Probing the Reactivity of Oxomanganese–Salen Complexes: An Electrospray Tandem Mass Spectrometric Study of Highly Reactive Intermediates

Derek Feichtinger and Dietmar A. Plattner*[a]

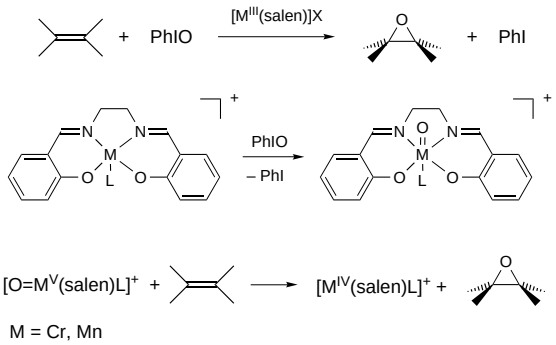
Abstract: Electrospray ionization in combination with tandem mass spectrometric techniques has been employed to study the formation of oxomanganese–salen complexes upon oxidation of $[Mn^{III}(salen)]^+$ cations as well as the properties and reactions of the oxidized species in the gas phase. Two species could be characterized as the principal oxidation products: the oxomanganese(v) complex, $[Mn{=}O(salen)]^+$, which is the actual oxygen-transfer agent in epoxidation reactions, and the dinuclear, μ-oxo bridged $[L(salen)Mn{-}O{-}Mn(salen)L]^{2+}$ with two terminal ligands L; the latter acts as a reservoir species. The effects of various substituents in the 5- and 5′-positions, respectively, of the salen ligand on the reactivity of the epoxidation catalyst were determined quantitatively from CID (collision-induced dissociation) experiments and B3LYP density functional calculations. Accordingly, the effect of axial donor ligands on the reactivity of the epoxidation catalyst was studied. Electron-withdrawing substitutents on the salen ligand and additional axial ligands decrease the stability and thus enhance the reactivity of the Mn=O moiety, while electron-donating salen substituents have a strong stabilizing effect.

Keywords: density functional calculations · epoxidations · gas-phase chemistry · manganese · mass spectrometry

Introduction

The oxidation of organic substrates in biological systems is accomplished by oxygenase enzymes with high-valent oxometalloporphyrin moieties in the active site.[1–9] The study of cytochrome P-450 and porphyrin model complexes designed to mimic its reactivity has yielded a number of synthetically useful catalysts for the epoxidation and hydroxylation of organic substrates.[10–12] The insight gained by the study of metal–porphyrin-based systems was readily transferred to metal–salen complexes (salen = *N*,*N*′-bis(salicylidene)ethylenediamine), introduced by Kochi and co-workers as versatile epoxidation catalysts in the 1980s.[13–17] A breakthrough was achieved in the field of enantioselective epoxidation through the introduction of chiral manganese–salen catalysts by Jacobsen and co-workers,[18] with a similar system developed by Katsuki and co-workers at about the same time.[19] The Jacobsen – Katsuki reaction is universally recognized as one of the most useful and widely applicable methods for the epoxidation of unfunctionalized olefins.[20, 21]

The mechanistic scheme adopted for oxygen transfer to organic substrates by salen complexes is based on the isolation and characterization of an oxochromium(v) species by Kochi and co-workers (Scheme 1).[13–15] This mechanism was in accordance with the properties and reactivity of an analogous oxoporphinatochromium(v) complex studied earlier by Groves and Kruper, who coined the term "oxygen-rebound mechanism".[22] Switching from chromium to manganese, Kochi and co-workers discovered a much more versatile salen-based oxidation catalyst.[16, 17] However, mechanistic studies on these systems have so far been hampered by the



Scheme 1. The mechanism of alkene epoxidation catalyzed by metal–salen complexes.

[a] Dr. D. A. Plattner, Dr. D. Feichtinger
Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule Zürich, ETH-Zentrum
Universitätstrasse 16, 8092 Zürich (Switzerland)
Fax: (+41) 1-632-1280
E-mail: plattner@org.chem.ethz.ch

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fact that the catalytically active species appear only as fleeting putative intermediates.

We have found that the reactivity of short-lived intermediates in the oxidation process can readily be addressed by transferring 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; due to high-vacuum conditions, the intermediates' short solution-phase lifetimes do not pose a problem. Electrospray ionization provides a powerful tool for the transfer of medium-to-large molecular ions to the gas phase with minimum fragmentation.[23–25] Recently, electrospray mass spectrometry (ESMS) has become increasingly popular as an analytical tool in inorganic/organometallic chemistry.[26, 27] We have demonstrated the usefulness of electrospray tandem mass spectrometry for mechanistic and thermochemical analysis in organometallic chemistry in accounts on the C–H activation by $[CpIr(PMe_3)(CH_3)]^+$,[28] gas-phase olefin oligomerization by "naked" alkylzirconocene cations,[29] and the oxygen-transfer reactivity as well as coordination chemistry of $[O{=}Mn^{V}(salen)]^+$.[30–32] In this report, we present a systematic study of substituent and ligand effects on the intrinsic reactivity of high-valent oxomanganese–salen complexes that are the catalytically active species in the Kochi – Jacobsen – Katsuki epoxidation.

