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Coordination chemistry of manganese–salen complexes studied by electrospray tandem mass spectrometry: the significance of axial ligands

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Abstract

Tandem mass spectrometric techniques in combination with high-level quantum chemical calculations have been employed to study the coordination chemistry of manganese– and oxomanganese–salen complexes in the gas phase. Electrospray ionization was used to transfer the ionic complexes from solution to the gas phase. The formation of five- versus six-coordinate manganese(III) species was subsequently probed by ion–molecule reactions with neutral ligands, e.g. acetonitrile, pyridine, alcohols, etc. The reactivity of the so far elusive oxomanganese(V)–salen complexes, readily accessible by fragmentation of μ-oxomanganese(IV) dimers, and their coordination chemistry was studied in the same way. Hybrid Hartree-Fock/density functional calculations have been performed to assess the geometries and energies of the triplet and quintet states of the manganese complexes in question. The effects of axial ligation on the geometry and reactivity of the oxo complex were found to be quite drastic. Finally, the epoxidation of olefins by oxomanganese(V)–salen was studied intramolecularly by tethering the substrate to the metal center. No indication for precoordination of the substrate as prerequisite for oxidation was found. (Int J Mass Spectrom 195/196 (2000) 351–362) © 2000 Elsevier Science B.V.

Keywords: Electrospray ionization; Epoxidation catalysts; Salen complexes

1. Introduction

High-valent oxomanganese and oxoiron complexes play a crucial role in oxygen transfer to otherwise unreactive organic substrates. Numerous studies point to oxoiron intermediates being involved in the mechanism of cytochrome P-450 [1–3]. In addition to their importance in enzymatic oxygenations, oxometal complexes have often been suggested as the catalytically active species in epoxidations catalyzed by metal–salen and porphyrin complexes. The mechanistic scheme adopted for oxygen transfer to organic substrates by manganese–salen complexes [salen = *N*,*N*′-bis(salicylidene)ethylenediamine], one of the most versatile epoxidation procedures developed by Kochi and co-workers, is shown in Scheme 1 [4,5]. The metal-oxo species is acting as a staging post for oxygen transfer, which is why the mechanism was named "oxygen-rebound." However, mechanistic studies on manganese–salen

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Dedicated to Bob Squires for his many seminal contributions to mass spectrometry and ion chemistry.

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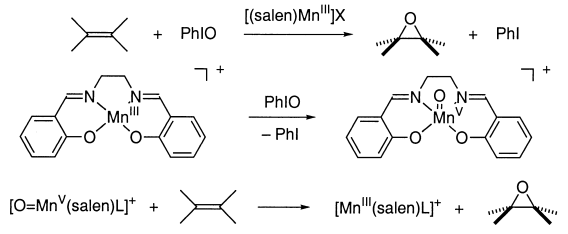

Scheme 1. The mechanism of alkene epoxidation catalyzed by manganese(III)–salen complexes.

and porphyrin oxidation catalysts have so far been hampered by the fact that the catalytically active oxomanganese species appear only as fleeting putative intermediates.

In view of the fact that oxygen transfers are so common and important in biological systems as well as in 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. (1) Oxygen transfer to the transition metal by dioxygen or some oxygen atom donor can yield several different species with quite diverse reactivities. In the case of manganese–porphyrin complexes, Groves and Stern were able to isolate several different oxomanganese(IV) complexes, none of which showed the reactivity typical for the intermediate in question [6]. Moreover, insight into the detailed mechanism of oxygen transfer by cytochrome P-450 is enormously complicated by the different reaction steps which can be envisioned after the initial formation of the ferric peroxocomplex: heterolytic O–O cleavage [→ (porphyrin)Fe^{V}=O], homolytic O–O cleavage [→ (porphyrin)Fe^{IV}=O], or direct nucleophilic attack on enzyme-bound substrate. (2) The transient nature of the catalytically active species. Recently, Groves and co-workers measured the conversion of a reactive intermediate in the manganese–porphyrin catalyzed oxidation, to which they assigned an oxomanganese (V) structure. They determined that the reaction followed a first-order rate constant of 5.7 s^{-1} [7].

Both problems can easily be overcome by transfer of the metal-oxo complexes to the gas phase and subsequent study of ion-molecule reactions. 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 ionization provides a powerful tool for the transfer of medium-to-large molecular ions to the gas phase with minimum fragmentation [8–10]. Most applications to inorganic/organometallic chemistry have so far focused on analytical aspects [11,12]. Our group has recently demonstrated the usefulness of electrospray-tandem mass spectrometry for mechanistic and thermochemical analysis in organometallic chemistry with regard to C–H activation by $[CpIr(PMe_3)(CH_3)]^+$ [13], oxo-transfer reactions by $[O{=}Mn^{V}(salen)]^+$ [14,15], gas-phase olefin oligomerization by "naked" alkylzirconocene cations [16], olefin metathesis by $[Cl_2Ru(=CHPh)(Cy_2PCH_2CH_2NMe_3)]^+$ [17], reversible hydrogenation/dehydrogenation of olefins by $[Rh(PMe_3)_2]^+$ ions [18], and olefin polymerization by Brookhart-type palladium(II) catalysts [19]. In this report, we present a study of the coordination chemistry of manganese(III) and oxomanganese(V)–salen complexes, the latter being the catalytically active species in the Kochi-Jacobsen-Katsuki epoxidation.

