.
6 E. N. Jacobsen and M. H. Wu, in *Comprehensive Asymmetric Catalysis*, eds. A. Pfaltz, E. N. Jacobsen and H. Yamamoto, vol.2, Springer-Verlag, Berlin, 1999, p. 649.
7 D. Feichtinger and D. A. Plattner, *Angew. Chem., Int. Ed.*, 1997, **36**, 1718.
8 K. P. Bryliakov, D. E. Babushin and E. P. Talsi, *J. Mol. Catal. A: Chem.*, 2000, **158**, 19.
9 K. A. Campbell, M. R. Lashley, J. K. Wyatt, M. H. Nantz and R. D. Britt, *J. Am. Chem. Soc.*, 2001, **123**, 5710.
10 X.-D. Du and X.-D. Yu, *J. Mol. Catal. A: Chem.*, 1997, **126**, 109.
11 A. R. Silva, C. Freire, B. de Castro, M. M. A. Freitas and J. L. Figueiredo, *Microporous Mesoporous Mater.*, 2001, **46**, 211; A. R. Silva, M. Martins, M. M. A. Freitas, A. Valente, C. Freire, B. de Castro and J. L. Figueiredo, *Microporous Mesoporous Mater.*, 2002, **55**, 275; A. R. Silva, C. Freire, B. de Castro, M. M. A. Freitas and J. L. Figueiredo, *Langmuir*, 2002, **18**, 8017; A. R. Silva, M. Martins, M. M. A. Freitas, C. Freire, B. de Castro and J. L. Figueiredo, submitted.
12 A. R. Silva, Ph. D. Thesis, Faculdade de Ciências, Universidade do Porto, 2002.
13 A. R. Silva, J. Vital, C. Freire, B. de Castro and J. L. Figueiredo, *New J. Chem.*, 2003, **27**, 1511; A. R. Silva, C. Freire, B. de Castro and J. L. Figueiredo, *Microporous Mesoporous Mater.*, in press.
14 M. Palucki, P. J. Pospisil, W. Zhang and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1994, **116**, 9333.
15 W. Zhang and E. N. Jacobsen, *J. Org. Chem.*, 1991, **56**, 2296.
16 R. Sayre, *J. Am. Chem. Soc.*, 1955, **77**, 6689.
17 P. Piaggio, P. McMorn, D. Murphy, D. Bethell, P. C. Bulman Page, F. E. Hancock, C. Sly, O. J. Kerton and G. J. Hutchings, *J. Chem. Soc., Perkin Trans. 2*, 2000, 2008.
18 H. Holm, G. W. E. Everett Jr. and A. Chakravorty, *Prog. Inorg. Chem.*, 1966, **7**, 83.
19 M. Calligaris and L. Randaccio, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, vol. 2, Pergamon Press, Oxford, 1987, and references therein.
20 B. Chiswell, E. D. McKenzie and L. F. Lindoy, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, vol. 6, PergamonPress, Oxford, 1987.
21 M. R. Bermejo, A. Castiñeiras, J. C. Garcia-Monteagudo, M. Rey, A. Sousa, M. Watkinson, C. A. McAuliffe, R. G. Pritchard and R. L. Beddoes, *J. Chem. Soc., Dalton Trans.*, 1996, 2935.
22 L. J. Boucher and M. O. Farrell, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3731.
23 D. L. Hughes, C. B. Smith, J. Liu, G. C. Dezeny, C. H. Senanayake, R. D. Larsen, T. R. Verhoeven and P. J. Reider, *J. Org. Chem.*, 1997, **62**, 2222.
24 D. L. Canali and D. C. S. Sherrington, *Chem. Soc. Rev.*, 1999, **28**, 85.
25 J. El-Bahraoui, O. Wiest, D. Feichtinger and D. A. Plattner, *Angew. Chem., Int. Ed.*, 2001, **40**, 2073.
26 H. Jacobsen and L. Cavallo, *Chem. Eur. J.*, 2001, **7**, 800.
27 M. Palucki, N. S. Finney, P. J. Pospisil, M. L. Güller, T. Ishida and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1998, **120**, 948.