Results and Discussion

***μ*-Oxomanganese complexes**: Previously, we reported the detection of oxomanganese(v)–salen complexes by electrospray of in situ mixtures of Mn^{III}(salen) and suitable oxygen transferring agents, for example, iodosobenzene.[30, 32] The oxidized species most prominent in the spectrum are the parent oxo-complex $[O{=}Mn^{V}(salen)]^+$ and the dinuclear, *μ*-oxo bridged complex with two terminal PhIO ligands $[PhIO(salen)Mn{-}O{-}Mn(salen)OIPh]^{2+}$; the latter acts as a reservoir species for parking the catalytically active complex in a more persistent form [Eq. (1)]. In addition to the analytical detection of the $[O{=}Mn^{V}(salen)]^+$ cation, we were able to demonstrate that $[O{=}Mn(salen)]^+$ displays oxygen-transfer reactivity with respect to suitable substrate molecules (olefins, sulfides).[30, 31]

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

μ-Oxomanganese(iv) complexes without terminal ligands or with acetonitrile instead of iodosobenzene were conspicuously absent in all the mass spectra recorded. Since acetonitrile binds readily to the .$[Mn^{III}(salen)]$ complex and can only be removed by applying moderate tube lens potentials (>40 V), we came to the conclusion that *μ*-oxo bridged species have to be coordinated by much better ligands in order to increase their lifetimes in solution to a level, at which they become detectable by ESMS. Iodosobenzene is clearly efficient in stabilizing a *μ*-oxo complex,[32] 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 been widely used as ligands for manganese–porphyrin and salen complexes.[16, 33] Since amine *N*-oxides are much poorer oxidants as compared with PhIO, the best method to prepare relatively stable *μ*-oxo complexes was found in the mixing of $[Mn^{III}(salen)]^+$ and the amine *N*-oxide (≈1:10) in a slurry of iodosobenzene in acetonitrile. A representative spectrum of the electrosprayed supernatant solution with *p*-CN–$C_6H_4NMe_2O$ as the ligand is shown in Figure 1. The species that appear most prominently

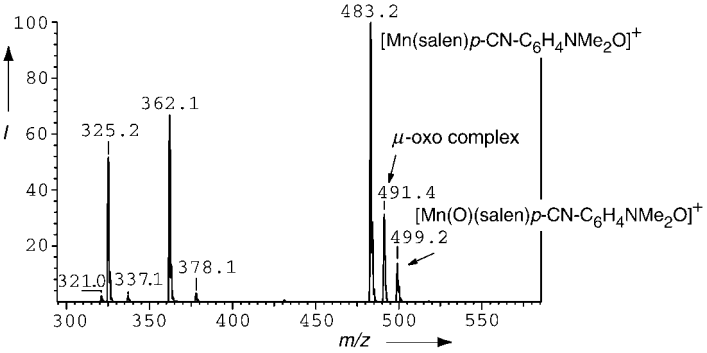

Figure 1. Electrospray mass spectrum of a solution of $[Mn(salen)]ClO_4$, *p*-CN-*N*,*N*-dimethylaniline *N*-oxide, and iodosobenzene in acetonitrile; this shows the formation of *N*-oxide ligated manganese(iii) and oxomanganese species.

in the spectrum are $[Mn^{III}(salen)p\text{-}CN{-}C_6H_4NMe_2O]^+$ (*m*/*z*: 483), $[Mn^{V}{=}O(salen)p\text{-}CN{-}C_6H_4NMe_2O]^+$ (*m*/*z*: 499), and $[p\text{-}CN{-}C_6H_4NMe_2O(salen)Mn^{IV}{-}O{-}Mn^{IV}(salen)OMe_2N\text{-}p\text{-}CN{-}C_6H_4]^{2+}$ (*m*/*z*: 491). The signal at *m*/*z*: 325 is due to the H^+-bridged *N*-oxide adduct $[p\text{-}CN{-}C_6H_4NMe_2O{-}H{-}ONMe_2\text{-}p\text{-}CN{-}C_6H_4]^+$. Amine *N*-oxides apparently are much better ligands than iodosobenzene or acetonitrile, which are both displaced, and they are very effective in stabilizing the *μ*-oxo bridged manganese(iv) complexes.

Effects of electronic tuning of the salen ligand: The possibility to generate and stabilize a species too reactive to be detectable in condensed phases tempted us to extend our experiments to study electronic effects of salen substituents on the reactivity of the catalytically active oxomanganese(v) species. Evidently, the way to probe the influence of electronic tuning, namely CID (collision-induced dissociation) threshold measurements[34] of differently substituted $[Mn^{III}(salen)\cdot PhIO]$ adducts, was precluded by the sheer size of the molecules. In the case of the cyclometallation reaction $[CpIr(PMe_3)(CH_3)]^+ \rightarrow [CpIr(\eta^2\text{-}CH_2PMe_2)]^+ + CH_4$, we were able to demonstrate that reliable thermochemical data can be obtained by CID threshold measurements with our experimental setup,[28b] but it also became clear from this study that the number of degrees of freedom and the quality of the frequencies obtained from quantum chemical calculations needed for the RRKM (Rice – Ramsperger – Kassel – Marcus) correction pose a serious problem when solution-phase species with a full ligand sphere are studied.

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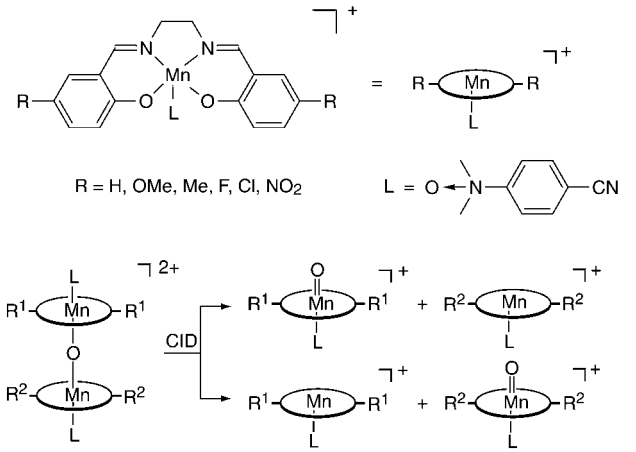
The presence of the μ-oxomanganese(IV) complexes led us to devise an alternative experiment to assess substituent effects on the reactivity of the Mn=O species. When a dinuclear μ-oxo complex with different salen ligands on each side is fragmented, the ratio of the resulting two oxomanganese(V) complexes (and, accordingly, the corresponding Mn^{III}(salen) fragments) will reflect their kinetic stability (Scheme 2). On the assumption that the reverse barrier for



Scheme 2. Possible fragmentation products upon CID of μ-oxomanganese(IV)–salen complexes with salen ligands with different substituents in the 5- and 5′-positions.

both reaction channels is roughly equal, entropic factors cancel out, and the energy distribution of the reactant ions can be approximated by a Boltzmann distribution; the observed difference in kinetic stability will reflect the difference in thermodynamic stability as well (the assumptions used for the evaluation of the branching ratios and the physical background on which they are based are specified in the Supporting information).[35] Thus, it is possible to establish an ordering of the relative stabilities of oxomanganese(V)–salen complexes; this stability depends on the electronic influence of the salen substituents.

