Laser Flash Photolysis Study of Jacobsen Catalyst and Related Manganese(III) Salen Complexes. Relevance to Catalysis

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Abstract: The laser flash photolysis and emission properties of a set of five-coordinate manganese(III) Schiff−base complexes have been examined. In contrast to the intramolecular electron transfer between Mn^{3+} and the equatorial salen ligand reported to occur in the absence of axial coordination, our laser flash photolysis study has shown that the reactivity of the respective excited states is appreciably influenced by the electron donor strength of the apical ligand at the metal center. In fact, homolytic and heterolytic photocleavage of the metal−ligand apical bond can be the most important processes upon laser excitation, their relative contribution being influenced by medium effects and the σ-charge donation of the axial ligand. On the other hand, the detection of reactive intermediates such as the oxomanganese(V) salen complex (λ_{max} 530 nm) by laser flash photolysis opens the way to apply this fast detection technique to the study of reaction mechanisms in catalysis by metallic complexes. As a matter of fact, quenching of oxomanganese(V) salen by simple alkenes has been observed by laser flash.

Introduction

Manganese(III) salen complexes have been the subject of intensive investigations over the past years, reflecting that they are excellent catalysts for the chiral and achiral epoxidation of alkenes.[1,2] In sharp contrast, there is a paucity of reports dealing with the photochemistry of manganese complexes in general, and specifically the photochemical and photophysical properties of the pentacoordinate manganese salen commonly used in catalysis remain unexplored. From the limited information available on related complexes, it has been rationalized that the emission mechanism of Mn(II)-bipyridine complexes immobilized in different zeolites involves a charge-transfer [Mn(III)-bipyridine[•−]] excited state from which luminescence is observed.[3] Excited states of similar nature, generated upon irradiation of chiral Mn(II) salen complexes within the cavities of zeolite Y, are reported to be enantioselectively quenched by chiral 2-butanols.[4] In both cases, light is able to instantaneously generate a reactive metallo fragment within the polar environment of the zeolite.

Likewise, a product study on the photochemical decomposition of four-coordinate cationic Mn(III) Schiff base complexes has been rationalized assuming a photochemical pathway closely related to those mentioned above for the tetradentate Mn(II) salen complexes. Thus, the photoproducts would be formed through an initial intramolecular metal−ligand electron transfer that can lead either to oxidative cyclization or to the dimerization of the salen ligand.[5,6]

Interestingly, deactivation of electronic excited states of azido pentacoordinated Mn(III) salen complexes occurs through a redox alternate pathway in which only the metal and the apical azido ligand are mechanistically implicated, while the robust equatorial salen ligand remains unaltered.[7] In fact, photolysis of azidomanganese complexes is a general reaction route to obtain salen-derived nitridomanganese(V) complexes by azide photodenitrogenation and simultaneous oxidation of the metal.[7] Chiral nitridomanganese(V) salen are also relevant complexes in asymmetric catalysis because they can effect the enantioselective aziridation of alkenes.

Taking into consideration the importance in catalysis of pentacoordinate Mn(III) salen complexes, the present work reports the first laser flash photolysis study of the transient UV−vis absorption spectra of a series of salen-derived Mn(III) complexes including the so-called Jacobsen catalyst. Assignment of the photogenerated intermediates is mainly based on the influence of the axial coordinating ligand around the Mn(III) salen moiety on the transient absorption spectra.

Results and Discussion

This study deals with the photochemistry of a set of five-coordinate Mn(III) Schiff base complexes, namely Mn(III)-

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Scheme 1. Preparation of Five-Coordinate Salen-Derived Mn(III) Complexes with Different Axial Ligands
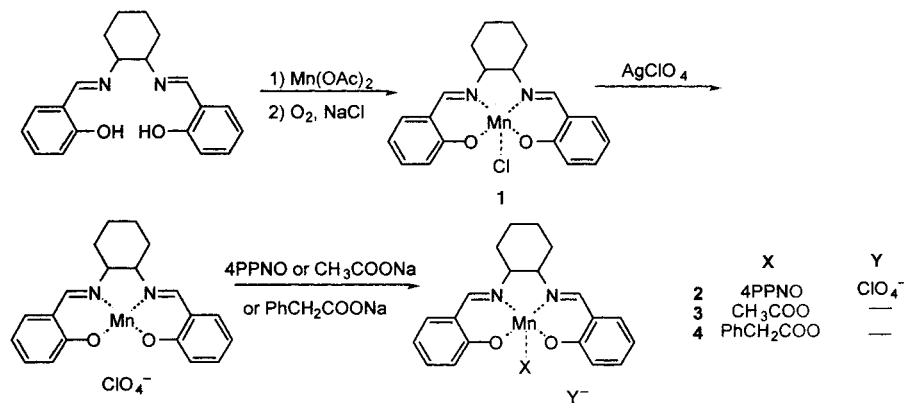
(salchd)Cl **1** [salchd = 1,2-bis(salicylidenimino)cyclohexane], Mn(III)(salchd)(4-phenylpyridine-*N*-oxide)ClO$_4$ **2**, Mn(III)-(salchd)CH$_3$CO$_2$ **3**, and Mn(III)(salchd)PhCH$_2$CO$_2$ **4** (Scheme 1). Complex **1** was synthesized by adding Mn(CH$_3$CO$_2$)$_2$ to previously obtained salchd ligand followed by air oxidation in the presence of chloride ions according to the general procedure reported by Jacobsen for the *tert*-butyl analogues (Scheme 1).[8] The new complexes **2**–**4** were prepared starting from complex **1** by precipitating the apical chloride ligand as AgCl and replacing it by good coordinating anions such as 4-phenylpy-ridine-*N*-oxide (4PPNO), acetate, and phenylacetate.[9] It is worth remarking that other alternate routes for the synthesis of complexes **2**–**4** proved to be much less efficient. For example, direct reaction of Mn(II) salen complex with 4PPNO, or with the sodium salts of acetate and phenylacetate, led predominantly to decomposition of the complexes into brown insoluble solids.

