Oxygen transfer to manganese–salen complexes: an electrospray tandem mass spectrometric study

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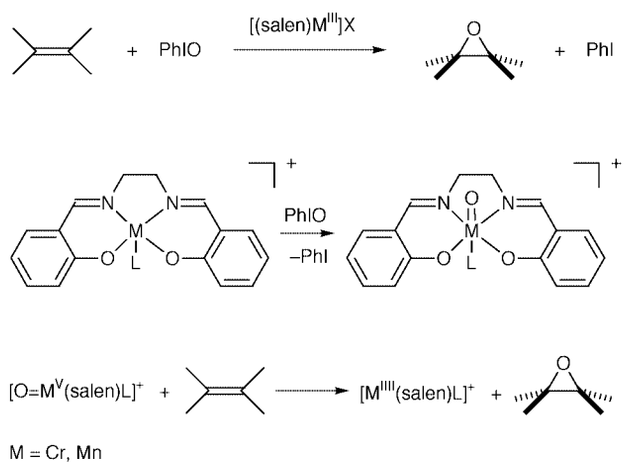
Electrospray ionisation in combination with tandem mass spectrometric techniques has been employed to study the formation of oxomanganese–salen complexes upon oxidation of $[(salen)Mn^{III}]^+$ salts with iodosylbenzene [H_2salen = *N*,*N*′-bis(saliclyidene)ethylenediamine]. Two species were characterised as the principal oxidation products: the oxomanganese(v) complex $[(salen)Mn{=}O]^+$, the actual oxygen-transfer agent in epoxidation reactions, and the dimeric, μ-oxo bridged $[PhIO(salen)Mn–O–Mn(salen)OIPh]^{2+}$ with two terminal iodosylbenzene ligands, which acts as a reservoir species. For the first time, the coordination chemistry of iodosylbenzene with regard to the manganese–salen system was studied in detail. In addition, the mechanism of oxygen transfer by PhIO to the metal centre was studied by collision-induced dissociation (CID) of $[(salen)MnOIPh]^+$. An alternative way to generate oxomanganese–salen complexes was found in the ligation of tertiary amine *N*-oxides to the manganese centre and subsequent fission of the N–O bond in the gas phase by CID. The electrospray-MS technique presents a convenient approach for the study of the coordination chemistry of highly reactive solution-phase species.

Introduction

The transition metal-catalysed oxidation of various organic substrates is of utmost importance in synthetic applications as well as in biochemical transformations.[1,2] The bulk of reactions involving direct oxygen transfer to the organic substrate is accomplished by reactive intermediates bearing a metal–oxo moiety. The paradigmatic system for oxidative transformations in biological systems is the enzyme cytochrome P-450.[3–6] For synthetic purposes, metal–salen complexes (H_2salen = *N*,*N*′-bis(salicylidene)ethylenediamine), which can be viewed as simplified synthetic models of the porphyrin analogs, were introduced by Kochi and co-workers as versatile epoxidation catalysts in the 1980's.[7–11] A breakthrough was achieved in the field of enantioselective epoxidation through the introduction of chiral manganese–salen catalysts by Jacobsen and co-workers,[12] with a closely related but somewhat less effective system by Katsuki and co-workers developed at about the same time.[13] The Jacobsen–Katsuki reaction is now recognised as one of the most useful and widely applicable methods for the epoxidation of non-functionalised olefins.[14,15]

The mechanistic scheme adopted for oxygen transfer to organic substrates by salen complexes is based on the isolation and characterisation of the oxochromium(v) species by Kochi and co-workers (Scheme 1).[7,9] The (salen)Cr–oxo complex was prepared by oxidation of the chromium(III) precursor with PhIO, isolated, and shown to be capable of epoxidising alkenes under stoichiometric and catalytic conditions.[8] This result was in accordance with the properties and reactivity of an analogous oxoporphinatochromium(v) complex studied earlier by Groves and Kruper.[16] The metal–oxo species in these reactions are acting as a staging post for oxygen transfer, which is why the mechanism was termed "oxygen-rebound". The chromium complexes were useful for mechanistic studies, but their utility as epoxidation catalysts is limited to electron-rich olefins. Switching to manganese as the metal centre, Kochi and co-workers established a much more versatile salen-based oxidation catalyst.[10,11] However, mechanistic studies on these systems have so far been hampered by the fact that the catalytically active oxomanganese species appear only as fleeting putative intermediates.