It is known from the literature that substituents in the 5- and 5′-positions of the salen ligand strongly perturb the redox properties of [metal(salen)] complexes.[36] We chose the following salen derivatives for our studies: 5,5′-dinitro-, 5,5′-difluoro-, 5,5′-dichloro-, 5,5′-dimethyl-, 5,5′-dimethoxy-, and the unsubstituted salen itself. The results of the fragmentation of the "mixed" μ-oxo complexes are shown in Table 1. The destabilizing effect on the oxomanganese(V) complex is in the following order: $NO_2 > Cl \cong H > F > CH_3 > OMe$. The net effect of the 5,5′-dichloro-substituted ligand as compared with the unsubstituted salen is zero within the limits of experimental error. With the electron-donating substituents, the 5,5′-dimethyl-oxomanganese(V) complex is twice as stable as the unsubstituted one. The maximum stability is achieved by the 5,5′-dimethoxy substitution, which yields an oxomanganese(V) species fifteen times more stable than the unsubstituted salen complex (Figure 2). A small stabilizing effect was found with the 5,5′-difluorosubstituted salen. Conversely, substitution with electron-withdrawing groups decreases the stability of the oxygen transferring species markedly. The dinuclear μ-oxo complex with the 5,5′-dinitrosubstituted salen can only be seen right after mixing with amine *N*-oxide/PhIO and disappears within seconds from the spectrum. Accordingly, the formation of mixed dinuclear complexes with 5,5′-dinitrosalen is very difficult to detect, and we found them to be too short-lived for conducting fragmentation experiments.

Table 1. Branching ratios (I_R/I_H) and differences in activation energies for the two principal pathways of the dissociation of the "mixed" μ-oxo complex. A value >1 indicates a stabilizing effect of the substituent on the oxomanganese(V) species.

Substituent	OMe	Me	F	H	Cl	NO_2[a]
I_R/I_H	14.6	2.16	1.39	(1)	1.03	–
	±2.6	±0.16	±0.10		±0.11	
σ_p^+	−0.78	−0.32	−0.07	0	0.11	0.79
ΔE	3.93	1.56	0.35	0	−0.55	(−3.98)

[a] The branching ratio could not be determined due to the extremely fast decay of the μ-oxo complex.

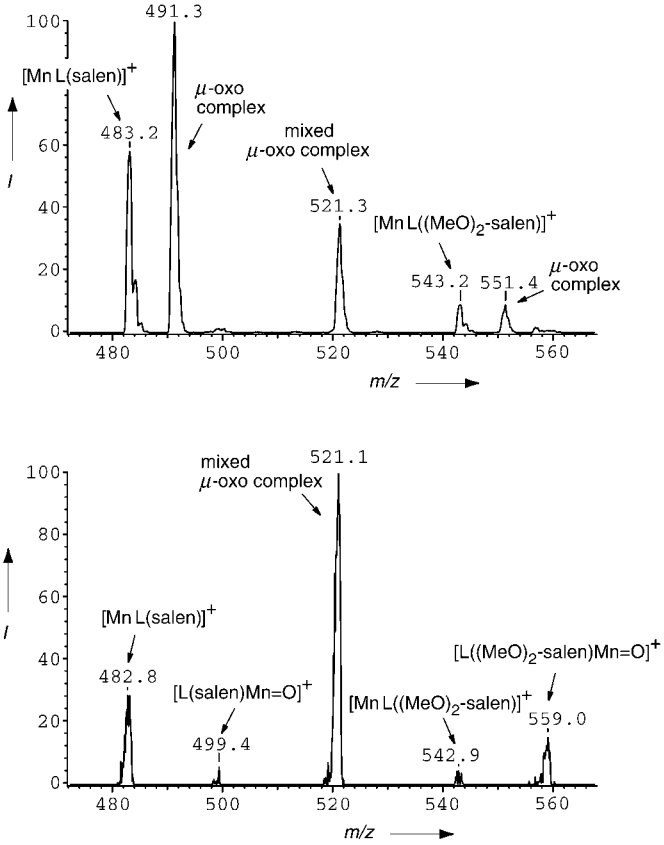


Figure 2. Top: electrospray mass spectrum of a solution of $[Mn((MeO)_2$–salen$)]ClO_4$, $[Mn(salen)]ClO_4$, *p*-CN-*N*,*N*-dimethylaniline *N*-oxide, and iodosobenzene in acetonitrile, and this shows the formation of homogeneous and mixed μ-oxo complexes with terminal *N*-oxide ligands; bottom: daughter-ion spectrum (0.09 Pa Ar, collision energy 34 eV) of the mixed dinuclear complex $[L((MeO)_2$–salen$)Mn$–O–Mn-(salen)$L]^{2+}$ (*m*/*z*: 521, L = *p*-CN-*N*,*N*-dimethylaniline *N*-oxide), and this shows both the fragmentation to $[MnL((MeO)_2$–salen$)]^+$ (*m*/*z*: 543) and to the corresponding oxo complex (*m*/*z*: 559).