The complexes were isolated in high yields, recrystallized, and characterized by analytical and spectroscopic techniques (see Experimental Section). Thus, the infrared spectra of complexes **1**–**4** showed prominent absorptions in the region around 2900 and 2800 cm^{-1}. This is due to ν(C–H) vibrations of the alkyl groups and two characteristic bands around 1620 and 1540 cm^{-1} that were assigned to C=N and C–O stretching vibrations, respectively.[10] The sharp and intense absorption at 1094 cm^{-1} in the case of complex **2** is within the wavenumber range expected for a ClO$_4^-$ anion not coordinated to manganese (reported strong Cl–O stretching absorption at 1085 cm^{-1}).[11] Thus, the most likely structure of complex **2** can be described as a cationic five-coordinate complex, presumably square pyramidal, where the *N*-oxide is axially coordinated to the metal, and the ClO$_4^-$ is acting as a noncoordinating counteranion. This structure is analogous to those obtained by X-ray diffraction for other related (salen)Mn(III) perchlorate complexes.[12]

The electronic spectra of the complexes were recorded in dichloromethane solutions. The UV–vis spectra of complexes **1**, **3**, and **4** exhibited a broad and featureless absorption that resembled that of the Jacobsen catalyst, with shoulders at 228, 255, and 318 nm (Figure 1). In striking contrast, complex **2** showed three well-defined bands with absorption maxima at 235, 305, and 420 nm, reflecting the stronger contribution of the ligand-centered absorption bands to the global UV–vis absorption spectrum of the complex (Figure 1, spectrum e).
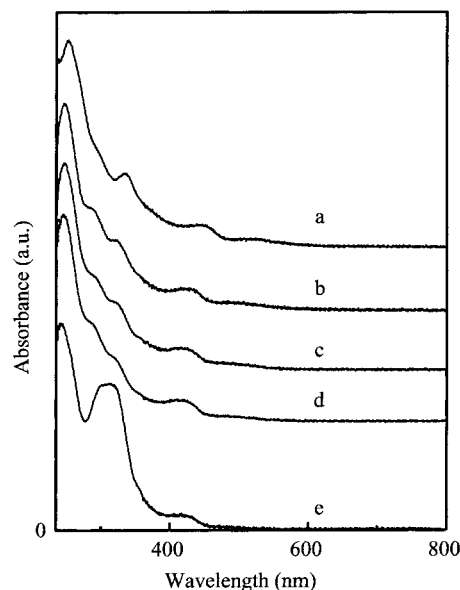
Figure 1. UV–vis absorption spectra of 10^{-3} M dichloromethane solutions of the Jacobsen catalyst (a) and complexes **1** (b), **3** (c), **4** (d), and **2** (e).

The complexes were photolyzed in solution (~10^{-4} M) using the 266 nm output of a pulsed Nd:YAG laser (10 ns, energy/pulse ~14 mJ). Hence, laser flash excitation of a nitrogen-purged dichloromethane solution of **1** or *tert*-butylated Jacobsen catalyst did not lead to the observation of any transient. In contrast, upon 266 nm excitation, the time-resolved changes in the UV–vis spectrum of a deaerated dichloromethane solution of **2** (~10^{-4} M) resulted in the prompt appearance of a transient absorption band with maximum at 410 nm, which decayed following a first-order kinetics (Figure 2). In agreement with literature data for aromatic *N*-oxides, direct laser flash photolysis of 4PPNO did not lead to the observation of any transient.[13] This rules out the possibility that the observed transient spectrum would correspond to a 4PPNO localized state. However, given that intramolecular electron transfer between the metal center and the ligand is a common process in the known photochemistry of metallic complexes, we explored the possibility that the transient observed in the photolysis of complex **2** would correspond to an *N*-oxyl radical generated through electron transfer from the *N*-oxide to Mn(III).[14]