Scheme 1 The mechanism of alkene epoxidation catalysed by chromium(III)– and manganese(III)–salen complexes.

In view of the fact that oxygen transfers are so common and important in nature and chemical synthesis it may seem surprising that our knowledge of the detailed mechanisms of these reactions leaves so much to be desired. Two factors are mainly responsible for the lack of mechanistic insights: (i) oxygen transfer to the transition metal by dioxygen or some oxygen atom donor can yield several different species with quite diverse reactivities; (ii) the transient nature of the catalytically active species. Both problems can easily be overcome by transfer of the metal–oxo complexes to the gas phase. By mass selection, the species of interest can be singled out and studied separately without interference by additional complexes present in solution. The reactivity of the crucial intermediates can be monitored by directed collision with an appropriate substrate; otherwise their short solution-phase lifetimes do not pose a problem due to high-vacuum conditions.

Electrospray ionisation provides a powerful tool for the transfer of medium-to-large molecular ions to the gas phase with minimum fragmentation.[17–19] Only in the last few years has electrospray mass spectrometry been widely used for analytical

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purposes in the area of inorganic/organometallic chemistry,[20,21] but so far it has not been coupled systematically[22] with the broad range of ion–molecule reaction techniques which have been exploited for mechanistic work on gas-phase transition-metal and small organometallic ions, respectively.[23] Our group has recently demonstrated the usefulness of electrospray-tandem-mass spectrometry for mechanistic and thermochemical analysis in organometallic chemistry in accounts on the C–H activation by $[CpIr(PMe_3)(CH_3)]^+$,[24] oxo-transfer reactions by $[O{=}Mn^V(salen)]^+$,[25] gas-phase olefin oligomerisation by "naked" alkylzirconocene cations,[26] olefin metathesis by $[Cl_2Ru(=CHPh)(Cy_2PCH_2CH_2NMe_3)]^+$,[27] reversible hydrogenation/dehydrogenation of olefins by $[Rh(PMe_3)_2]^+$ ions,[28] and olefin polymerisation by Brookhart-type palladium(II) catalysts.[29]

Our complete lack of knowledge about the mechanism of oxygen transfer to the manganese–salen complex and the exact nature and reactivity of the catalyst's active form is mainly due to the inherent reactivity of the catalyst in solution. Many open questions concerning the mechanism of the catalytic oxidation can be addressed in a unique way by using electrospray tandem mass spectrometry. In this report, we focused our studies on two basic questions: (i) how is the oxygen transfer to the metal centre achieved; and (ii) what are the species produced upon oxidation under typical reaction conditions. We present a systematic study of oxygen transfer from iodosylbenzene, the oxygen transfer reagent commonly used in solution-phase chemistry, to manganese(III)–salen complexes and of the high-valent oxomanganese–salen complexes formed in this process that are the catalytically active species in the Kochi–Jacobsen–Katsuki epoxidation.

Experimental

Chemicals

(Diacetoxyiodo)benzene and pyridine *N*-oxide were purchased from Aldrich and Fluka, respectively, acetonitrile (HPLC grade quality) for the preparation of the electrospray solutions from Fluka and H_2salen from Fluka and used as received. Iodosylbenzene was prepared from (diacetoxyiodo)benzene following the procedure of Saltzman and Sharefkin.[30]

Synthesis of manganese(III)–salen salts

Manganese(III) salen chloride Mn(salen)Cl was prepared following the procedure of Zhang and Jacobsen.[31] Acetonitrile solutions of the chloride were treated with an equimolar amount of silver perchlorate and stirred for 15 minutes. After removal of AgCl by filtration the solution was diluted to 10^{-5} M.

Synthesis of *para*-substituted dimethylaniline *N*-oxides

p-Cyano-*N*,*N*-dimethylaniline *N*-oxide was prepared according to the procedure of Cymerman Craig and Purushothaman[32] by MCPBA oxidation of the respective *N*,*N*-dimethylaniline (bought and used as received from Fluka). All *N*-oxide spectra matched the analytical data given in the literature. For the experiments with amine *N*-oxide as terminal ligand it was used at a concentration of 10^{-4} M. Solutions containing μ-oxomanganese–salen complexes were prepared by adding stock solutions (10^{-3} M) of the terminal ligands to a suspension of iodosylbenzene in acetonitrile, and then adding the manganese(III) salen salts just prior to data acquisition.