The product yields in the fragmentation experiments reflect the trend in stability of the oxomanganese(V) ions that one would conceive intuitively when one considers the electronic

properties of the substituted salen ligands. The Mn=O moiety in these high-valent complexes is stabilized by electron-donating and destabilized by electron-withdrawing substitutents. This result can easily be rationalized by the electron deficiency imposed on the manganese center upon oxidation to Mn^{V}=O. The differences in stability derived from gas-phase experiments are quite pronounced. The ordering of the substituent effects suggests an underlying linear free energy relationship. When we plotted $\ln(k_1/k_2)$ versus Hammett parameters found in the literature, the best correlation was obtained with the σ^+ values given by H. C. Brown et al. (Figure 3).[37] These electrophilic substituent constants are

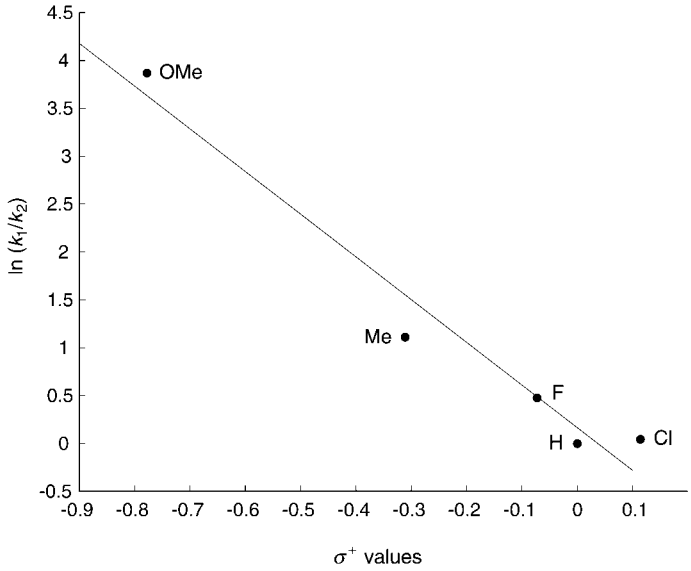


Figure 3. Correlation of the branching ratios of "mixed" μ-oxomanganese(IV)–salen complexes and σ^+ values of the 5,5′-substituents.

based on the solvolysis of *tert*-cumyl chlorides, that is, for reactions, in which an electron-donating group interacts with a developing positive charge in the transition state. The good correlation with the σ^+ values in our experiments can be rationalized by the analogy between a developing carbocation and the increase in oxidation state of the manganese center in the course of the fragmentation.

Two different approaches have been taken in order to relate the experimental branching ratio of *one* dissociation reaction to absolute differences in activation energy (see Supporting information). Based on the linear free energy relationship displayed in Figure 3, all the remaining dissociation energies can be interpolated. The thermochemistry of the homodesmotic reaction shown in Equation (2) reflects the energy

$$[Mn(salen)]^+ + [O{=}Mn(5,5'\text{-}(CH_3)_2{-}salen)]^+ \longrightarrow [O{=}Mn(salen)]^+ + [Mn(5,5'\text{-}(CH_3)_2{-}salen)]^+ \quad (2)$$

difference of the transition states of the two possible fragmentation pathways. For an accurate determination of the thermochemistry, the hybrid Hartree–Fock/density functional method (B3LYP) together with the 6–311G* basis set was employed. The fully optimized structures of reactants and products are shown in Figure 4.[38]

In an alternative approach, the energetics of the dissociation reaction (Scheme 2) have been calculated using a statistical model of the collision process and of the unimolecular reaction kinetics (see Supporting information for details). The DFT (density functional theory) calculation gave a difference between the activation energies of 5.0 kJ mol^{-1}, whereas the statistical kinetic model gave an energy difference of 2.3 kJ mol^{-1}. The DFT calculations should give a very accurate description of the thermochemistry as a result of the high level of theory employed and the homodesmotic nature of the reaction. The kinetic model, on the other hand, provides an approximate lower boundary for the energy differences by treating the dication as an ideally ergodic system. However, the major substructures (Mn(salen), terminal ligands) are only linked by Mn–O bonds and thus probably weakly coupled. Because of the approximations used in the statistical model, we are inclined to favor the energetics derived from the DFT calculation.

How do our results (displaying the "intrinsic" reactivity of the active catalyst) compare with those for the reactivity in solution? It was recognized at an early stage by Kochi that [Mn(salen)] complexes with electron-donating substituents, such as the 5,5′-dimethoxy derivative, give only poor yields of epoxide, whereas the catalyst with 5,5′-dinitro substituents gave the best product yields.[16] While the reactivity differences seen with differently substituted achiral salens suggest

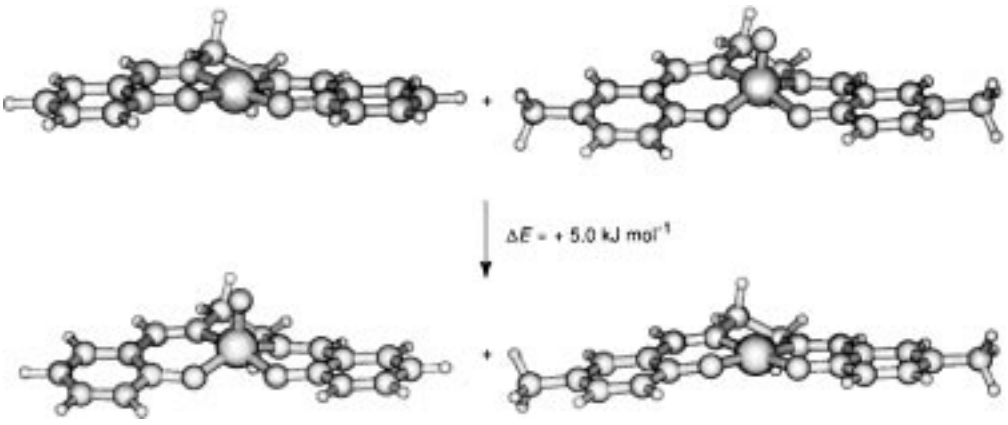


Figure 4. B3LYP/6–311G* structures of the manganese(III) and oxomanganese(V)–salen complexes of the homodesmotic reaction given in Equation (2).

