

Role of Mn^{IV} species in Mn(salen) catalyzed enantioselective aerobic epoxidations of alkenes: an EPR study

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Abstract

Using EPR spectroscopy, high valence Mn(salen) complexes were monitored in Mn^{III}(salen)/isobutyraldehyde/O₂ and Mn^{III}(salen)/pivalaldehyde/O₂ catalytic systems in the absence and in the presence of *N*-methylimidazole (*N*-Me-Imd), where Mn^{III}(salen) (**1**) is (*S,S*)-(+)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino-manganese(III) chloride. Inter-action of **1** with aliphatic aldehydes in the presence of O₂ was found to give a mixture of oxo manganese(IV) species L₁(salen)Mn^{IV} = O (**2**) with various axial ligands L₁ (L₁ = Cl⁻, RCOO⁻). They display EPR signals having close *g* values of ca. 5.2 with resolved hyperfine structures from one manganese (*A* = 75 G, ⁵⁵Mn, *I* = 5/2). In the presence of *N*-Me-Imd, new manganese(IV) complexes were detected. The first one was shown to be an antiferromagnetically coupled mixed-valence [(salen)Mn^{IV}(μ₂-O)₂Mn^{III}(salen)]⁻ dimer having 16-line EPR signal at *g* = 2. The second one is probably (salen)Mn^{IV}(OOCOR)*N*-Me-Imd acylperoxo complex (**2**) (*g* = 4.2 (R = CH(CH₃)₂), or *g* = 4.7 (R = C(CH₃)₃), unresolved manganese hyperfine structure). Possible roles of each complex in the enantioselective alkene epoxidations are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Epoxidations; Enantioselective; Chiral schiff bases; Mn(salen) complexes; Mixed-valence dimers; EPR

1. Introduction

Asymmetric synthesis is a promising and rapidly developing branch of chemistry. One of the significant challenges in this area is a catalytic asymmetric oxidations of unfunctionalized alkenes [1]. In 1992, Mukaiyama reported an enantioselective epoxidation of unfunctionalized olefins with molecular oxygen in the presence of branched aliphatic aldehydes as sacrificial reductants and optically active chelate Mn(III) complexes as catalysts [2]. An acylperoxo manganese complex was supposed to be the reactive intermediate responsible for enantioselectivity.

Addition of *N*-alkylimidazoles (*N*-Alk-Imd) to the above system leads to increase of the epoxide yield and enantiomeric excess (e.e.) as well as the reversal of the epoxide absolute configuration [3,4]. The active species in this reaction was considered to be a (salen)Mn^{VO} complex [4]. However, the mechanism proposed has not been confirmed spectroscopically and remains hypothetical. Recently, it has been found that (salen)Mn^{III} complexes has EPR signal at *g* ≈ 8 [5,6]. EPR spectroscopy was used to monitor intermediates in Jacobsen's catalytic system, (salen)Mn^{III}/*meta*-chloroperbenzoic acid (*m*-CPBA) [6] and Mukaiyama's system Mn^{III}(salen)/isobutyraldehyde/O₂ [7]. Role of Mn(IV) species in Jacobsen–Katsuki epoxidations has been elucidated using combined EPR/ESI-MS study [8].

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Here we report a comparative EPR study of manganese species formed in $\text{Mn}^{\text{III}}(\text{salen})/\text{isobutyraldehyde}/\text{O}_2$ and $\text{Mn}^{\text{III}}(\text{salen})/\text{pivalaldehyde}/\text{O}_2$ catalytic systems and discuss their possible roles in the enantioselective alkene epoxidations.

2. Experimental

2.1. Materials

(*S,S*)-(+)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino-manganese(III) chloride ($[\text{Mn}^{\text{III}}(\text{salen})]$ or **1**), *m*-CPBA, isobutyraldehyde, pivalaldehyde, *trans*- β -methylstyrene, 1,2-dihydronaphthalene, *N*-methylimidazole (*N*-Me-Imd) were purchased from Aldrich. Isobutyraldehyde and pivalaldehyde were distilled prior to use. *Trans*- β -methylstyrene oxide and 1,2-epoxy-1,2,3,4-tetrahydronaphthalene were prepared by oxidation of the corresponding olefins with *m*-CPBA in CHCl_3 .