To provide support to the assignment of Figure 2 as a 4PPNO• radical, a photoinduced electron transfer from 4PPNO to the

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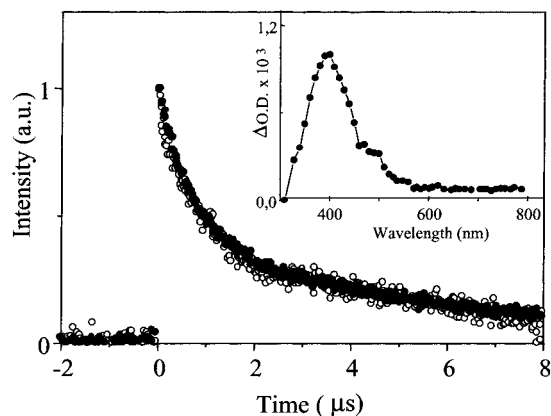
Figure 2. Decay traces of (●) complex **2** in dichloromethane solution under nitrogen monitored at 410 nm after 266 nm excitation and (□) of a dichloromethane solution under nitrogen containing triphenylpyrilium tetrafluoroborate and 4-phenylpyridine-*N*-oxide monitored at the same wavelength after 355 nm excitation. The inset shows the transient spectrum recorded 2 μs after 266 nm laser-pulse excitation of **2** in dichloromethane under nitrogen.

2,4,6-triphenylpyrylium (TP$^+$) excited state was carried out (eq 1).
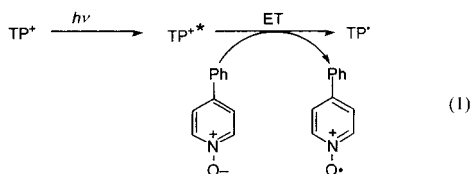
TP$^+$ tetrafluoroborate is a good electron-acceptor photosensitizer upon selective 355 nm laser excitation (a control experiment established that the direct 355 nm photolysis of 4PPNO does not give any transient).[15] Importantly, this TP$^+$-photosensitized photolysis of 4PPNO leads to the same transient spectrum observed for complex **2**. Furthermore, the normalized decays of the transient obtained in dichloromethane through both alternate procedures superimpose exactly. According to eq 1, these results strongly support that the 4PPNO$^\bullet$ radical is the most reasonable assignment for the species observed in the direct photolysis of complex **2** (Figure 2).

Thus, these experimental observations firmly indicate that the prevalent pathway after light absorption is an unprecedented homolytic photocleavage of the exchangeable 4PPNO axial ligand, yielding the corresponding oxygen-centered radical, plus the concurrent (salen)Mn(II) (eq 2).
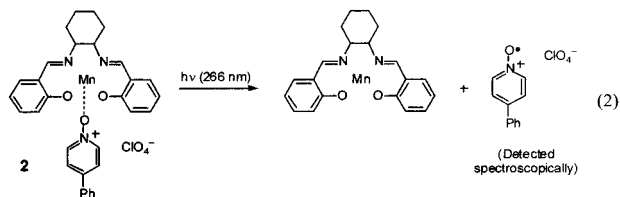
We note that the behavior of 4PPNO in complex **2** contrasts sharply with the tendency of aromatic *N*-oxides to lose atomic oxygen upon direct excitation with no detectable formation of any transient.[13] We note that even though a (salen)Mn(II) complex must be formed concomitantly with the pyridinyloxyl radical, the transient UV−vis spectrum is dominated by the latter, and spectroscopic evidence for the Mn(II) moiety was
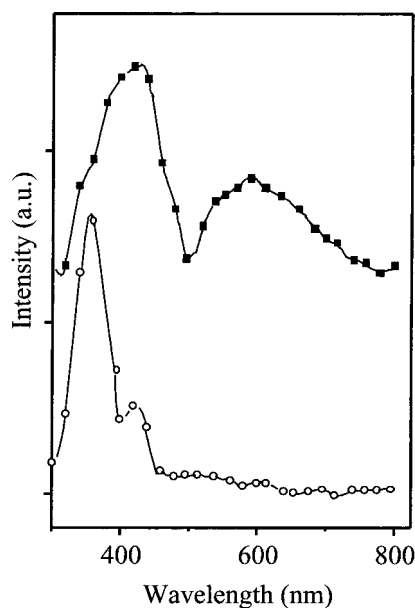
Figure 3. Transient spectra recorded under nitrogen 0.3 μs after 266 nm laser-pulse excitation of complex **3** in dichloromethane (full dots) and acetonitrile (open circles). The spectrum in dichloromethane has been vertically shifted.