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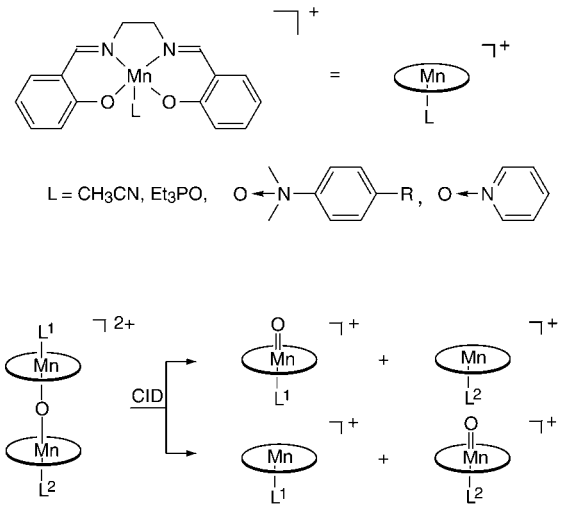
that the more electron-deficient ligand will give the more effective catalyst, the interplay between epoxidation efficiency and selectivity is much more subtle and less predictable for asymmetric epoxidation. In 1991, Jacobsen reported the dramatic effects of electronic tuning, that is, using different substituents in the *para*-position to the ligating oxygens (5,5′-disubstitution), on the enantioselectivity of the [Mn(salen)] catalyzed epoxidation of *cis*-disubstituted olefins.[39] In a more recent account, Jacobsen and co-workers systematically investigated the correlation between enantioselectivity and the electronic character of the Jacobsen catalyst by varying the substituents in the 5,5′-positions (NO_2, Cl, H, Me, and OMe).[40] In all cases, electron-donating groups on the catalyst were found to give higher enantioselectivities in epoxidation, whereas electron-withdrawing substitutents led to decreased enantioselectivity. The possibility that the substitutents might induce conformational distortions in the oxygen transferring complexes or provoke changes in the Mn–O bond lengths and thus in the substrate–ligand interactions was dismissed as highly improbable by these authors. Instead, the electronic effect on the enantioselectivity was attributed to changes in the reactivity of the Mn^{V}=O moiety.

Our gas-phase experiments provide the first direct probe for the intrinsic properties of the reactive intermediates in the Jacobsen–Katsuki epoxidation. The intermolecular experiment, in which the two metal centers in the "mixed" μ-oxo complex compete for the bridging oxygen atom, provides us with a direct measure of the oxygen-transfer capabilities of the oxomanganese(v) species, without the need for an olefinic substrate. We have shown that electron-donating substituents indeed stabilize the oxomanganese(v) moiety, which should attenuate its reactivity and give a relatively milder oxidant. Electron-withdrawing substituents, on the other hand, destabilize the oxomanganese(v) moiety and make it a more reactive oxidant. Accordingly, the milder oxidant, which delivers the oxygen to the substrate in a more product-like transition state, will achieve a higher degree of stereochemical communication between substrate and catalyst, whereas the more reactive oxidant's differentiation of the diastereomeric transition structures will be much poorer. The analogous trends in the reactivities seen in solution-phase and in our gas-phase stability measurements indicate that the mechanism of oxygen transfer to the substrate in solution is primarily governed by the intrinsic reactivity of the oxomanganese(v) complexes.

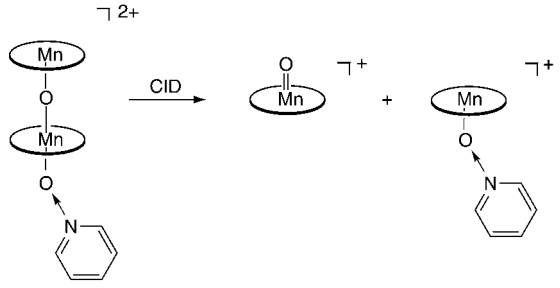
Effects of axial ligands: The reactivity of salen catalysts in epoxidation reactions cannot only be tuned by substitution of the salen, but also by adding donor ligands to the reaction mixture.[14, 17] The question arises whether or not donor ligands directly modulate the reactivity of the oxygen transferring species by ligation.[33, 41] The methodology employed by us for the investigation of electronic influences on the stability of the oxomanganese(v) complexes can be extended to study the effects of additional axial ligands. For this purpose, a μ-oxomanganese(iv) complex with two different terminal ligands has to be prepared, which upon fragmentation will give rise to two differently ligated Mn^{V}=O species (Scheme 3). This experiment provides us with a direct probe for possible stabilizing/destabilizing effects of donor ligands on the Mn=O moiety. The following ligands were studied: *p*-CN-*N*,*N*-dimethylaniline *N*-oxide, *p*-Me-*N*,*N*-dimethylaniline *N*-oxide, *p*-Br-*N*,*N*-dimethylaniline *N*-oxide, *N*,*N*-dimethylaniline *N*-oxide, acetonitrile, pyridine *N*-oxide, and triethylphosphine oxide.



Scheme 3. Possible fragmentation products upon CID of μ-oxomanganese(iv)–salen complexes with two different terminal ligands on each side.

The first axial ligand studied was pyridine *N*-oxide. Kochi had already reported the use of pyridine *N*-oxide in manganese- and chromium–salen catalyzed epoxidations, which resulted in a significant enhancement of epoxide yields.[14, 16] By carefully adjusting the stoichiometry of the in situ mixture of $[Mn^{III}(salen)]ClO_4$, iodosobenzene, and pyridine *N*-oxide as well as the spraying conditions, we succeeded in generating the asymmetrical dinuclear μ-oxo complex $[pyO(salen)Mn–O–Mn(salen)]^{2+}$ (m/z: 376.5) in the gas phase. The primary fragmentation products observed are $[Mn{=}O(salen)]^{+}$ (m/z: 337) and $[Mn^{III}pyO(salen)]^{+}$ (m/z: 416), with no traces of alternative fragmentation detectable (Scheme 4). Fragmentation of the bridging μ-oxo bond takes place exclusively on the side where the terminal ligand is bound.