Instrumentation

For the mass spectrometric measurements the slightly modified Finnigan MAT TSQ7000 electrospray tandem mass spectrometer described previously[24] (octopole, quadrupole, octopole, quadrupole set-up) was used. The first octopole was fitted with an open cylindrical sheath around the rods into which a collision gas could be bled up to 20 mTorr for thermalisation. In the collision-induced dissociation (CID) experiments, argon was used as target gas in the second octopole at pressures ranging from 0.4 to 1.5 mTorr. According to an estimation based on a hard-sphere model, this corresponds to 4 to 15 collisions.

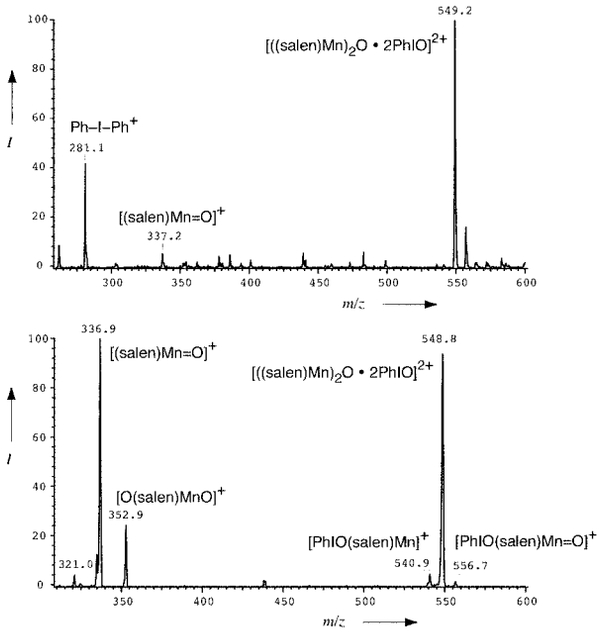

Fig. 1 Top: electrospray mass spectrum of an acetonitrile solution of $[(salen)Mn]ClO_4$ and iodosylbenzene. Bottom: daughter-ion spectrum (0.4 mTorr Ar, collision energy 54 eV) of $[PhIO(salen)Mn–O–Mn(salen)OIPh]^{2+}$ (m/z = 549).

General ESMS set-up for the experiments

All CID measurements were carried out in daughter-ion mode, *i.e.* the first quadrupole is used to mass select ions of a single mass, which are then collided with a target gas in the second octopole. The second quadrupole is operated in scanning mode and serves to detect the ionic fragments. The collision energy can be varied by applying different potentials (to a lens in front of the second octopole) which serves to alter the velocity of the ions on their way into the collision region (the collision energies are given in eV, laboratory frame). The incoming ions were thermalised in the first octopole with argon at a pressure of ≈10 mTorr and at a temperature of 70 °C. The tube lens was typically operated at 70 V (referenced to m/z = 500).

Results and discussion

μ-Oxomanganese(IV) dimers

Previously, we reported on the detection of oxomanganese(V) complexes by electrospray of *in situ* mixtures of Mn^{III}(salen) and suitable oxygen transferring agents, *e.g.* iodosylbenzene.[25] The oxidised species most prominent in the spectrum (Fig. 1 top) are the parent oxo complex $[O{=}Mn^V(salen)]^+$ (m/z = 337) and the μ-oxo bridged dimer with two terminal PhIO ligands $[PhIO(salen)Mn–O–Mn(salen)OIPh]^{2+}$ (m/z = 549). The coordination of iodosylbenzene to manganese finds a precedent in the field of Mn–porphyrin chemistry. Hill and co-workers found that oxidation of a (tetraphenylporphinato)-manganese complex with PhIO leads to the formation of a dimeric species containing one iodosylbenzene molecule per Mn atom.[33] By analogy to the corresponding dimer with terminal azido ligands,[34] an antiferromagnetically coupled dimeric μ-oxomanganese(IV) structure was assumed (Fig. 2). In the case of the (salen)Mn catalysed epoxidation, Kochi and