not obtained. In this regard, it should be noted that the typical UV−vis absorption spectra of salen manganese complexes are characterized by very broad bands with low extinction coefficients (see for instance Figure 1, spectra a−d, and the explanatory comments above). This type of spectra may be difficult to detect by time-resolved techniques in the presence of other transients having much more intense absorption bands. Examples of photocleavages where only a single fragment is spectroscopically detected are not uncommon in laser flash photolysis.[16]

In view of the photochemical behavior of complex **2** that undergoes homolytic photocleavage of the apical 4PPNO ligand, it is of interest to determine whether this process may be a general pattern for related (salen)Mn(III) complexes coordinated to ligands with a negative oxygen terminus, and if this photoprocess can lead to the generation of proposed intermediates in Mn-salen-catalyzed epoxidations.

The transient spectra of complex **3** in dichloromethane, recorded at two different times after 266 nm laser flash excitation, are shown in Figure 3. At shorter time scales, this spectrum exhibits two absorption bands at 430 and 630 nm, and a shoulder at 360 nm. All these bands decay in the microsecond time scale with different kinetics, indicating that the spectrum corresponds to more than one species. The disappearance kinetics of the 430 nm band can be fitted to a first-order decay with a lifetime of 4.9 μs. In oxygen-saturated dichloromethane, the decay kinetics of the 430 nm band also followed first-order decay kinetics with a much shorter lifetime (0.24 μs), giving an approximate oxygen quenching rate constant of 3.9 × 10^9 M^{-1} s^{-1}. Interestingly, a different transient spectrum with absorption maxima centered at 360 and 430 nm was recorded in acetonitrile (Figure 3). The presence of these two bands indicates that the same two transients observed in dichloromethane are also generated in acetonitrile, but in different proportions. This must reflect the difference in polarity between CH$_2$Cl$_2$ and CH$_3$CN, the more polar intermediate being presumably that characterized by the 360 nm band.

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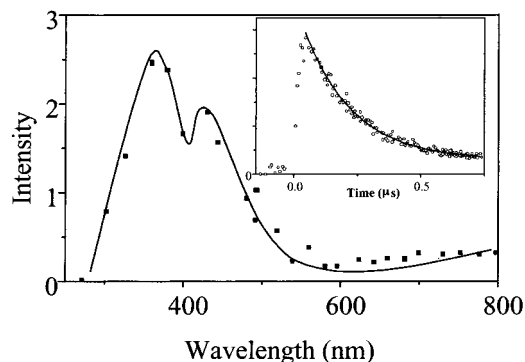
Figure 4. Transient spectrum of Jacobsen catalyst in hexane under nitrogen recorded 1.5 μs after 266 nm laser excitation. The inset shows an initial growth followed by a decay of the ΔO.D. monitored at 450 nm.

It is known that tetracoordinated cationic Mn(III) complexes having the apical position free are characterized by an absorption band at 360 nm tailing beyond 400 nm.[17] Hence, a reasonable assignment for the transient species with absorption maximum at 360 nm observed predominantly in acetonitrile is the cationic Mn(III) complex formed by heterolytic photodetachment of the acetoxy ligand present in complex **3** (eq 3).
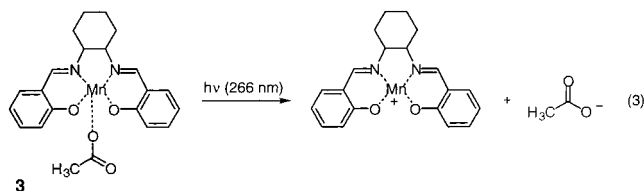
Contrary to what is observed for complex **2**, the fact that the acetoxy ligand or any of the species derived from it does not absorb in the monitored region of the UV−vis spectrum permits recording the absorption of the (salen)Mn fragments without interference. In this regard, it is worth noting that either the +II or +III oxidation state of manganese-in-salen complexes can be easily distinguished by its electronic spectra, which are very different depending on the metal oxidation state. Hence, the transient with an absorption band at 430 nm would be the Mn(II) salen complex arising from a competitive homolytic photodissociation of the metal−acetoxy bond. In support of this assignment is the decrease in the quantum yield observed for the generation of the 430 nm transient when increasing the solvent polarity. On the other hand, the fact that the transient characterized by the 430 nm band is quenched by oxygen indicates that this species reacts to give oxygenated products, a chemical behavior that is compatible with salen Mn(II) complexes, but not with cationic Mn(III)salen$^+$ that is air stable. This scheme parallels the work of Steenken, McClelland, and co-workers on the heterolytic versus homolytic cleavage of benzylic derivatives in various solvents.[18]