2. Experiment

2.1. Chemicals

Diacetoxyiodobenzene, pyridine, pyridine *N*-oxide, 2,3-dihydrofuran, allyl alcohol, 3-buten-1-ol, 4-penten-1-ol, and 5-nitro-2-hydroxybenzaldehyde were purchased from Aldrich and Fluka, respectively, and used as received. Salen [*N*,*N*′-bis(salicylidene) ethylenediamine] was bought from Fluka. Triethylphosphine oxide was obtained from Strem. Acetonitrile (HPLC grade quality) for the preparation of the electrospray solutions was purchased from Fluka.

2.2. Synthesis of 5,5′-dinitrosalen

The 5,5′-dinitrosubstituted salen was synthesized from the respective aldehyde and ethylene diamine according to the procedure by Jacobsen et al. [20]. The spectra obtained matched the analytical data given in the literature.

2.3. Synthesis of p-CN-N,N-dimethylaniline N-oxide

The *N*-oxide was prepared according to the procedure of Cymerman Craig and Purushothaman [21] by MCPBA oxidation of the respective *p*-CN-*N*,*N*-dimethylaniline.

2.4. Synthesis of manganese(III)–salen salts

[(Salen)Mn]Cl was prepared following the procedure of Jacobsen et al. [20], whereas Mn(5,5′-dinitrosalen)PF_6 was prepared by the method of Kochi et al. [4]. In the case of the manganese(III) PF_6^- salt, electrospray solutions were prepared by dissolving the salt in CH_3CN and diluting to 10^{-5} M concentration. Acetonitrile solutions of the chloride salts were treated with an equimolar amount of silver perchlorate and stirred for 15 min. After removal of AgCl by filtration the solution was diluted to 10^{-5} M.

2.5. Electrospray solutions

For experiments with manganese(III) complexes, the stock solution of the manganese(III) salt was either simply diluted with CH_3CN to a 10^{-5} M concentration or added to a ca. 100-fold volume of a 10^{-4} M solution of the ligand (pyridine, Et_3PO, etc.) in acetonitrile. For the experiments with oxomanganese species, the solutions were prepared by adding the stock solution of the manganese(III) salt to a slurry of PhIO and Et_3PO (10 equivalents) in acetonitrile, resulting in a $\sim 10^{-5}$ M concentration of the manganese complex.

2.6. Instrumentation

For the mass spectrometric measurements the slightly modified Finnigan MAT TSQ7000 electrospray tandem mass spectrometer described previously [13b] (octopole O1, quadrupole Q1, octopole O2, quadrupole Q2 setup) was used. The first octopole O1 was fitted with an open cylindrical sheath around the rods into which a collision gas could be bled for thermalization or reaction pressures up to 20 mTorr.

2.7. ESMS setup

In all experiments, the incoming ions were thermalized in the first octopole with argon or the volatile ligand at a pressure of ~10 mTorr and at a temperature of 70 °C. For an ESMS analysis of the complex ions in solution, the instrument was operated with Q1 in scanning mode and Q2 acting as an ion guide. All gas-phase reactivity measurements were carried out in daughter-ion mode, i.e. the first quadrupole was used to mass select ions of a single mass, which were then collided with a target gas in the second octopole. The second quadrupole Q2 was operated in scanning mode and served to detect the ionic collision products. Experiments with pickup of substrates/ligands in O1 were carried out by first setting the tube lens such as to optimize the yield of the desired complex ion and then bleeding in the gaseous ligand with a needle valve. The liquid ligands used as reactants were thoroughly degassed by freeze–pump techniques. Collision-induced dissociation (CID) experiments on the generated ions could then be conducted by collision with argon or xenon in O2 (the collision energy can be varied by applying different field potentials which alters the velocity of the ions on their way into the collision region). Experiments involving pickup in O2 were performed by selecting the species studied with Q1 and colliding the ions with the target gas at very low collision energies (0–1 eV) and gas pressures of 0.5–1 mTorr (measured by a cold-cathode gauge). The tube lens setting was typically in the range of 50–70 V (referenced to a mass of *m*/*z* 500) except in cases where a high fragment yield was crucial (>100 V).

2.8. Computational methods

Ab initio molecular orbital calculations for the compounds studied have been performed using the

G98 series of programs [22] on SGI Origin 2000 computers at the University of Notre Dame and the National Center for Supercomputing Applications (NCSA) University of Illinois, Urbana-Champaign. Both the triplet and quintet states of $[(salen)Mn{=}O]^+$ and $[Me_3NO(salen)Mn{=}O]^+$ were fully optimized without symmetry constraints using the hybrid Becke3 Lee-Yang-Parr (B3LYP) exchange correlation functional [23]. A 6-311G* valence triple zeta + polarization basis set [24] was used for the calculation of $[(salen)Mn{=}O]^+$. Preliminary results for $[Me_3NO(salen)Mn{=}O]^+$ were obtained by geometry optimization using a 3-21G* basis [25] set, followed by 6-311G* single point calculations. All bond lengths are given in angstroms, all bond angles in degrees. Relative energies are in kilocalories per mole and are not corrected for zero point energies.