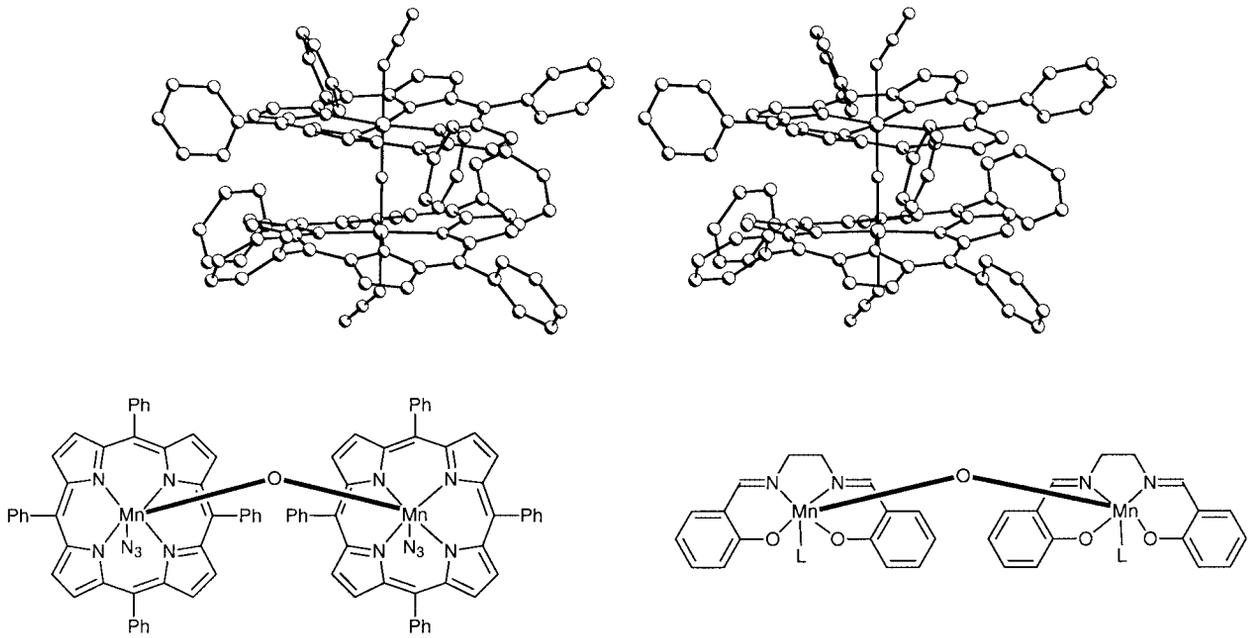

Fig. 2 Top: stereo plot of the structure of N_3(TPP)Mn–O–Mn(TPP)N_3 in the solid state.[34] Bottom: structures of the dimeric, μ-oxo bridged manganese–TPP and manganese–salen complexes, respectively.

co-workers identified a transient species with $\lambda_{max} \approx 530$ nm and with a half-life of approximately 4 min at 25 °C.[10] The analysis of the decay of this absorption band clearly showed that the principal mode of decomposition is not dependent on the olefin. Therefore, this transient species cannot be the reactive intermediate which is directly responsible for oxygen transfer to the substrate. Based on Hill's results, Kochi assigned a dimeric μ-oxomanganese(IV) structure $[(salen)Mn–O–Mn(salen)]^{2+}$ to this transient, whose formation was attributed to a coupling of the putative reactive species $[O=Mn^{V}(salen)]^{+}$ with $[(salen)Mn^{III}]^{+}$ (eqn. (1)). If disproportionation of the manganese(IV)

$$[O=Mn^{V}(salen)]^{+} + [Mn^{III}(salen)]^{+} \rightleftharpoons [(salen)Mn^{IV}–O–Mn^{IV}(salen)]^{2+} \quad (1)$$

dimer were to be relatively slow, it would be the rate-limiting step in the overall epoxidation kinetics and thus explain the zero-order dependence of the decay rate, owing to the rapid subsequent reaction of the oxygen transferring species with the substrate.