To seek support for the above mechanistic rationalization of the photochemistry of salen manganese complexes **2** and **3**, complex **4** having the UV-detectable chromophore phenylacetate as apical ligand was prepared and photolyzed under the same conditions. According to the previous discussion we anticipated

that laser flash photolysis of **4** at 266 nm could lead to the spectroscopic observation of the benzyl anion and/or the benzyl radical by heterolytic or homolytic photodetachment of the apical ligand and CO_2 loss as depicted in eqs 4 and 5.
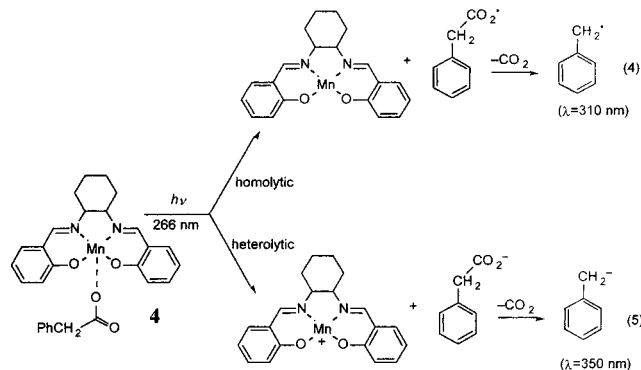
Both benzylic intermediates have characteristic absorption bands at 350 and 310 nm for the anion and the radical, respectively.[16] In fact, after laser excitation of complex **4** in dichloromethane or acetonitrile, an absorption band at 350 nm, attributable to the benzyl anion, was clearly detected, decaying with first-order kinetics and a lifetime of 0.15 μs. This benzyl anion is quenched by ethanol and other protic solvents due to protonation of the carbanionic center.

On the other hand, although the laser flash photolysis of complex **1** in dichloromethane or acetonitrile did not lead to the observation of any transient, we undertook the same study using the Jacobsen catalyst (the tetra-*tert*-butyl derivative of complex **1**) but also failed to detect any transient in either dichloromethane or acetonitrile. However, since the *tert*-butyl groups of the Jacobsen catalyst confer it some solubility in apolar solvents, the laser flash photolysis of Jacobsen catalyst was also pursued in hexane. Unexpectedly, 266 or 355 nm laser excitation in hexane led to observation of two bands at 360 and 420 nm (see Figure 4) which are compatible with the formation of the (salchd)Mn(II) complex.

In light of these results, we propose that excited states of pentacoordinate Mn(III) Schiff base complexes can undergo heterolytic and homolytic axial ligand photodissociation as a general process. The relative efficiency of these two photodissociations depends not only on the medium polarity but also on the σ electron-donor character of the coordinating axial base and the stability of the resulting radical or ionic species. Effectively, the prevalence of the homolytic pathway with the *N*-oxide derivative as axial ligand can be related to the lower oxidation potential of this compound relative to poorer donors such as acetate and phenylacetate.[19]

It is worth noting the different photochemical reactivities of the five-coordinate complexes studied here compared to those reported for four-coordinate Mn(salen), either Mn(II) or Mn(III). In both cases four-coordinated Mn(II) or Mn(III) complexes undergo intramolecular metal-to-ligand electron transfer to generate a transient species having a ligand with radical anion character. For tetracoordinated Mn complexes this transient species can be considered as an excited state, since light emission repopulates the ground state of manganese salen complexes. According to this, observation of photoluminescence will provide sound evidence that the same process occurs for

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(19) The oxidation potential of 4PPNO in acetonitrile using 0.1 M tetrabutylammonium perchlorate as electrolyte was 1.45 V vs saturated calomel electrode (SCE). In contrast, acetate and phenylacetate do not undergo anodic oxidation under these conditions in the range of potentials available in acetonitrile.
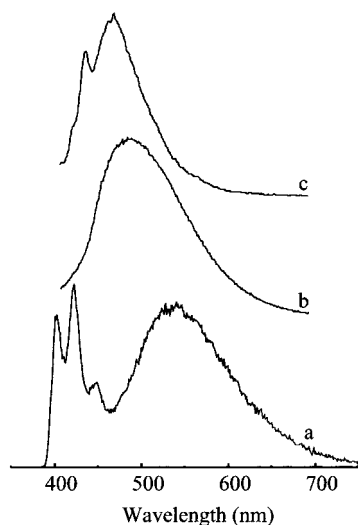
Figure 5. Emission spectra in dichloromethane solution under nitrogen of (a) Jacobsen catalyst and complexes (b) **2** and (c) **4**.