2.2. Preparation of samples for EPR investigations

All samples were prepared directly in EPR tubes. Typically, isobutyraldehyde (660 μmol , 60 μl) or pivalaldehyde (360 μmol , 40 μl) was added to the samples containing 400 μl of toluene, 14.2 μmol (9 mg) of **1** and, if necessary, 125 μmol (10 μl) of *N*-Me-Imd, and air was blown through the system. If necessary, 10 μl of alkene (77.1 μmol of *trans*- β -methylstyrene or 76.6 μmol of dihydronaphthalene) was added, before or after the addition of aldehyde. When reactivities of *N*-Me-Imd(*salen*) $\text{Mn}^{\text{IV}}(\text{OOCOR})$ complexes (**3**) were probed, the latter were generated by blowing air through the samples containing **1**, *N*-Me-Imd and aldehyde, during 1–2 min. Then alkene was added at reduced temperature (-20°C), and the samples were covered to switch off further access of air. Epoxides of *trans*- β -methylstyrene and dihydronaphthalene were separated from the reaction mixture by column chromatography on silica gel immediately after the disappearance of **3** was indicated by EPR, and epoxide yields and e.e. values were measured. Reaction times were 10 min for both **3a** ($\text{R} = \text{CH}(\text{CH}_3)_2$) and **3b** ($\text{R} = \text{C}(\text{CH}_3)_3$).

2.3. EPR measurements

EPR spectra (-196°C) were recorded on a Bruker ER-200D spectrometer at 9.4 GHz. Measurements were performed in quartz tubes ($d = 5\text{ mm}$, $l = 150\text{ mm}$) placed into a quartz dewar with liquid nitrogen. Periclase crystal (MgO) with impurities of Mn^{2+} and Cr^{3+} , which served as a side reference, was placed into the second compartment of the dual cavity. The half-life times of high-valence Mn complexes were estimated by monitoring the intensities of the corresponding EPR signals.

2.4. ^1H NMR measurements

^1H NMR spectra were recorded on a Bruker DPX-250 spectrometer at 250.13 MHz, using 5 mm cylindrical tubes. Chemical shifts were referenced to CDCl_3 residual protons ($\delta = 7.30\text{ ppm}$). Typical operation conditions for ^1H measurements were the following: sweep widths 5000 Hz, spectrum accumulation frequency 0.2 Hz, number of scans 16–160, 3 μs of pulse, 32 K data points.

2.5. UV–VIS measurements

UV–VIS spectra were recorded on a Shimadzu UV-300 spectrophotometer in quartz cells ($l = 1\text{ cm}$). A toluene solution containing **1** ($1 \times 10^{-4}\text{ M}$) and, if necessary, *N*-Me-Imd (0.14 M) was blown with air during 5 min and then isobutyraldehyde (0.4 M) was added and spectra were run immediately.

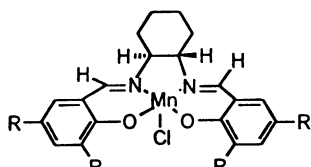
2.6. Analysis of oxidation products

Oxidation products were identified by GC–MS and ^1H NMR [4] and quantified by (glass capillary column (GC) 35 m \times 0.3 mm, SE-54). Typically, epoxide yields were calculated based on initial substrate. Epoxides of *trans*- β -methylstyrene and dihydronaphthalene were separated from the reaction mixture by using column chromatography on silica gel, and e.e. values were determined by using ^1H NMR in CH_2Cl_2 with $\text{Eu}(\text{hfc})_3$ as a chiral shift reagent, and by GC (Chiraldex-B, 30 m \times 0.25 mm ID \times 0.25 μm μm film, J&W), respectively.