The detection of $[PhIO(salen)Mn–O–Mn(salen)OIPh]^{2+}$ in our electrospray experiments is the first direct evidence for the conproportionation of Mn^{III} and Mn^{V}–oxo species as the mechanism for parking the catalytically active complex in a more persistent form. The microscopic reverse process of eqn. (1), the disproportionation of the μ-oxo bridged dimer, leads to the release of the active $[O=Mn^{V}(salen)]^{+}$. This reaction can be triggered by collision with argon in the gas phase, thus providing a structural proof for the parent dication as well as for the putative reactive oxomanganese(V) cation. The daughter-ion experiment with $[PhIO(salen)Mn–O–Mn(salen)OIPh]^{2+}$ ($m/z = 549$, collision with Ar at 54 eV) gives the expected disproportionation products $[PhIO(salen)Mn^{III}]^{+}$ ($m/z = 541$) and $[PhIO(salen)Mn^{V}=O]^{+}$ ($m/z = 557$), thus suggesting the presence of the μ-oxo bridge in the parent and a terminal Mn–oxo functionality in the daughter ion (Fig. 1 bottom). The two primary daughter ions formed by collisional activation immediately fragment further, leading to quite a complex product pattern. This provoked us to study in detail the properties of iodosylbenzene as a ligand and the mechanism of oxygen transfer to the metal center. By carefully adjusting the tube lens potential in the electrospray source we were able to generate the complexes $[(salen)Mn^{III}\cdot PhIO]^{+}$ and

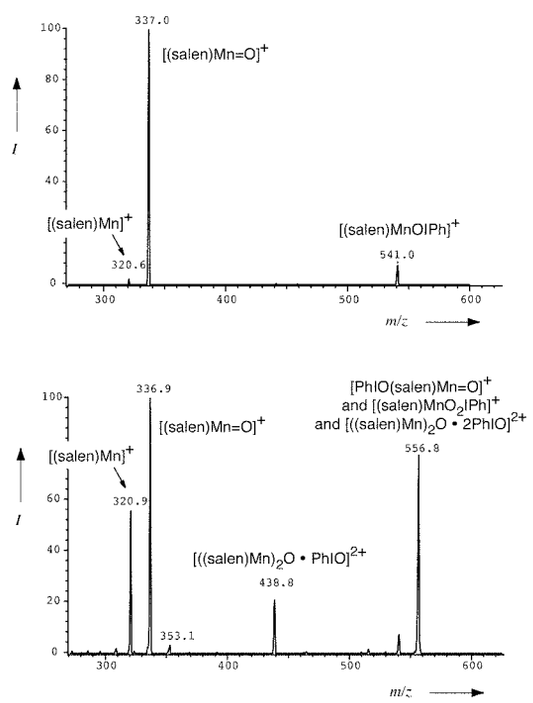

Fig. 3 Top: daughter-ion spectrum (0.4 mTorr Ar, collision energy 17 eV) of $[(PhIO)Mn^{III}(salen)]^{+}$ ($m/z = 541$), showing the predominant loss of PhI and formation of $[(salen)Mn=O]^{+}$ ($m/z = 337$). Bottom: daughter-ion spectrum (0.4 mTorr Ar, collision energy 27 eV) of the species with $m/z = 557$.

$[O=Mn^{V}(salen)\cdot PhIO]^{+}$ in high enough yields to conduct MS/MS experiments. The daughter-ion spectrum of $[PhIO(salen)Mn^{III}]^{+}$ ($m/z = 541$, collision gas Ar) is shown in Fig. 3 (top): the main product peak observed is the complex $[O=Mn^{V}(salen)]^{+}$ due to predominant fragmentation of the O–I bond. Loss of PhIO leading to $[(salen)Mn^{III}]^{+}$ ($m/z = 321$) is only a minor pathway. The following conclusions for the mechanism of oxidation by iodosylbenzene can be drawn from this experiment. Owing to the polymeric structure (with an O–I–O backbone) in the solid state,[35] the solubility of PhIO in organic solvents is very low and there are only small amounts available for ligation to the Mn complex. The detection of the Mn(salen)·PhIO