The relative destabilizing effects of different amine *N*-oxides on the Mn–oxo moiety can be seen from the fragmentation of the μ-oxomanganese(iv) complex with *p*-CN-*N*,*N*-dimethylaniline *N*-oxide and pyridine *N*-oxide, re-



Scheme 4. Fragmentation of the asymmetrical μ-oxo complex $[(salen)Mn–O–Mn(salen)Opy]^{2+}$ upon CID.

spectively, as terminal ligands (Figure 5). Fragmentation of the Mn–O bond occurs predominantly on the side where the aniline *N*-oxide is bound; this means that pyridine *N*-oxide is much less destabilizing and should thus be the less effective

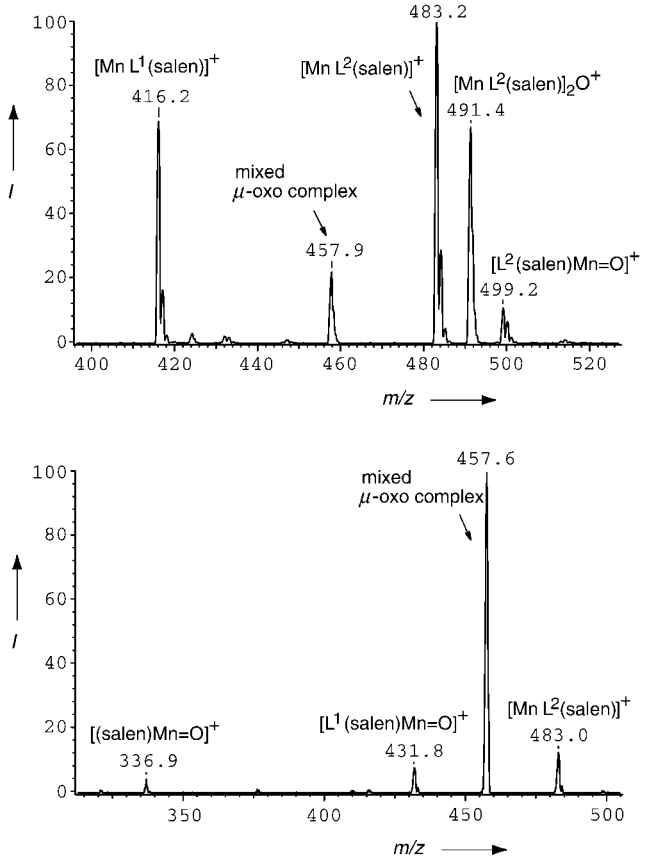


Figure 5. Top: electrospray mass spectrum of a solution of [Mn(salen)]-ClO_4 and iodosobenzene with pyridine *N*-oxide and *p*-CN-*N*,*N*-dimethylaniline *N*-oxide in acetonitrile; bottom: daughter-ion spectrum (0.08 Pa Ar, collision energy 14 eV) of the dinuclear μ-oxo complex $[L^1(salen)Mn–O–Mn(salen)L^2]^{2+}$ (*m*/*z*: 457.5, L^1 = pyridine *N*-oxide, L^2 = *p*-CN-*N*,*N*-dimethylaniline *N*-oxide), and this shows exclusive fragmentation to $[MnL^2(salen)]^+$ (*m*/*z*: 483) and to the oxo complex $[L^1(salen)Mn{=}O]^+$ (*m*/*z*: 432).

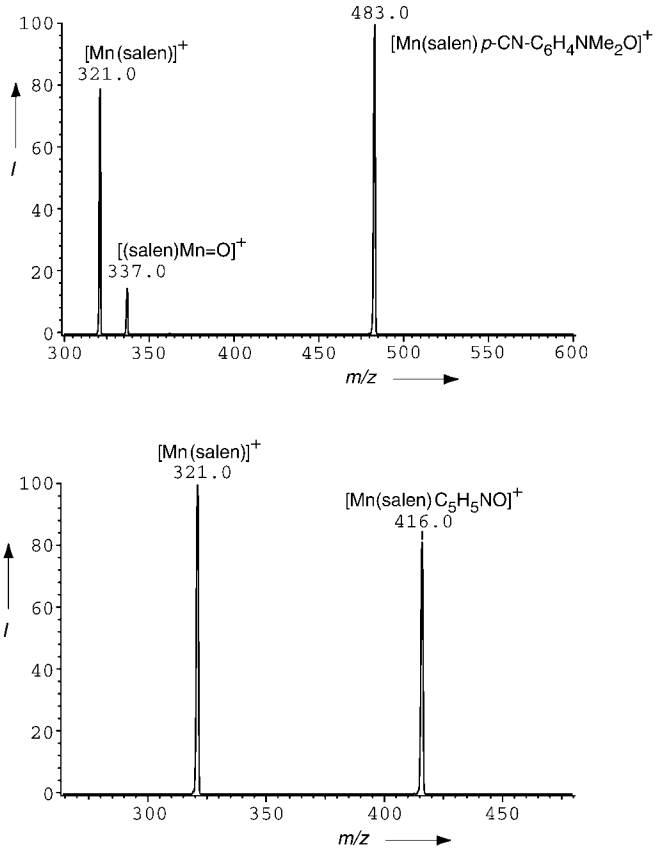


Figure 6. Top: daughter-ion spectrum (0.13 Pa Ar, collision energy 20 eV) of $[p\text{-}CN–C_6H_4NMe_2O–Mn^{III}(salen)]^+$, and this shows fragmentation of the Mn–O as well as of the N–O bond; bottom: daughter-ion spectrum (0.13 Pa Ar, collision energy 20 eV) of $[Mn^{III}(pyO)(salen)]^+$, and this shows exclusive loss of pyridine *N*-oxide.

promoter for oxidation catalysis. *N*,*N*-dimethylaniline *N*-oxide and its derivatives are not only capable of oxygen transfer to manganese–porphyrin,[42] but also to manganese–salen complexes (see Figure 6 top), albeit less efficiently than iodosobenzene.[43] Pyridine *N*-oxide, on the other hand, does not transfer oxygen to Mn–salen complexes, as can be seen from the fragmentation depicted in Figure 6 (bottom). The only loss observed is that of pyridine *N*-oxide (95 mass units). The alternative fragmentation of the N–O bond cannot be detected even at collision energies of up to 50 eV.