3. Results and discussion

3.1. *1*/Aldehyde/ O_2 catalytic system

It is commonly accepted that (salen)Mn^{III} complexes are EPR silent due to non-Kramers spin state [8]. However, it has been shown recently that complex **1** displays EPR signal at $g = 8.0 \pm 0.2$ readily detectable at 77 K on conventional X-band EPR spectrometer (we note that hereinafter g -values are not true ones but are only used to define the field positions) [5–7]. The shape and intensity of this signal allow to monitor concentration and coordination environment of manganese(III) [5,6,9,10].



1. R = t-Bu

When isobutyraldehyde was added to the solution of complex **1** in toluene and air was blown through the reaction mixture, EPR signal of complex **1** at $g = 8.0 \pm 0.2$ (Fig. 1a) converted fast into a more intense one at $g = 5.2 \pm 0.2$ with partially resolved hyperfine structure from manganese ($A = 75$ G) (Fig. 1b). When air was blown through the sample over a period of 4 min, all the manganese(III) originally present in the solution converted into manganese species exhibiting EPR signal at $g = 5.2$ (Fig. 1c). UV–VIS spectra showed appearance of a green species with a maximum at $\lambda = 645$ nm (Fig. 2). We will further refer this species as complex **2**. Additionally, formation of a small amount of (salen)Mn^{II} (signal at $g = 2$, $A = 85$ G) was observed (Fig. 1b). **2** appeared to be unstable and almost quantitatively converted back into **1** with $\tau_{1/2} \approx 90$ min when the flow of air was switched off. It is worth noting that besides the signal at $g = 5.2$, **2** exhibits a very broad high-field component in the range of 2500–4000 G (Fig. 1b). Such a spectrum is characteristic of mononuclear Mn(IV) species with $D > h\nu$ [5–8,11].

Blowing air through the sample containing **1** and pivalaldehyde also lead to the formation of **2** (Fig. 1d). Like in the system with isobutyraldehyde,

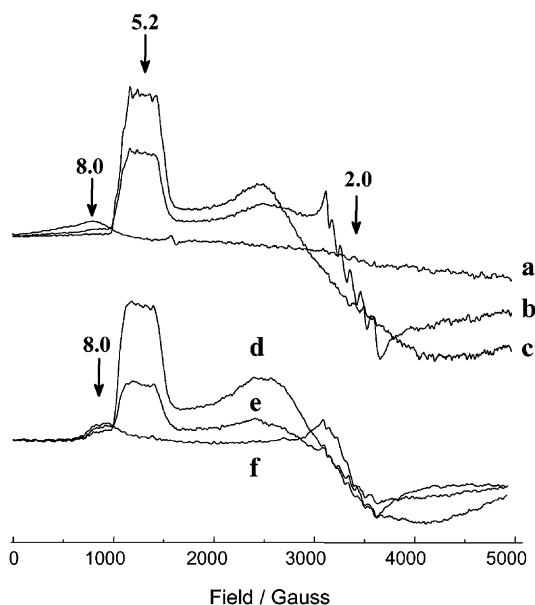


Fig. 1. X-band EPR spectra (-196°C) of complex **1** (14.2 μmol) in 400 μl of toluene (a); after addition of 660 μmol of isobutyraldehyde (b); after blowing air through the sample (b) during 4 min (c). X-band EPR spectra (-196°C) of complex **1** in different moments of time after addition of 360 μmol (40 μl) of pivalaldehyde and blowing air through the sample for 4 min: immediately after blowing air (d); in 5 min (e); in 25 min (f).