3. Results and discussion

Electrospray of unsubstituted manganese(III) salen complexes in acetonitrile gives mainly the singly charged, five-coordinate cation $[CH_3CN(salen)Mn^{III}]^+$ [*m/z* = 362, Fig. 1(a)]. When the spraying conditions are changed such that the ions are energized by applying higher tube lens potentials of ~130 V, some of the ligated acetonitrile molecules can be dissociated from the manganese centers resulting in the detection of the "naked" salen complex $[(salen)Mn^{III}]^+$ [*m/z* = 321, Fig. 1(b)]. It is known from numerous crystallographic studies that manganese(III)–salen complexes can bind one or two ligands (usually the solvent used for recrystallization, i.e. acetone, ethanol, etc.) in the axial positions, thus forming five- or six-coordinate species in the solid state [26]. It has been found that in the tetra- and penta-coordinate modes of these complexes, there always is a planar arrangement of the salen ligand. In the octahedral coordination mode, an alternative arrangement has been occasionally observed, where one of the oxygens of the salen ligand moves out of the plane and occupies an apical position. The axial ligands can easily be exchanged in solution, indicating that they are only weakly bound to the manganese

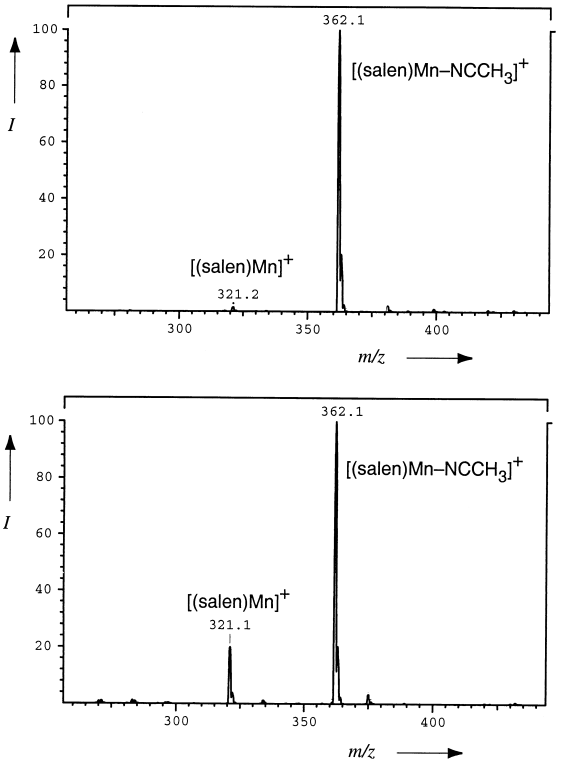

Fig. 1. Electrospray mass spectrum of an acetonitrile solution of $[(salen)Mn]ClO_4$, taken with a tube lens potential of (a) 70 and (b) 130 V, respectively, showing the dissociation of the axial ligand upon collisional activation.

center [27]. Although we do not see any six-coordinate manganese–salen complexes bearing two acetonitrile ligands in our electrospray experiments, the presence of the five-coordinate species posed the question whether or not acetonitrile is bound strongly enough to survive the spraying process. When a 10^{-3} M stock solution of $[(salen)Mn]ClO_4$ in acetonitrile was diluted to 10^{-5} M with CH_2Cl_2 and electrosprayed, only small traces of the five-coordinate complex with CH_3CN as a ligand could be detected. The acetonitrile could then be completely removed at tube lens potentials on the order of 90 V. We therefore conclude that the presence of $[CH_3CN(salen)Mn^{III}]^+$ is due to recombination during the electrospray process when acetonitrile is used as a solvent rather than to the inherent stability of the $Mn–NCCH_3$ bond. To further test the stability of the axially ligated com-

plexes, we performed ligand-pickup experiments in the collision cell at pressures of ~1 mTorr. Although the naked salen complex readily picks up one molecule of acetonitrile, no traces of the acetonitrile bisadduct could be detected. Accordingly, when the five-coordinate complex $[CH_3CN(salen)Mn^{III}]^+$ was mass selected in the first quadrupole, no addition of acetonitrile could be induced.

A similar picture emerges from experiments performed with methanol as axial ligand. When methanol is used as collision gas in the second octopole, pickup of only one equivalent of alcohol can be detected. The picture changes somewhat when a stronger ligand is used, namely pyridine. Pickup experiments in the collision cell lead to exclusive formation of the five-coordinate complex. However, when a solution of $[(salen)Mn]ClO_4$ with a large excess of pyridine in CH_3CN is electrosprayed, a small amount of the six-coordinate species $[py(salen)Mn^{III}py]^+$ bearing two axial pyridine ligands can be detected. Dissociation of the first pyridine ligand is extremely facile, while the second pyridine can only be removed at collision energies >10 eV. Electronic factors play a decisive role in the formation of six- versus five-coordinate manganese–salen complexes. One would conceive intuitively that Mn–salen complexes with a more electron-deficient metal center bind axial ligands more strongly. This can be demonstrated by experiments with the 5,5′-dinitrosubstituted salen ligand. The peak corresponding to the complex with two axial acetonitrile ligands (m/z = 493) is present in the electrospray MS of a 10^{-5} M acetonitrile solution of $[(5,5'\text{-dinitrosalen})Mn]ClO_4$. Accordingly, pickup experiments with $[(salen)Mn]^+$ in the collision cell clearly show addition of one and two molecules CH_3CN [28].