The surprisingly big difference in destabilization between *p*-CN-*N*,*N*-dimethylaniline *N*-oxide and pyridine *N*-oxide prompted us to test *N*,*N*-dimethylaniline *N*-oxides with different substituents in the *para*-position. As can be seen from Table 2, the only ratio significantly deviating from 1 comes from the competition experiment between the *p*-CN and the *p*-Br derivatives. As the site of substitution is far removed from the site of coordination, the ratios of ≈ 1 between the Br-, Me-, and H-substituted aniline *N*-oxides are not unexpected. A small but significant difference is observed between *p*-CN-*N*,*N*-dimethylaniline *N*-oxides and Et_3PO; the latter also acts as a promoter in metal–salen catalyzed epoxidations.[14] Triethylphosphine oxide binds very strongly to $[Mn^{III}(salen)]^+$ and has only a slightly less destabilizing effect on the Mn=O moiety than *p*-CN-*N*,*N*-dimethylaniline *N*-oxide. As a result of the very strong P=O bond, however, the phosphine oxide does not transfer oxygen to the metal center.

Table 2. Branching ratios (I_{L1}/I_{L2}) for the two principal pathways of the dissociation of the "mixed" μ-oxo complex with two different terminal ligands (L^2 = *p*-$CN–C_6H_4NMe_2O$). A value >1 indicates a stabilizing effect of the terminal ligand on the Mn=O moiety with respect to the reference ligand L^2.

Ligand	$C_6H_5NMe_2O$	*p*-$Br–C_6H_4NMe_2O$	*p*-$Me–C_6H_4NMe_2O$[a]	Et_3PO	pyO
I_{L1}/I_{L2}	1.12 ±0.17	1.30 ±0.13	1.30 ±0.15	1.33 ±0.12	>10

[a] Value extrapolated from a competition experiment against L^2 = *p*-$Br–C_6H_4NMe_2O$ because of overlap between parent and daughter peaks in the daughter-ion spectrum of $[p\text{-}Me–C_6H_4NMe_2O(salen)Mn–O–Mn(salen)OMe_2N\text{-}p\text{-}CN–C_6H_4]^{2+}$.

The following picture emerges from our electrospray MS data. Since we have never detected μ-oxo complexes without terminal ligands in the in situ mixtures, we conclude that the additional axial ligands strongly promote formation of

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dinuclear complexes. This can easily be rationalized by regarding the formation of the μ-oxomanganese(IV) species as a partial oxygen transfer from $[L(salen)Mn{=}O]^+$ to $[MnL(salen)]^+$. As evidenced in our stability measurements, axial ligands enhance the oxygen-transfer capability and thus the formation of dinuclear μ-oxo complexes. The conproportionation can be viewed as an escape route for the extremely reactive oxomanganese(V) species to "hide" in a more persistent form. After disproportionation of the dinuclear complex, that is, after the release of $[L(salen)Mn{=}O]^+$, the coordinating ligand stays at the metal center and will now promote the reactivity of the catalyst in the epoxidation (or in the back reaction to the μ-oxo complex).

Conclusion

Electrospray ionization tandem mass spectrometry is a convenient approach to the study of transition metal catalyzed reactions and reactive intermediates that are too elusive for solution-phase characterization, as has been demonstrated for the oxomanganese–salen complex $[O{=}Mn(salen)]^+$. Once in the gas phase, reactivity studies of species that have so far escaped any solution-phase characterization can be conducted both qualitatively as well as quantitatively. As shown for electronic and ligand effects on oxomanganese(V)–salen complexes, insight into the intrinsic reactivity of transient species can be gained far beyond the limits of solution-phase techniques. The similarities and the differences between the observed gas-phase and solution-phase chemistry will then yield the information that is necessary to dissect the complex mechanisms of transition metal catalysis.

Experimental Section

Materials: Diacetoxyiodobenzene, pyridine *N*-oxide, 5-chloro-2-hydroxybenzaldehyde, 5-methyl-2-hydroxybenzaldehyde, 5-methoxy-2-hydroxybenzaldehyde, and 5-nitro-2-hydroxybenzaldehyde were purchased from Aldrich and Fluka, respectively, while 5-fluoro-2-hydroxybenzaldehyde was obtained from Melford Laboratories (UK). Triethylphosphine oxide was obtained from Strem. Acetonitrile (HPLC grade quality) for the preparation of the electrospray solutions was purchased from Fluka.

Synthesis of salen ligands: Salen (*N*,*N*′-bis(salicylidene)ethylene diamine) was bought from Fluka and used as received. The 5,5′-substituted salen ligands were synthesized from the respective aldehydes and ethylene diamine according to the procedure given by Jacobsen et al.[44] All spectra matched the analytical data given in the literature. The 5,5′-difluorosalen ligand has so far not been described in the literature.

N,N′-Bis(5,5′-difluorosalicylidene)ethylene diamine (*5,5′-Difluorosalen*): Yield 50%. M.p. 205–206.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.32$ (s, 2H; ArCH=N), 6.89–7.05 (m, 6H; Ar), 3.98 (4H; NCH_2CH_2N); IR (KBr pellet): $\tilde{\nu} = 3447$(w), 2939(w), 2909(w), 2853(w), 1634(s), 1498(s), 1364(m), 1140(m), 831(m), 702(s) cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{14}N_2O_2F_2$ (304.3): C 63.15, H 4.64, N 9.21; found C 63.09, H 4.77, N 9.01.

Synthesis of manganese(III)–salen complexes: The manganese(III)–salen complexes were prepared either following the procedure of Kochi et al.[16] ($[Mn(5,5'\text{-dinitrosalen})]PF_6$ and $[Mn(5,5'\text{-difluorosalen})]PF_6$) or the procedure of Jacobsen et al.[44] [(Mn(salen)]Cl, [Mn(5,5′-dimethoxysalen)]Cl, [Mn(5,5′-dimethylsalen)]Cl, and [Mn(5,5′-dichlorosalen)]Cl). In the case of manganese(III)PF_6^- salts, the electrospray solutions were prepared by dissolving the salt in CH_3CN and diluting to 10^{-5} M concentration. Solutions of the chlorides in acetonitrile were treated with an equimolar amount of silver perchlorate and stirred for fiveteen minutes. After removal of AgCl by filtration, the solution was diluted to 10^{-5} M.