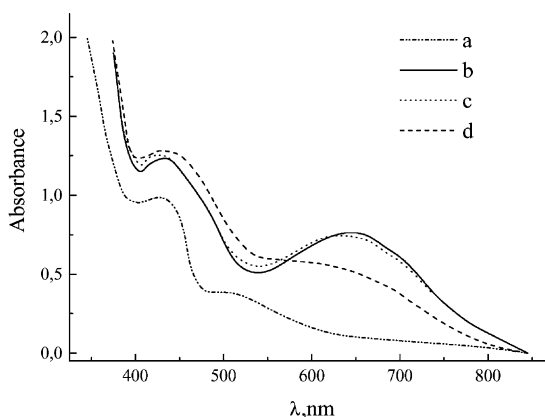


Fig. 2. UV–VIS spectra of complex **1** (1×10^{-4} M) in toluene (a); after blowing air during 5 min followed by addition of isobutyraldehyde (0.4 M) (b); immediately after addition of *N*-Me-Imd (0.14 M) (c); after addition of *N*-Me-Imd (0.14 M) followed by blowing air during 5 min and adding isobutyraldehyde (0.4 M) (d).

formation of a small amount of (salen)Mn^{II} can be observed. The half-life time of **2** in the system with pivalaldehyde ($\tau_{1/2} \approx 4$ min) was much shorter than that in the system with isobutyraldehyde ($\tau_{1/2} \approx 90$ min).

Recently, we revealed the same Mn^{IV} species **2** ($g = 5.2$, $A = 75$ G) upon interaction of **1** with one equivalent of perisobutyric acid [7]. We believe that **2** are two oxo Mn^{IV} complexes [(salen)Mn^{IV}OL]⁻, where L = Cl⁻ and RCOO⁻ (R = CH(CH₃)₂). Most probably, they form according to Eq. (1):



The half-life times of self-decomposition of complex **2a** was about 100 min at ambient conditions both in the presence and in the absence of alkene substrate (*trans*- β -methylstyrene). Under N₂ atmosphere, $\tau_{1/2}$ decreased to 40 min. Benzaldehyde and 3-phenylacrylaldehyde were the main oxidation products when species **2** were generated in situ via the reaction of **1** with perisobutyric acid and then allowed to react with *trans*- β -methylstyrene (the total product yield was less than 10%). This reactivity pattern is similar to that of oxo manganese (IV) porphyrin complexes [12,13] that supports our assignment of complex **2** as oxo manganese (IV) species.

On the contrary, when *trans*- β -methylstyrene was added to the reaction mixture prior to the oxidant, corresponding epoxide was formed in 49% (based on the oxidant) and 31% yield, with perisobutyric acid and isobutyraldehyde/O₂, respectively. We may suppose that the actual reactive intermediate responsible for the enantioselectivity in the Mn^{III}(salen)/aldehyde/O₂ catalytic system can be Mn^{III} acylperoxo complex formed via interaction of **1** with the peroxyacid, which is formed in the course of aldehyde autoxidation process [3]. Recently, experimental data in favor of the formation of Mn(III) acylperoxo complexes were obtained for the Mn^{III}(salen)/*m*-CPBA system in CH₂Cl₂ at -90 °C using EPR [6]. Unfortunately, we failed to detect such intermediates by EPR in the Mn^{III}(salen)/perisobutyric acid system, probably, because of their high reactivity towards alkenes and very rapid conversion into the oxo Mn^{IV} species **2** in the alkene-free system.

3.2. **1**/Aldehyde/O₂/*N*-Me-Imd catalytic system

3.2.1. Detection of complexes **3a** and **3b**

The situation changed dramatically in the presence of *N*-Me-Imd (Fig. 3). Blowing air through the solution containing **1**, isobutyraldehyde, *trans*- β -methylstyrene and *N*-Me-Imd, led to appearance of a new signal at $g = 4.2$ with unresolved hyperfine structure from manganese along with the six-line signal at $g = 5.2$, ($A = 75$ G, assigned to *N*-Me-Imd(salen)Mn^{IV}O