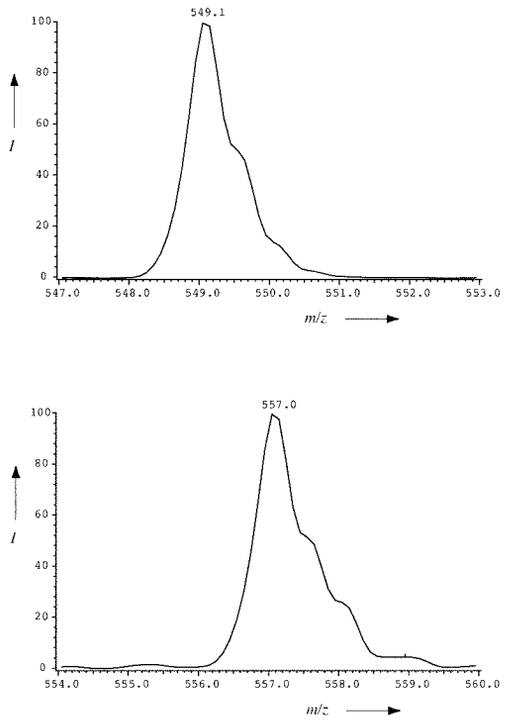

Fig 4 Top: isotope pattern of the doubly charged μ-oxomanganese(IV) complex $[PhIO(salen)Mn\text{-}O\text{-}Mn(salen)OIPh]^{2+}$ ($m/z = 549$). Bottom: isotope pattern of the peak at $m/z = 557$, indicating the presence of a doubly charged, dinuclear species.

species shows that iodosylbenzene coordinates strongly enough to the metal center to survive electrospray conditions, thus indicating that the major part of dissolved PhIO will effectively be bound to the manganese complex. From the fragmentation experiments we know that O–I bond scission dominates by far over the alternative O–Mn breakdown in the energy range of our CID experiments, leading to the preferred formation of $[O{=}Mn^{V}(salen)]^{+}$ and PhI over $[(salen)Mn^{III}]^{+}$ and PhIO. The products observed are the result of heterolytic bond fission in the gas phase. Products related to radical processes are not detected, but cannot be excluded on the basis of the MS experiments for solution-phase reactions. There is no evidence for iodobenzene bound as a ligand to one of the Mn(salen) species, but in all experiments using iodosylbenzene as oxygen transferring agent to the manganese(III) complex, $[Ph\text{–}I\text{–}Ph]^{+}$ (m/z 281) gives rise to a prominent peak in the mass spectrum (see Fig. 1 top).

At first glance, the fragmentation products in the daughter-ion spectrum of $[PhIO(salen)Mn^{V}{=}O]^{+}$ ($m/z = 557$, collision gas Ar) cause some puzzlement (Fig. 3 bottom). The main fragmentation is loss of iodosylbenzene leading to $[(salen)Mn^{V}{=}O]^{+}$ ($m/z = 337$), while the much less prominent peak at $m/z = 353$ is due to loss of iodobenzene. When compared to the daughter-ion spectrum of $[PhIO(salen)Mn^{III}]^{+}$, it is obvious that fragmentation of the Mn–O bond by far dominates over I–O fragmentation leading to formation of $[O(salen)MnO]^{+}$ ($m/z = 353$; we regard the rearrangement to a peroxomanganese(V) complex highly improbable). The occurrence of the bare $[(salen)Mn]^{+}$ at $m/z = 321$, however, cannot be explained as the result of the fragmentation of an oxomanganese(V) species. In our earlier work, we have shown that $[O{=}Mn^{V}(salen)]^{+}$ does not fragment when collided against argon with energies of up to 30 eV.[25] Closer inspection of the parent peak reveals where the unexpected fragment peaks stem from (Fig. 4). While the signal at $m/z = 549$ (Fig. 4 top) has isotope peaks compatible with the doubly charged dinuclear μ-oxomanganese(IV) complex (^{13}C isotope peaks separated by 0.5 mass unit), the isotope pattern of the signal at $m/z = 557$ (Fig. 4 bottom) suggests the presence of another doubly charged species of the same m/z ratio as