Oxomanganese(V)–salen and porphyrin complexes have so far remained elusive in condensed-phase studies. If those species are present in not-too-low steady-state concentrations, electrospray of authentic reaction mixtures will transfer all ionic species to the gas phase and thus provide us with a tool to study the coordination chemistry and reactivity of the active species of the catalytic cycle. Electrospray of in situ mixtures of $[(salen)Mn^{III}]ClO_4$ and suitable oxygen transferring agents, e.g. iodosobenzene, reveals the presence of several oxidation products. Two oxidized species readily identifiable in the spectrum 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) [14]. The coordination of iodosobenzene to manganese finds its precedent in the field of Mn-porphyrin chemistry. Hill and co-workers found that oxidation of a (tetraphenylporphinato)Mn complex with PhIO leads to the formation of a dimeric species containing one iodosobenzene molecule per Mn atom [29]. By analogy to the products found upon oxidation of manganese(III)–porphyrin complexes, we assign an antiferromagnetically coupled dimeric μ-oxomanganese(IV) structure to the iodosobenzene ligated dimer.

Further evidence for the presence of a μ-oxo bridged dimeric species arises from the product distribution of a CID experiment. The daughter-ion experiment with $[PhIO(salen)Mn–O–Mn(salen)OIPh]^{2+}$ (m/z = 549, collision with Ar at 20 eV) gives the expected disproportionation products $[PhIO(salen)Mn^{III}]^+$ and $[PhIO(salen)Mn^{V}{=}O]^+$, which proves the presence of the μ-oxo bridge in the parent and a terminal Mn-oxo moiety in the daughter ion. Due to the lability of the O–I bond and the facile dissociation of iodosobenzene, the two primary daughter ions formed by collisional activation immediately fragment further, leading to a rather complex product pattern [15].

μ-Oxomanganese(IV) complexes without terminal ligands or with acetonitrile replacing iodosobenzene are conspicuously absent in all the mass spectra recorded. Iodosobenzene is obviously efficient in stabilizing μ-oxo dimers, but the lability of the I–O bond and the problems experienced with different samples of varying properties caused us to search for alternatives. Acetonitrile binds readily to the manganese(III)-salen complex to form a five-coordinate species (vide supra), but is not effective in stabilizing μ-oxo dimers. Obviously, much better ligands are needed for the formation of stable six-coordinate manganese complexes. Amine *N*-oxides have been widely used as ligands for manganese-porphyrin and

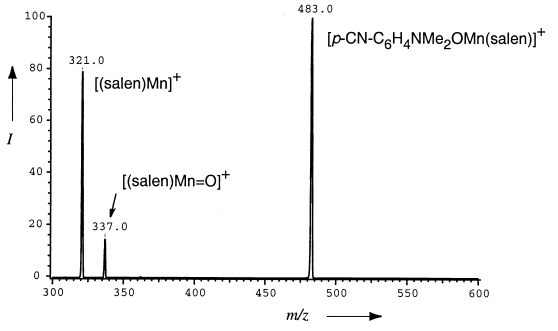

Fig. 2. Daughter-ion spectrum of $[(p\text{-CN–C}_6\text{H}_4\text{NMe}_2\text{O})\text{Mn}^{\text{III}}(\text{salen})]^+$, showing fragmentation of the Mn–O as well as of the N–O bond.

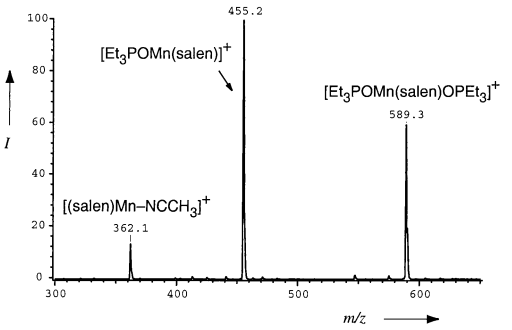

Fig. 3. Electrospray mass spectrum of an acetonitrile solution of $[(\text{salen})\text{Mn}]\text{ClO}_4$ and triethylphosphine oxide, showing the formation of both the five- and six-coordinate manganese(III) cation.

salen complexes [4,30], and they have proven to be effective ligands as well as oxygen-transferring agents in our studies on the oxidation of (tetraphenylporphinato)manganese(III) [31]. With $p\text{-CN–C}_6\text{H}_4\text{NMe}_2\text{O}$ present in a tenfold excess, electrospray of a 10^{-5} M solution of $[(\text{salen})\text{Mn}]\text{ClO}_4$ shows both the five- and—to a smaller extent—the six-coordinate complexes being present. The same result is obtained with a variety of para-substituted *N*,*N*-dimethylaniline *N*-oxides. With pyridine *N*-oxide, the peak corresponding to the axially bisligated species is considerably smaller. In the case of the five-coordinate complex with an axial pyridine *N*-oxide ligand, fragmentation gives exclusively loss of *N*-oxide, with no detectable traces of the oxomanganese(V) complex.