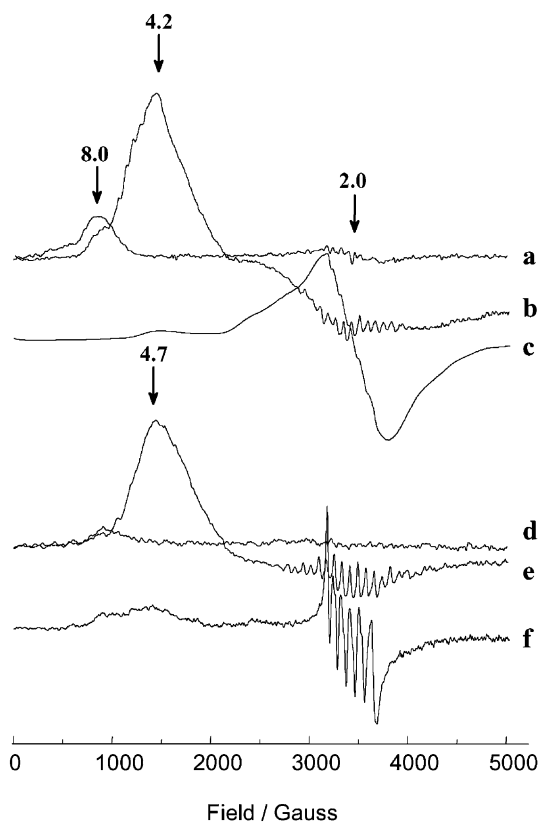


Fig. 3. X-band EPR spectra (-196 °C) of complex **1** (14.2 μmol) in 400 μl of toluene (a); after addition of 77 μmol of *trans*- β -methylstyrene, 125 μmol of *N*-Me-Imd and 880 μmol of isobutyraldehyde and blowing air through the sample (b); sample (b) in 20 min with exclusion of air, the intensity was scaled down twice (c). X-band EPR spectra (-196 °C) of complex **1** (19 μmol) in 400 μl of toluene containing 250 μmol of *N*-Me-Imd (d); in different moments of time after addition of 1.44 mmol of pivalaldehyde and blowing air through the sample for 1 min: immediately after blowing air (e); in 10 min (f).

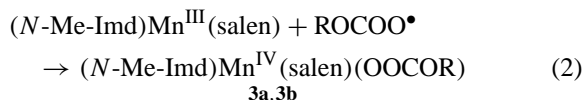
(**2-N-Me-Imd**) complex) (Fig. 3). Slight changes in the UV–VIS spectrum of (salen)Mn^{IV}O green species observed upon addition of *N*-Me-Imd may also indicate axial ligation of *N*-Me-Imd to (salen)Mn^{IV}O (Fig. 2). Both EPR signals were also detected in the alkene-free system. The signal at $g = 4.2$ disappeared more rapidly than the signal at $g = 5.2$ ($\tau_{1/2} = 5$ min at room temperature) and might be assigned to an unstable Mn(IV) complex, further denoted as complex **3a**. The rate of decomposition of **3a** was independent on the presence of *trans*- β -methylstyrene in the reaction mixture. When *trans*- β -methylstyrene was added to the solution prior to blowing air, the system afforded *trans*- β -methylstyrene epoxide in the yield of 64% and e.e. 34%.

We also detected a new Mn^{IV} complex in **1**/pivalaldehyde/O₂/*N*-Me-Imd catalytic system. When air was blown through the sample containing 30 μ mol of **1**, 250 μ mol of *N*-Me-Imd and 1.44 mmol of pivalaldehyde, a new signal at $g = 4.7$ with unresolved hyperfine structure from one manganese appeared (Fig. 3). The resonance at $g = 4.7$ belongs to an unstable Mn^{IV} complex **3b** ($\tau_{1/2} < 2$ min) which is believed to be analogous to complex **3a**.