Table 1. Wavelength for the Maximum Intensity of the Excitation and Emission Spectra of Some of the Salen Complexes (2×10^{-7} M)

compound	λ_{ex} (nm)	λ_{em} (nm)
Jacobsen catalyst[a]	340	420 and 530
2[b]	375	468
3[b]	365	440

[a] Hexane. [b] Dichloromethane.

pentacoordinate Mn(III) salen complexes. In fact, the Jacobsen catalyst and complexes **2** and **4** exhibit a broad featureless photoluminescence band characteristic of the metal-to-ligand transition in the 500−600 nm region. Although these emissions could be easily recorded with good signal-to-noise ratio (see Figure 5), the corresponding photoluminescence quantum yields were low and could not be measured (<0.01). In some cases, a ligand-centered emission at much shorter wavelength showing vibrational fine structure was also observed upon excitation at the ligand-localized absorption bands (see spectrum a in Figure 5). Table 1 summarizes the wavelength maxima for excitation and emission for the above-mentioned complexes. Concerning the laser flash photolysis study discussed above, what is relevant from the luminescence spectra is that the emission−time profile is too rapid to be monitored within the time resolution of our system. This implies that the emitting excited-state lifetime is too short (<1−2 ns), and cannot be responsible for any of the transients detected in the laser flash photolysis experiments that typically expand in the microsecond time scale. Thus, the emitting excited state that probably corresponds to the intramolecular metal−ligand electron transfer (the only photochemical process yet reported for other manganese complexes) is also generated in pentacoordinate Mn(III) salen complexes, but it does not correspond to any of the transient species observed by laser flash photolysis that are much longer lived.

We suggest that the different photochemical behavior of pentacoordinate Mn(III) salen complexes can be related to the relative energy of the new orbital system having a labile apical ligand that is reflected in the coordination geometry. Effectively, in four-coordinate complexes the manganese is centered in the basal salen plane. In this geometry there is a stronger metal−salen orbital overlap favoring a more efficient intramolecular metal−ligand electron transfer than when the manganese ion moves away from the main salen plane. However, axial complexation induces the displacement of the manganese ion
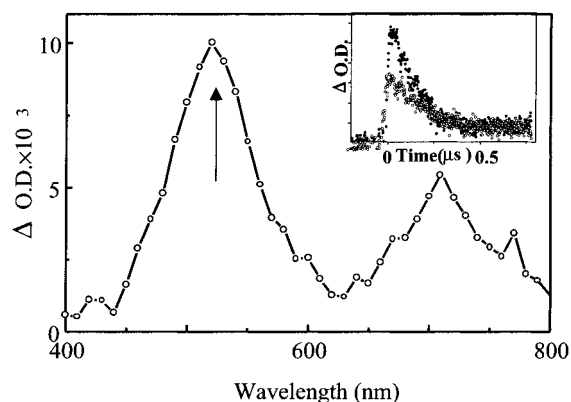
Figure 6. Transient spectrum recorded 0.2 μs after 266 nm laser-pulse excitation of binuclear complex **5** in dichloromethane. The arrow shows the band that has been previously assigned to (salchd)Mn(V)= O. The inset shows the decays monitored at 530 (●) and 710 (○) nm.

above the equatorial salen plane and the resulting geometry is roughly square pyramidal, in which the manganese atoms are located above the main salen plane.[12] This geometry disfavors the metal−salen orbital interaction, making less favorable the manganese salen single-electron transfer, and shortening the lifetime of the intramolecular charge-separated species. From our laser flash photolysis study, it appears that the essential role of the labile axial ligand in the photochemistry of pentacoordinate Mn(III) salen complexes is to provide an efficient pathway for competitive excited-state deactivation.

Given the relevance of these types of complexes as oxidation catalysts, we were interested in applying the laser flash photolysis technique to the generation of transients proposed as intermediates in epoxidation reactions. Aimed at this purpose, and having determined the photoreactivity of pentacoordinate Mn salen complexes, we prepared a binuclear oxobridged salen complex [Mn(III)(salchd)-O−Mn(IV)(salchd)]$^+$ (**5**) and submitted it to photolysis in dichloromethane solution. The mixed III/ IV valence was deduced from the magnetic susceptibility measurements (see the Experimental Section). Laser flash photolysis led to the formation of a transient absorption band with maximum at 530 nm which decayed with a first-order kinetics with a lifetime of 1.56 μs (Figure 6). On the basis of the reported UV spectrum of Mn(III)salen in highly concentrated oxidizing media, this transient was assigned to the reactive oxomanganese(V) complex that has been postulated as the oxygen-transferring species in the epoxidation reaction with manganese salen systems.[17,20,21] This intermediate may have been formed through homolytic photocleavage of the oxygen− metal bond as depicted in eq 6. There is also a different transient (λ_{max} 710 nm) that accompanies the oxomanganese but decays differently (see Figure 6). This second transient could be formed through a photocleavage (either homo- or heterolytic) different than that indicated in eq 6.
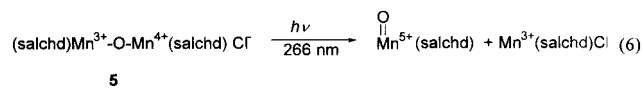
Related binuclear oxobridged salen complexes have already been proposed in equilibrium with the active oxomanganese- (V) during the thermal alkene epoxidation catalyzed by Mn(III)