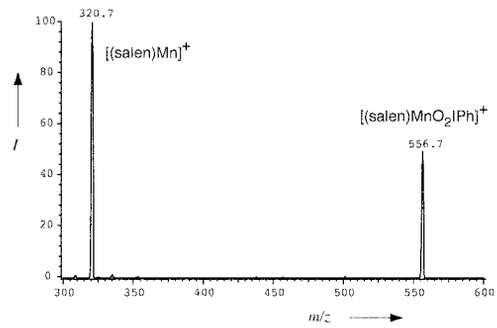

Fig. 5 Daughter-ion spectrum (1 mTorr Ar, collision energy 17 eV) of $[(PhIO_2)Mn^{III}(salen)]^{+}$ ($m/z = 557$), showing exclusive fragmentation to $[(salen)Mn^{III}]^{+}$ ($m/z = 321$).

$[PhIO(salen)Mn^{V}{=}O]^{+}$. This species could either be $[(salen)Mn^{III}O_2IPh]_2^{2+}$, a dinuclear Mn(salen) complex with two iodylbenzene molecules coordinated (possibly in a bridging manner), or the μ-oxo dimer $[PhIO_2(salen)Mn\text{–}O\text{–}Mn(salen)OIPh]^{2+}$. This assignment is based on the occurrence of a signal at $m/z = 439$, which is the product of loss of iodylbenzene $PhIO_2$. The disproportionation of PhIO to $PhIO_2$ and PhI is a well known reaction,[36] and we can safely assume that there will always be some iodylbenzene present in solution. From our experience, the amount of disproportionation depends entirely on the consistency of solid iodosylbenzene, which varies strongly from batch to batch. In some cases, the only species detectable upon mixing of $[(salen)Mn]^{+}$ and PhIO in acetonitrile was $[(salen)Mn^{III}O_2IPh]^{+}$, which can be identified readily by its exclusive fragmentation to $[(salen)Mn]^{+}$, *i.e.* loss of iodylbenzene (Fig. 5). The knowledge that $PhIO_2$ is not capable of transferring oxygen to manganese(III) corroborates the assignment for $m/z = 439$. The amount of $[(salen)Mn]^{+}$ present in the daughter-ion spectrum (Fig. 3 bottom) probably reflects the presence of the third isomeric species with $m/z = 557$, namely $[(salen)Mn^{III}O_2IPh]^{+}$.

μ-Oxomanganese(IV) complexes without terminal ligands or with acetonitrile replacing iodosylbenzene are conspicuously absent in all the mass spectra recorded. Since acetonitrile binds readily to the $(salen)Mn^{III}$ complex and can only be removed by applying moderate tube lens potentials (>40 V), we were led to the conclusion that μ-oxo bridged dimers have to be coordinated by much better ligands in order to have high enough lifetimes in solution to be detectable. Iodosylbenzene is obviously efficient in stabilising μ-oxo dimers, but the lability of the I–O bond and the problems experienced with different samples of varying properties caused us to look for alternatives. Amine *N*-oxides have widely been used as ligands for manganese–porphyrin and –salen complexes,[10,37] and they have proven to be effective ligands as well as oxygen-transferring agents in our studies on oxidation of (tetraphenylporphinato)manganese(III).[38] Since amine *N*-oxides are much poorer oxidants as compared to PhIO, the best method to prepare relatively stable μ-oxo dimers was found in the mixing of $[(salen)Mn^{III}]^{+}$ and the amine *N*-oxide in a 1 : 10 ratio in a slurry of iodosylbenzene in acetonitrile. A representative spectrum of the electrosprayed supernatant solution with *p*-$NCC_6H_4NMe_2O$ as a ligand is shown in Fig. 6 (top). The species which appear most prominently in the spectrum are [*p*-$NCC_6H_4NMe_2O(salen)Mn^{III}]^{+}$ ($m/z = 483$), [*p*-$NCC_6H_4NMe_2O(salen)Mn^{V}{=}O]^{+}$ ($m/z = 499$), and [*p*-$NCC_6H_4NMe_2O(salen)Mn^{IV}\text{–}O\text{–}Mn^{IV}(salen)$ *p*-$NCC_6H_4NMe_2O]^{2+}$ ($m/z = 491$). The signal at $m/z = 325$ is due to the H^{+}-bridged *N*-oxide dimer. Amine *N*-oxides apparently are much better ligands than iodobenzene or acetonitrile, which are both largely displaced (the residual peak for $[(salen)Mn^{III}NCCH_3]^{+}$ is probably due to recombination in the course of the electrospray process), and they are very effective in stabilising the μ-oxo bridged manganese(IV) dimers. Electrospray experiments with $[(salen)Mn^{III}NCCH_3]^{+}$