3.2.2. Nature of complexes **3a** and **3b**

The present EPR study reveals the principal difference between the **1**/aldehyde/O₂ and **1**/aldehyde/*N*-Me-Imd/O₂ catalytic systems: unstable complex **3a** (or **3b**, depending on the aldehyde used) appears in the latter system. Complexes **3a** and **3b** cannot be obtained by plain addition of *N*-Me-Imd to the solution containing (salen)Mn^{IV}O oxo species **2** and thus are not products of *N*-Me-Imd ligation to (salen)Mn^{IV}O. Indeed, UV–VIS spectra differ significantly when *N*-Me-Imd is added before and after the formation of the green (salen)Mn^{IV} oxo species (Fig. 2). The addition of one equivalent of perisobutyric acid to the solution of **1** and *N*-Me-Imd caused immediate conversion into (salen)Mn^{III} [7], so complex **3a** is not a product of the peroxy acid interaction with *N*-Me-Imd(salen)Mn^{III}. It is tentative to suppose that **3a** and **3b** are acylperoxy complexes of manganese(IV), *N*-Me-Imd(salen)Mn^{IV}(OOCOR), (R = CH(CH₃)₂ and R = C(CH₃)₃, for isobutyraldehyde and pivalaldehyde, respectively), formed via capturing of acylperoxy radicals present in the catalytic

system by (salen)Mn^{III}*N*-Me-Imd complex [14]:



When 76.6 μ mol of dihydronaphthalene were added to the sample containing generated in situ complex **3a**, dihydronaphthalene oxide was formed in the yield of 25% and e.e. 0%. Similar results were obtained with complex **3b**. Previously, we supposed **3a** to be the precursor of the active intermediate responsible for the stereoselectivity in Mukaiyama's system [7]. However, the data obtained in this work show unambiguously that while complexes **3a** and **3b** are reactive towards alkenes, they can be neither true intermediates responsible for the enantioselectivity nor the intermediate precursors.

3.2.3. Mixed-valence dinuclear Mn^{III}/Mn^{IV} complexes

One can observe a slow growth of the 16-line signal at $g = 2$ (Fig. 2b and e) in **1**/aldehyde/O₂/*N*-Me-Imd catalytic systems. This signal is characteristic of antiferromagnetically coupled mixed-valence dinuclear manganese complex having an overall spin of $S = \frac{1}{2}$ [15–19]. These species can be generated either by consecutive treatment of **1** with perisobutyric acid and *N*-Me-Imd, or isobutyraldehyde/O₂ and *N*-Me-Imd, or pivalaldehyde/O₂ and *N*-Me-Imd, respectively. At the first step, *N*-Me-Imd(salen)Mn^{IV}O complex forms which then converts into mixed-valence dimers. Like in [19], our attempts to simulate the experimental spectrum with either isotropic or axial models for g and A tensors were unsuccessful in that we could not reproduce simultaneously the splitting pattern and peak intensities of the spectrum. Its best fit parameters are $g_x = 2.0030$, $g_y = 2.0030$, $g_z = 2.0015$, $A_{1x} = 162$ G, $A_{1y} = 160$ G, $A_{1z} = 150$ G, $A_{2x} = 87.5$ G, $A_{2y} = 83$ G, $A_{2z} = 61.5$ G, line width $d_x = d_y = d_z = 20$ G, Gaussian line shape. The total spectrum width is 1340 G. Fig. 3 represents both the experimental and the simulated spectra. Theory predicts that, using these values, one can estimate the hyperfine constants in the corresponding monomers [15,18]:

$$a_i^1 = A_i^{1/2} \cdot \left(\frac{\vec{S}_i \cdot \vec{S}_i}{\vec{S}_i \cdot \vec{S}_i} \right) \quad (3)$$