Tertiary amine *N*-oxides are able to oxidize the manganese(III) complex, as can be seen from the product distribution of the CID experiment shown in Fig. 2. Collisions at 20 eV do not only induce ligand loss, but also lead to fragmentation of the N–O bond and thus to the formation of an oxomanganese(V) complex. Because of the ambiguities in the fragmentation of ligated *N*-oxides, we were prompted to look for alternative neutral ligands. Phosphine oxides turned out to be the ligands of choice because of the oxophilicity of Mn^{III} on the one hand and the strong, fragmentation-stable P=O bond on the other. The electrospray MS of an acetonitrile solution of $[(\text{salen})\text{Mn}]\text{ClO}_4$ with 10 equivalents Et_3PO present demonstrates the formation of both singly and doubly ligated Mn^{III}–salen species (Fig. 3). Since triethylphosphine oxide cannot act as an oxidant, a good method to prepare relatively stable μ-oxo dimers was the mixing of $[(\text{salen})\text{Mn}^{\text{III}}]^+$ and the phosphine oxide in a 1:10 ratio in a slurry of iodosobenzene in acetonitrile. A representative spectrum of the electrosprayed supernatant solution with Et_3PO as a ligand is shown in Fig. 4. The species that appear most prominently in the spectrum are $[\text{Et}_3\text{PO}(\text{salen})\text{Mn}^{\text{III}}]^+$ (m/z = 455), $[\text{Et}_3\text{PO}(\text{salen})\text{Mn}^{\text{V}}{=}\text{O}]^+$ (m/z = 471), and $[\text{Et}_3\text{PO}(\text{salen})\text{Mn}^{\text{IV}}\text{–O–Mn}^{\text{IV}}(\text{salen})\text{Et}_3\text{PO}]^{2+}$ (m/z = 463). Phosphine oxides apparently are much better ligands than either iodosobenzene or acetonitrile, which are both largely displaced (the residual peak for $[(\text{salen})\text{Mn}^{\text{III}}\text{NCCH}_3]^+$ is hardly noticable and probably due to recombination in the course of the electrospray process), and they are very effective

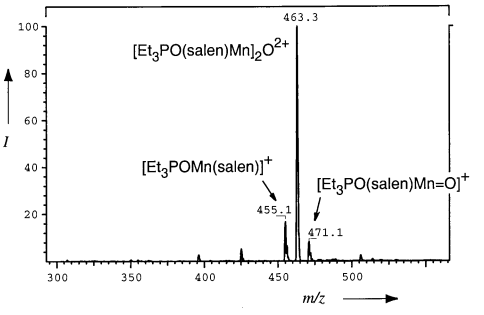

Fig. 4. Electrospray mass spectrum of an acetonitrile solution of $[(\text{salen})\text{Mn}]\text{ClO}_4$, triethylphosphine oxide, and iodosobenzene, showing the formation of phosphine oxide-ligated manganese(III) and oxomanganese complexes.

in stabilizing the μ-oxo bridged manganese(IV) dimers.

Fragmentation of the μ-oxo bridged dimer provides us with a reliable source for oxomanganese(V) complexes. With ~20 mTorr argon in the first octopole and high tube lens potentials, the yield of the fragmentation products $[(salen)Mn^{V}{=}O]^{+}$ and $[Et_3PO(salen)Mn^{V}{=}O]^{+}$ is high enough to conduct MS/MS experiments in the collision cell. We have shown earlier that $[(salen)Mn{=}O]^{+}$ is not only present in typical in situ epoxidation mixtures, but that the oxomanganese(V) species is also capable of transferring oxygen to organic substrates, e.g. sulfides and electron-rich olefins [14]. The search for a reliable method of preparing fairly stable μ-oxomanganese(IV) complexes was originally motivated by an experiment aimed at the elucidation of electronic influences of salen substituents on the reactivity of the catalytically active oxomanganese(V) species. We were able to demonstrate that the effect of salen substituents on the reactivity of the oxomanganese(V) complex can be analyzed from the product distribution of CID on dimeric μ-oxomanganese(IV) salen species with two differently substituted salen ligands. Accordingly, by CID of μ-oxomanganese(IV) salen species with two different terminal ligands, the effect of axial donor ligands on the stability of the epoxidation catalyst could be studied. Electron-withdrawing substituents on the salen ligand and axial ligands were shown to decrease the stability and thus to enhance the reactivity of the oxygen-transferring $[(salen)Mn{=}O]^{+}$, while electron-donating salen substituents have a strong stabilizing effect.