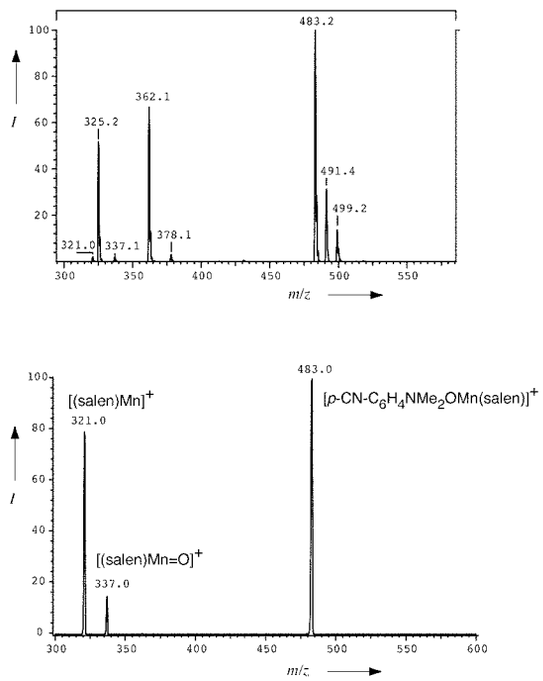

Fig. 6 Top: electrospray mass spectrum of an acetonitrile solution of [(salen)Mn]ClO_4, *p*-cyano-*N*,*N*-dimethylaniline *N*-oxide, and iodosylbenzene, showing the formation of *N*-oxide ligated manganese(III) and oxomanganese species. Bottom: daughter-ion spectrum (1.5 mTorr Ar, collision energy 20 eV) of $[(p\text{-}NCC_6H_4NMe_2O)Mn^{III}(salen)]^+$ (m/z = 483), showing fragmentation of the Mn–O as well as of the N–O bond.

ClO_4^- in non-coordinating solvents, *e.g.* CH_2Cl_2, have shown that the major part of acetonitrile dissociates from the manganese complex under "normal" spraying conditions (150 °C capillary temperature, tube lens potential ≈ 50 V). Thus, we conclude that the species detected with acetonitrile as a solvent are mainly due to recombination with the solvent in the spraying process. Tertiary amine *N*-oxides can also act as oxidants for the manganese–salen system. Dimethylaniline *N*-oxides do not only bind strongly to the metal centre, but are also able to transfer oxygen to the manganese(III)–salen complex. As shown in Fig. 6 (bottom), upon CID of $[p\text{-}NCC_6H_4NMe_2O(salen)Mn^{III}]^+$ both the loss of the *N*-oxide as well as of dimethylaniline can be induced. Further evidence for the aniline *N*-oxide acting as an oxidant comes from the observation that μ-oxomanganese(IV)–salen complexes are also detected without the addition of PhIO, albeit in small quantities. The oxidised oxomanganese(IV) and oxomanganese(V) species are fairly stable under these conditions and can be detected for several minutes. However, as already noted by Kochi and co-workers,[10,11] degradation of the intermediates sets in even without substrates present, and after 15 min essentially all oxomanganese complexes have disappeared.

Conclusion

Electrospray ionisation tandem mass spectrometry is a new approach for the study of the coordination chemistry of transient transition metal compounds. By transferring condensed-phase species with intact ligand spheres to the gas phase, the coordination chemistry of otherwise elusive species can be studied. By applying electrospray tandem mass spectrometry to the analysis of the oxidation chemistry of the manganese–salen system, we were able to dissect the detailed mechanism of oxygen transfer from iodosylbenzene to the manganese(III) complex and to identify the oxomanganese species formed upon oxidation. By employing electrospray ionisation for the transfer of catalytically active solution species to the gas phase and studying their gas-phase ion chemistry, insight into the reactivity of transient species can be gained far beyond the limits of solution-phase techniques.

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