Where a^1 and $A^{1/2}$ are the hyperfine constants in the mono- and dinuclear complex, respectively; S and S_i stand for the total spin ($S = \frac{1}{2}$) and electron spin of the i th metal atom in the dinuclear complex. For the trapped $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$ pair and for the case where the exchange coupling is large versus other effects we have:

$$\begin{aligned} a^1(\text{Mn}^{\text{II}}) &= \frac{3}{7}A^{1/2}(\text{Mn}^{\text{II}}) \\ a^1(\text{Mn}^{\text{III}}) &= -\frac{3}{4}A^{1/2}(\text{Mn}^{\text{III}}) \end{aligned} \quad (4)$$

and for $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ dinuclear complex one obtains:

$$\begin{aligned} a^1(\text{Mn}^{\text{III}}) &= \frac{1}{2}A^{1/2}(\text{Mn}^{\text{III}}) \\ a^1(\text{Mn}^{\text{IV}}) &= -A^{1/2}(\text{Mn}^{\text{IV}}) \end{aligned} \quad (5)$$

So, if this species were $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$ dimer, $a_{\text{Mn}^{\text{(III)}}}^1$ and $a_{\text{Mn}^{\text{(II)}}}^1$ would be expected to be 58.0 and 67.4 G, respectively. These values are too small as compared to those reported in the literature [16–18]. On the contrary, if this species were $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ dimer, $a_{\text{Mn}^{\text{(III)}}}^1$ and $a_{\text{Mn}^{\text{(IV)}}}^1$ would be expected to be 78.7 and 77.3 G, respectively. The latter values are much closer to those found for mononuclear manganese complexes with chelate ligands [16–18]. Thus, we assigned the dimeric complex to bis- μ_2 -oxo- $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$ dinuclear species $[(\text{salen})\text{Mn}^{\text{III}}-(\mu_2\text{-O})_2\text{-Mn}^{\text{IV}}(\text{salen})]^-$. The dimer was shown to be inert towards alkenes. In the presence of high excess of isobutyraldehyde or pivalaldehyde, when all the oxygen originally present in the sample was consumed, the $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$ signal converted into the signal of $(\text{salen})\text{Mn}^{\text{II}}$ ($g = 2.025$, $A = 85$ G) (Fig. 3f). This may be rationalized taking into account the following reaction steps [17–19]:

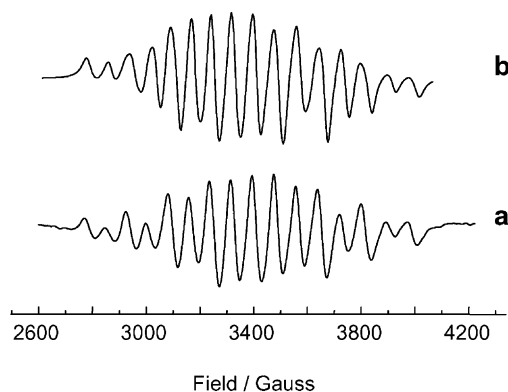
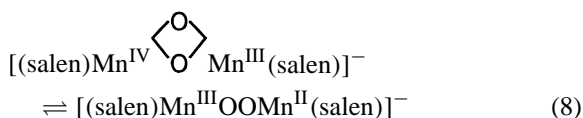
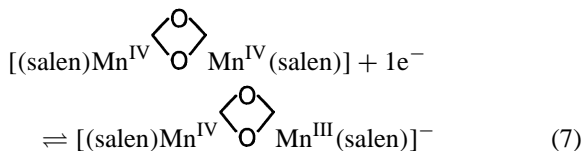
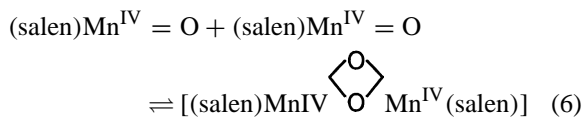
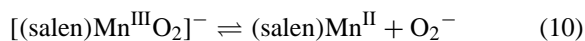
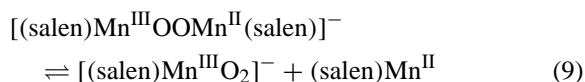


Fig. 4. X-band EPR spectra (-196°C) of toluene ($400\ \mu\text{l}$) solution of bis- μ_2 -oxo- $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$ dinuclear complex obtained as described in the capture to Fig. 3 (a); the simulated spectrum of bis- μ_2 -oxo- $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$ dinuclear complex obtained using the parameters and approach described in the text (b).