In addition to the gas-phase experiments, we performed hybrid Hartree-Fock/density functional calculations in order to obtain information about the structures and energetics of oxomanganese(V)–salen complexes. It is well known from the literature that an accurate quantum mechanical description of first row transition metals requires the adequate treatment of electron correlation [32]. For the calculation of manganese complexes, which can be present in multiple spin states, the use of hybrid density functional methods was found to be particularly promising [33]. For the problem studied in this article, a sufficiently flexible basis set for the description of the five- and six-coordinated manganese complexes is necessary. We therefore decided to use the B3LYP/6-311G* method for the calculation of $[(salen)Mn{=}O]^{+}$ and the B3LYP/6-311G*//B3LYP/3-21G* method for preliminary studies of $[Me_3NO(salen)Mn{=}O]^{+}$. So far, only mechanical force-field calculations of oxomanganese–salen complexes and the intermediates of the epoxidation reaction have been reported [34,35]. High-level quantum chemical calculations have been restricted to simplified model systems [33c]. With no single-crystal x-ray data available, most of the discussions and models applied to the stereochemical course of the epoxidation catalyzed by chiral manganese-salen complexes were based on structures derived from the manganese(III) precursors, i.e. structures in which the active species has a planar salen ligand [36]. We calculated the triplet and the quintet state of $[(salen)Mn{=}O]^{+}$ which could both be engaged in non-synchronous reactions with olefins [33c]. The results of our calculations are summarized in Fig. 5. The energy difference between these states is small; the triplet is the ground state with the quintet only 6.8 kcal/mol higher in energy. The oxo-manganese bond is 1.576 Å in the triplet and 1.650 Å in the quintet state, both significantly shorter than in the smaller model system described earlier [33c]. As in the experimental structures of oxochromium(V)–salen complexes [37], the metal center is displaced above the plane of the four coordinating heteroatoms, 0.43 Å in the triplet and 0.25 Å in the quintet state. Both structures are slightly twisted: the angle between the two planes formed by the aromatic rings is 4.8° (quintet) and 12.4° (triplet), respectively. This leads to a distortion of the coordination sphere of the manganese in the triplet state, making the two manganese–oxygen and manganese–nitrogen bonds differ by 0.06 Å.

Thus far, the influence of additional axial ligands on the catalyst structure has not been addressed. Amine *N*-oxides have already been introduced as promoters in the epoxidation catalysis by Kochi and co-workers [4,5] and Jacobsen and co-workers [38], and we have recently demonstrated that the axial coordination of tertiary amine *N*-oxides on

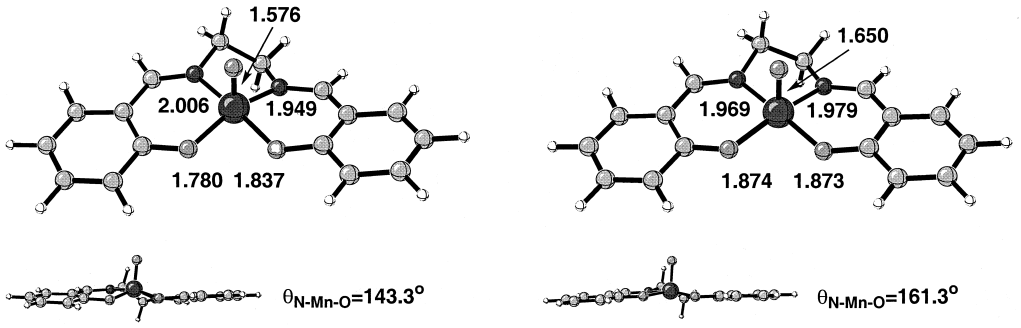

Fig. 5. B3LYP/6-311G* Structures of $[(salen)Mn{=}O]^+$ in the triplet (left) and quintet (right) states.

$[(salen)Mn{=}O]^+$ increases the oxygen-transfer reactivity of the complex dramatically [15]. We therefore chose trimethylamine *N*-oxide as a suitable model ligand for our calculations. Due to the large size of the system, preliminary calculations were performed at the B3LYP/6-311G*//B3LYP/3-21G* level of theory. The results of these calculations are summarized in Fig. 6. It can be seen that the axial *N*-oxide ligand has a strong influence on the geometry of the complex. The axial oxo-manganese bond is lengthened by 0.14 Å, even though the axial *N*-oxide ligand has a fairly long manganese–oxygen bond. The overall shape of the molecule is also strongly influenced by the additional axial ligand. The metal center is in the plane of the four heteroatoms, which in turn forms 150°/174° and 159°/153° angles with the phenyl rings in the triplet and quintet, respectively. Consequently, the coordination sphere of the manganese with the four equatorial heteroatoms is less distorted. It is likely that the transoid orientation of the phenyl rings in the triplet and the cisoid orientation in the quintet correspond to two local minima on the potential energy hypersurface. The energy difference between the two states is 4.7 kcal/mol at the B3LYP/6-311G*// B3LYP/3-21G* level of theory which is even smaller than in the case of $[(salen)Mn{=}O]^+$. The results of ongoing studies on the dependence of the overall shape of the molecules and their relative energies on the axial ligand and the spin state will be reported in due course.

With a reliable source for oxomanganese(V)–salen complexes at hand, we were able to conduct reactivity