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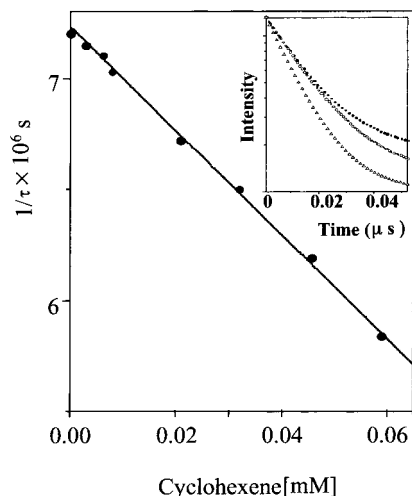
Figure 7. Plot of $1/\tau$ versus the concentration of cyclohexene for the decay of the oxomanganese(V)salen transient monitored at 530 nm. The inset shows three representative decay without and after addition of 1.5×10^{-6} and 2×10^{-5} M cyclohexene.

salen complexes.[17,22] However, as far as we know, the photochemical generation of a representative oxomanganese(V) salen complex is unprecedented and opens the way to study the chemical reactivity of these short-lived intermediates under reactive conditions through fast detection techniques. We note that the presence of a second transient does not interfere with the kinetic study of the oxomanganese salen complex.

In fact, the decay kinetics of the 530 nm band was significantly faster in the presence of alkenes. Thus, under the conditions of the laser flash photolysis experiments, the photogenerated oxomanganese(V) transient reacts with 1-hexene ($k_q = 5.3 \times 10^5$ M^{-1} s^{-1}), 1-octene ($k_q = 6.4 \times 10^5$ M^{-1} s^{-1}), and cyclohexene ($k_q = 2.0 \times 10^6$ M^{-1} s^{-1}), but not with 1-methylcyclohexene ($k_q < 10^5$ M^{-1} s^{-1}). As an example, Figure 7 presents the quenching for cyclohexene.

To confirm that the observed alkene quenching of the photogenerated oxomanganese(V) transient leads to the formation of epoxide, a preparative photolysis was carried out. Equivalent amounts of oxo dimer **5** and cyclohexene in dichloromethane were photolyzed under nitrogen using the 308 nm output of an excimer laser. After percolation of the solution through basic alumina, gas chromatography (GC) analysis reveals the presence of 1,2-cyclohexanediol (conversion 16%, selectivity > 95%). This diol is the known ring-opening product of the expected epoxide. This shows that laser flash photolysis can be a valuable tool in the investigation of reaction mechanisms in the field of metal complex catalysis.

Conclusions

Laser flash photolysis of a set of five-coordinate manganese-(III) salen complexes leads as general photoprocesses to the homolytic and heterolytic photodetachment of the axially ligated σ-electron donor from the salen manganese core. The relative efficiency of these processes can be related to the polarity of the solvent and to the oxidation potential of the apical substituent.

Comparison of our spectroscopic results with previous product studies reported in the literature for related four-coordinate cationic salen Mn(III) enables us to conclude that photodetach-

ment of the easily exchangeable axial ligand in pentacoordinate Mn(III) salen complexes is the predominant photoprocess arising from the initial charge-separated excited state.

On the other hand, laser flash photolysis of a binuclear mixed-valence complex [Mn(III)(salchd)−O−Mn(IV)(salchd)]$^+$ leads to the formation of the reactive oxo(salchd)manganese(V) complex (λ_{max} 530 nm), a species that has been proposed as key intermediate in the epoxidation reaction with manganese salen systems,[17,23−25] and we have observed that this species indeed reacts with aliphatic mono- and disubstituted alkenes. The fact that the quenching constant of 1-methylcyclohexene is much lower than those of cyclohexene and 1-alkenes agrees with the reported data that chiral induction of trisubstituted alkenes is much lower due to the higher steric encumbrance of these alkenes toward the side-on approach to the active Mn=O bond.[26,27] The possibility of generating intermediates proposed in the Mn(III)-salen-catalyzed epoxidation using the laser flash technique would enable the study of their reactivity and could open the way to the elucidation of reaction mechanisms in transition metal catalysis.