Synthesis of para-substituted dimethylaniline N-oxides: Dimethylaniline *N*-oxide, *p*-CN-dimethylaniline *N*-oxide, *p*-methyl-dimethylaniline *N*-oxide, and *p*-Br-dimethylaniline *N*-oxide were prepared according to the procedure of Cymerman Craig and Purushothaman[45] by MCPBA (*m*-chloroperoxybenzoic acid) oxidation of the respective *N*,*N*-dimethylanilines (all bought and used as received from Fluka). All *N*-oxide spectra matched the analytical data given in the literature. For the experiments with terminal ligands, the amine *N*-oxide or Et_3PO was used in a tenfold excess with respect to the manganese complex. Solutions that contained μ-oxomanganese–salen complexes were prepared by adding stock solutions (10^{-3} M in CH_3CN) of the terminal ligand to a suspension of iodosobenzene in acetonitrile, and then adding the manganese(III)–salen salt just prior to electrospray.

Instruments: For the mass spectrometric measurements, the slightly modified Finnigan MAT TSQ7000 electrospray tandem mass spectrometer described previously[28b] (octopole, quadrupole, octopole, quadrupole setup) was used. The first octopole was fitted with an open cylindrical sheath around the rods into which a collision gas could be bled for thermalization or reaction up to 2.5 Pa.

General ESMS setup for the experiments: All quantitative measurements were carried out in daughter-ion mode, that is, 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 was operated in scanning mode in order to detect the ionic fragments. The collision energy could be varied by applying different potentials (to a lens in front of the second octopole), which altered the velocity of the ions on their way into the collision region (the collision energies are given in eV, lab frame). The incoming ions were thermalized in the first octopole with argon at a pressure of $\approx$1.3 Pa and at a temperature of 70 °C. The tube lens was typically operated at 70 V (referenced to m/z: 500).

Determination of branching ratios

CID of complexes of the type $[p\text{-}CN\text{-}C_5H_4NMe_2O(salen)Mn{-}O\text{-}Mn(5,5'\text{-}R_2{-}salen)OMe_2N\text{-}p\text{-}CN\text{-}C_5H_4]$: A set of 122 separate measurements of $[p\text{-}CN\text{-}C_5H_4NMe_2O(salen)Mn{-}O{-}Mn(5,5'\text{-}(CH_3)_2{-}salen)OMe_2N\text{-}p\text{-}CN\text{-}C_5H_4]^{2+}$ was taken at collision energies ranging from 4–44 eV (lab frame, collision gas Ar, that is, 0.15–1.68 eV in c.o.m. frame) and from 4–24 eV (lab frame, collision gas Xe, that is, 0.46–2.76 eV in c.o.m. frame), respectively, in order to obtain information about the collision-energy dependence and the statistical errors of the experiments. The collision gas was at a pressure of 0.027 Pa as measured by a cold cathode gauge. Additional measurements at 0.013 and 0.007 Pa yielded the same branching ratios. The measurements of the remaining mixed dinuclear μ-oxo complexes were conducted at a pressure of 0.027 Pa Ar and 34 eV collision energy (lab frame). Under these conditions, the total fragment yield was about 10%, and secondary fragmentation products were only present in negligible amounts. Spectra were added in the course of 2–3 minutes at a rate of one scan per second. Please note that the CID spectra shown in Figures 2 and 5 were recorded at significantly higher gas pressures (0.07–0.13 Pa Ar) in order to represent all different parent and fragment peaks in an adequate size.

For the calculation of the branching ratio, the ratio between the intensities of the manganese(III) fragment masses corresponding to $[p\text{-}CN{-}C_5H_4NMe_2O{-}Mn(5,5'\text{-}R_2{-}salen)]^+$ and $[p\text{-}CN{-}C_5H_4NMe_2O{-}Mn(salen)]^+$ was chosen. To account for the secondary fragmentation products $[Mn(5,5'\text{-}R_2{-}salen)]^+$ and $[Mn(salen)]^+$ derived from the loss of the terminal ligand, the total ion yield for each channel was calculated by adding the intensity of the secondary fragment to its respective parent. The branching ratio of every experiment was assigned a statistical weighting factor proportional to the total fragment intensities in order to calculate mean values.

CID of complexes of the type $[L^1(salen)Mn{-}O{-}Mn(salen)L^2]^{2+}$: The branching ratio was calculated from the intensities of $[Mn(salen)L^1]^+$ and $[Mn(salen)L^2]^+$. In contrast to the experiments with different salen ligands on each side of the μ-oxo complex, the ratio could not be corrected for secondary fragmentation products in this case, as loss of the terminal ligand led to the same product $[Mn(salen)]^+$ for both channels. The experimental conditions were chosen such that the $[Mn(salen)]^+$ peak intensity never

exceeded 5% of the primary fragment intensities. In the case of acetonitrile or pyridine *N*-oxide, there was an additional reaction channel, and this yielded an asymmetrical $[(salen)Mn{-}O{-}Mn(salen)L]^{2+}$ fragment by dissociation of one of the terminal ligands. Those species could also be obtained in high enough intensities to conduct CID experiments by applying higher tube lens potentials ($\approx$90 V). The CID experiment on $[(salen)Mn{-}O{-}Mn(salen)NCCH_3]^{2+}$ turned out to be inconclusive, since the only fragment mass which can be unambiguously assigned to a specific reaction channel corresponded to $[Mn(salen)(NCCH_3)]^+$, which was only a minor peak in the spectrum.

Computational methods: Quantum chemical calculations for the compounds shown in Figure 4 have been performed using the Gaussian94 series of programs[46] on DEC Alpha 8400 computers at ETH Zürich. The quintet and triplet ground states of the manganese(III) and manganese(V) complexes, respectively, were fully optimized without symmetry constraints using the hybrid Becke3 Lee – Yang – Parr (B3LYP) exchange correlation functional.[47] A 6 – 311G* valence triple zeta + polarization basis set was used. The structure and energy of $[O{=}Mn(salen)]^+$ have been reported in a previous account.[31]

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