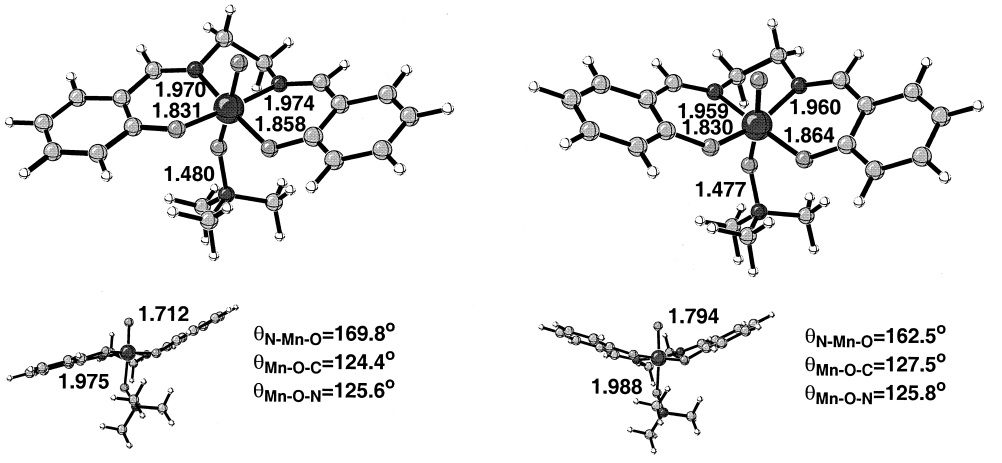

Fig. 6. B3LYP/3-21G* Structures of $[Me_3NO(salen)Mn{=}O]^+$ in the triplet (left) and quintet (right) states.

studies with both the naked $[(salen)Mn{=}O]^+$ and the six-coordinate $[L(salen)Mn{=}O]^+$. The first substrate tested was acetonitrile, the solvent of choice not only in our electrospray experiments, but also in the solution-phase studies of Kochi and co-workers [4,5]. The observation that all in situ mixtures containing PhIO as an oxidant gradually decompose until no manganese–salen species can be detected poses the question whether or not the solvent could be slowly oxidized. A species with *m/z* = 378 is always detected in varying degrees when the supernatant solution of a slurry of $[(salen)Mn]ClO_4$ and PhIO in acetonitrile is electrosprayed. Two structural assignments are possible: the six-coordinate oxomanganese(V) complex $[CH_3CN(salen)Mn{=}O]^+$ and the five-coordinate manganese(III) complex $[(salen)Mn–ONCCH_3]$, which could both be present in solution or formed in the electrospray process. CID on this acetonitrile adduct gives exclusively $[(salen)Mn{=}O]^+$. Daughter-ion experiments with $[(salen)Mn{=}O]^+$ and ~1 mTorr CH_3CN in O2 do not give conclusive results: the only daughter-ion detected is a species with *m/z* = 378; the reduction to $[(salen)Mn]^+$ is not observed. For the nitrile–oxide complex, fragmentation of the Mn–O bond would be expected unless the N–O bond were to be much weaker than the metal–ligand bond. We therefore regard the presence of the six-coordinate cation $[CH_3CN(salen)Mn{=}O]^+$ more likely. Corroboration for this assignment comes from a pickup experiment with a substrate which has similar ligation properties (vide supra) but is not oxidized: $[CH_3OH(salen)Mn{=}O]^+$ is formed to a significant amount with 1 mTorr methanol in O2. There is no experimental evidence for the oxidation of acetonitrile by oxomanganese(V).

Another substrate which could be oxidized at the N-atom is pyridine, already used as promoter in the epoxidation of Kochi and co-workers [4]. Upon addition of a tenfold excess of pyridine to a slurry of $[(salen)Mn]ClO_4$ and PhIO in acetonitrile, we detected a predominant species of *m/z* = 416. As in the case of acetonitrile, two structural isomers are conceivable: the six-coordinate oxomanganese(V) complex $[py(salen)Mn{=}O]^+$ and the manganese(III) complex bearing a pyridine *N*-oxide ligand $[(salen)Mn–Opy]^+$. The latter was prepared independently by adding 10 equivalents of pyridine *N*-oxide to the acetonitrile solution of $[(salen)Mn]ClO_4$, and its fragmentation was subsequently studied by CID with argon as collision gas. The only pathway observed is loss of pyridine *N*-oxide and formation of $[(salen)Mn^{III}]^+$. Since the same fragmentation is detected with the species of *m/z* = 416 of the in situ mixture, we concluded that the presence of $[py(salen)Mn{=}O]^+$ can safely be ruled out; as known from earlier experiments, the Mn=O bond cannot be fragmented even up to collision energies of 30 eV, hence the fragmentation expected for $[py(salen)Mn{=}O]^+$ would be loss of pyridine. This leads us to the conclusion that most of the pyridine in solution must have been consumed by catalytic oxidation by the manganese-salen complex. To further study the oxidation in detail, we performed reactions of $[(salen)Mn{=}O]^+$ with pyridine in the gas phase. With a pressure of ~1 mTorr pyridine in O2, the main reaction product is a pyridine monoadduct, with a very small but significant amount of the six-coordinate $[py(salen)Mn–Opy]^+$ also formed (Fig. 7). In an alternative experiment, pyridine was introduced in O1 and the species with *m/z* = 416 was fragmented in O2 (collision gas argon at ~0.2 mTorr, collision energy 10 eV). The only fragmentation detected is loss of pyridine and formation of $[(salen)Mn{=}O]^+$. In other words, ligation of pyridine to the metal center by far exceeds the reaction with the oxo ligand. In no case, oxygen transfer to pyridine could be confirmed: in all daughter-ion experiments

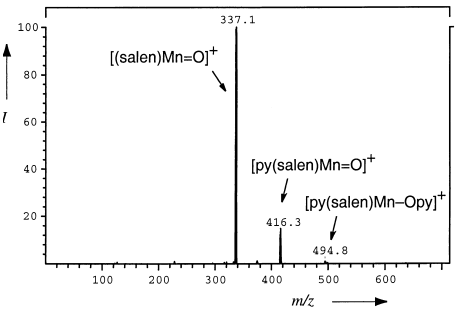

Fig. 7. Daughter-ion spectrum of $[(salen)Mn{=}O]^+$ (*m/z* = 337) with pyridine in O2, showing the pickup of two substrate molecules.

performed with $[(salen)Mn{=}O]^+$, no traces of $[(salen)Mn]^+$ or $[(salen)Mnpy]^+$ were detected.