Experimental Section

Fourier transformed infrared (FT-IR) spectra were recorded at room temperature in a KBr disk using a spectrophotometer (Nicolet 710 FT). Room-temperature transmission UV−vis spectra of transparent dichloromethane solutions were recorded in a UV−vis scanning spectrophotometer (Shimadzu). The emission spectra of pure complexes were recorded with a spectrofluorimeter (FS900 Edinburgh) with a monochromator (Czerny-Turner) in the 200−800 nm range. Excitation wavelengths were those corresponding to the charge transfer (CT) maxima. Samples dissolved in dichloromethane (10^{-2} M) contained in 7×7 quartz cuvettes were sealed with septum caps and purged with nitrogen at least 15 min before recording the luminescence spectra. Laser flash experiments were performed at concentrations in the 10^{-4} M range with a pulsed Nd:YAG laser (pulse width, 10 ns; energy pulse, $\sim$14 mJ).

Preparation of Manganese Salen Complexes 1−5. (1) Preparation of 1. Complex **1** was prepared according to a general procedure reported by Jacobsen.[7] Basically, this procedure consists of heating at reflux temperature a suspension of 6.72 g (0.027 mol) of Mn(OAc)$_2$·4H$_2$O in 60 mL of ethanol, and a solution of 8.69 g of salchd ligand (0.027 mol) in 20 mL of toluene, for 2 h. A gas dispersion tube was placed, and air was bubbled through the reaction mixture for 1 h. After this, heating and air bubbling were stopped, and a saturated NaCl solution (10 mL) was added. The mixture was cooled to room temperature, and **1** precipitated as a brown solid.

Characterization data for complex **1**. IR(KBr): 1620, 1603, 1541, 1447, 1305, 740 cm^{-1}. UV−vis (CH$_2$Cl$_2$): 246, 288, 325 426, 500 nm. MS(FAB): m/z 375 (M − Cl$^-$)$^+$. Anal. Calcd for C$_{20}$H$_{20}$N$_2$O$_2$-ClMn (%): C, 55.92; H, 4.96; N, 6.31; Measured: C, 55.91; H, 4.76; N, 6.73.

(2) Preparation of 2−4. Complexes **2−4** were prepared according to a protocol reported for related complexes.[8] Thus, a 50-mL round-bottom flask fitted with a dropping funnel was charged with 0.269 g (1.3 mmol) of AgClO$_4$ and 5 mL of dry CH$_3$CN. The dropping funnel was charged with a solution of 0.5 g (1.219 mmol) of complex Mn-(III)(salchd)Cl in 5 mL of dry CH$_3$CN, and this solution was added dropwise. The mixture was stirred for 24 h at room temperature, filtered

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through Celite, and washed with 10 mL of acetonitrile. The filtrate was concentrated to 15 mL, and 1.219 mmol of each specific ligand (4-phenylpyridine-*N*-oxide, sodium acetate, and sodium phenylacetate) was added. The solutions were stirred at room temperature for 24 h to give the complexes **2**–**4** as brown solids.

Characterization data for complex **2**. IR(KBr): 1623, 1600, 1544, 1472, 1447, 1395, 1311, 1223, 1094, 908 cm^{-1}. UV–vis (CH$_2$Cl$_2$): 242, 311, 423 nm. MS(FAB): *m/z* 546 (M − ClO$_4^-$)$^+$. Anal. Calcd for C$_{31}$H$_{31}$N$_3$O$_7$ClMn·1H$_2$O: C, 55.92; H, 4.96; N, 6.31. Found: C, 55.91; H, 4.76; N, 6.73.

Characterization data for complex **3**. IR(KBr): 1625, 1610, 1565, 1537, 1447, 1305, 1142, 910 cm^{-1}. UV–vis (CH$_2$Cl$_2$): 246, 290, 325, 426 nm. MS(FAB): *m/z* 375 (M − CH$_3$CO$_2^-$)$^+$. Anal. Calcd for C$_{22}$H$_{23}$N$_2$O$_4$Mn: C, 60.83; H, 5.38; N, 6.45. Found: C, 60.75; H, 5.41; N, 6.43.

Characterization data for complex **4**. IR(KBr): 1614, 1593, 1568, 1531, 1444, 1301, 1117, 906 cm^{-1}. UV–vis (CH$_2$Cl$_2$): 246, 290, 325, 426 nm. MS(FAB): *m/z* 375 (M − PhCH$_2$CO$_2^-$)$^+$.

(2) Preparation of 5. Complex **5** was prepared by adding 2 mL of NaOCl (4% active chlorine) to 5 mL of a dichloromethane solution containing 0.5 g (1.22 mmol) of complex **1**. The resulting biphasic system was stirred at room temperature for 24 h. A brown solid precipitated. The solid was filtered off, washed with dichloromethane and *n*-pentane and dried.

Characterization data for complex **5**. IR(KBr): 1616, 1605, 1542, 1447, 1305, 1142, 910, 747 cm^{-1}. UV–vis (CH$_2$Cl$_2$): 246, 288, 325, 426, 500 nm. MS(FAB): *m/z* 375, 391 (M − Mn(salchd)Cl − ClO$_4^-$)$^+$. Magnetic susceptibility: $X = 5.1$ emu·K/mol.