As for the reactions with olefinic substrates, we have already demonstrated that electron-rich olefins, e.g. dihydrofuran, are oxidized by $[(salen)Mn{=}O]^+$ [14]. On the other hand, no reduction of $[(salen)Mn{=}O]^+$ to $[(salen)Mn]^+$ could be observed when the substrate in the collision cell was 1-butene. A simple explanation for this failure to detect reaction products with nonactivated olefins would be that the reaction proceeds too slowly to be observed in our experimental setup (the residence time of the ions in a typical CID experiment in O2 was estimated to be on the order of a few microseconds [17]). An alternative explanation would result from the difference in the ligation properties of the two substrates: while 1-butene does not form adducts with $[(salen)Mn]^+$ or $[(salen)Mn{=}O]^+$ (no pickup in O1 or O2), dihydrofuran can add as a ligand to the manganese center. Thus, a mechanism is conceivable in which the substrate first binds to the metal center and further reacts as a substrate when the complex is collisionally activated. To test this possibility, we chose substrates which can bind to the manganese center via an alcohol group and also bear an olefinic unit which can be epoxidized: allyl alcohol, 3-buten-1-ol, and 4-penten-1-ol. Since these olefinic alcohols are electronically very similar, they should be equally good substrates for epoxidation. With ~1 mTorr allyl alcohol in O2, $[(salen)Mn{=}O]^+$ is reduced to $[(salen)Mn]^+$ by a significant amount. This observation is in striking contrast to the reaction with 1-butene (both olefinic units are not activated and should react similarly). Thus it is tempting to assume that precoordination does indeed play a crucial role in the epoxidation. Fortunately, this assumption can also be tested experimentally by adding allyl alcohol in O1 (~20 mTorr) and collisionally activating the resulting complex $[C_3H_5OH(salen)Mn{=}O]^+$ in O2. The only fragmentation product seen in this experiment is $[(salen)Mn{=}O]^+$, which proves that no oxidation has taken place in the collision cell. It also indicates that the epoxide alcohol which has been produced to some amount in O1 is not bound as a ligand, probably due to dissociation in the course of the epoxidation. We conclude that neither precoordination nor activation of the olefin by electron-donating groups are prerequisites for the epoxidation to occur in the gas phase. The reaction cross section is probably mainly determined by the polarizibility of the substrate, which would explain our experimental observations.

When the homologous alcohols 3-buten-1-ol and 4-penten-1-ol are added in O1, a different fragmentation pattern is observed. With longer chains between the alcohol and the olefinic moiety, intramolecular oxidation of the olefin becomes possible, i.e. a significant amount of $[(salen)Mn]^+$ is detected. We conclude that the axially bound substrate can reach around the salen ligand (between the two oxygen atoms) and thus be oxidized. Of course, we can make no statement whether this reaction has already occurred in O1, but this is of no relevance for the conclusions. Moreover, a second intramolecular reaction is observed, which seems to derive from a four-membered ring intermediate and leads to methylene transfer to the oxo group (m/z = 351). This observation is of great importance for the mechanistic discussion about radical versus manganaoxetane intermediates in the epoxidation and is currently under investigation in our group.

4. Conclusions

Electrospray ionization tandem mass spectrometry is a new approach for the study of the coordination chemistry of transition metal compounds. By employing electrospray ionization for the transfer of catalytically active condensed-phase species with intact ligand spheres to the gas phase, insight into the reactivity of transient species can be gained far beyond the limits of solution-phase techniques. Once in the gas phase, reactivity studies of catalysts which have so far escaped any solution-phase characterization can be conducted by taking advantage of established gas-phase ion chemistry techniques. By comparing the coordination chemistry of manganese(III) and oxomanganese(V) complexes, we arrive at the conclusion that the influence of axial ligation on the catalytically active species has so far been seriously

underestimated. The effects of axial ligation on the geometry and reactivity of the oxo complex are quite drastic and force a re-evaluation of the established models explaining the stereochemical course of the Jacobsen-Katsuki epoxidation. The results obtained for the gas-phase oxidation by oxomanganese(V)–salen have shown that precoordination of the substrate is not a prerequisite for efficient conversion and that a direct attack of the oxo ligand on the substrate in a bimolecular reaction is more likely.

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[Fe($TPPF_{20}$)Cl and Fe($TPPF_8$)Cl]. Less binding was observed for Fe(TPP)Cl, and virtually no binding was observed for Fe(TMP)Cl. Interestingly, these workers have shown that increased binding of second axial ligands to ferric and manganic porphyrin peroxo complexes leads to increased nucleophilic oxidations by these complexes. (a) M. Selke, J.S. Valentine, J. Am. Chem. Soc. 120 (1998) 2652; (b) M. Selke, D.L. Wertz, J.S. Valentine, private communication.

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