This is a formal scheme of chemical equations where O_2^- is not an end product but an intermediate one involved in equilibrium (11) that is to explain the fact observed that in the absence of dioxygen (Fig. 3c and f), $(\text{salen})\text{Mn}^{\text{II}}$ species predominated in solution:



$(\text{Salen})\text{Mn}^{\text{II}}$ complex with resolved six-line hyperfine structure (Fig. 3f) can be transformed back into **1** and then into **2** by further blowing air through the sample. At longer times, new Mn^{II} species having EPR with $g = 2$ and unresolved HFS forms irreversibly (Fig. 3c). This must be a product of $(\text{salen})\text{Mn}^{\text{II}}$ degradation. Note that the 16-line signal was not observed for the system without *N*-Me-Imd. Two molecules of *N*-Me-Imd are assumed to bind to the bis- μ_2 -oxo- $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$ species as axial ligands (Fig. 4).

4. Conclusions

As we mentioned already, different reactive intermediates were supposed to operate in Mykayama's

system in the absence and in the presence of *N*-Alk-Imd [3,4]. The reactive intermediate responsible for the alkene epoxidation in the Mn^{III}(salen)/aldehyde/O₂ catalytic system was supposed to be Mn^{III} acylperoxo complex. In the absence of an olefinic substrate, the initially formed (salen)Mn^{III}-(OOCOR) is converted rapidly into (salen)Mn^{IV}O complex. The latter species was detected in this work and appeared to be not capable of epoxidizing alkenes enantioselectively. In Mn^{III}(salen)/aldehyde/*N*-Alk-Imd/O₂ system, high valence oxo manganese complex was supposed to be the active intermediate [3]. We detected complexes **3a** and **3b** identified as *N*-Me-Imd(salen)Mn^{IV}(OOCOR) in Mukaiyama's system containing *N*-methylimidazole. These complexes turned out to be reactive towards dihydronaphthalene to give racemic dihydronaphthalene epoxide and could not be responsible for the enantiofacial selection in Mukaiyama's catalytic system. We conclude that the true intermediates should be either short-lived or EPR-silent (salen)Mn species. There are just a few examples of chelate Mn^VO complexes, all of them being low-spin and therefore diamagnetic [6,20–22]. Recently, oxo manganese(V) porphyrin complexes have been detected spectroscopically [22,23]. ESI-MS [24,25] and ¹H NMR [6] data in favor of the formation of Mn^VO reactive species in Mn^{III}(salen)/PhIO system were reported. However, spectroscopic evidence in favor of the Mn^VO reactive intermediate in Mn^{III}(salen)/aldehyde/*N*-Alk-Imd/O₂ system is yet to be obtained. Nevertheless, the main result of this study is EPR spectroscopic characterization of the major manganese species present in Mukaiyama's catalytic system. Complex **2** and complexes **3a** and **b** could act in the real catalytic system for the enantioselective alkene epoxidation. The former one, probably, accounts for the formation of undesirable radical-type epoxidation products, while the second one contributes to the formation of racemic alkene epoxides.

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References

- [1] E.N. Jacobsen, In: I. Ojima, (Ed.), *Catalytic Asymmetric Synthesis*, VCH, New York (1993).
- [2] T. Yamada, K. Imagawa, T. Nagata, T. Mukaiyama, *Chem. Lett.* (1992) 2231.
- [3] T. Yamada, K. Imagawa, T. Nagata, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* 67 (1994) 2248.
- [4] T. Nagata, K. Imagawa, T. Yamada, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* 68 (1995) 1455.
- [5] K.P. Bryliakov, D.E. Babushkin, E.P. Talsi, *Mendeleev Commun.* (1999) 29.
- [6] K.P. Bryliakov, D.E. Babushkin, E.P. Talsi, *J. Mol. Catal.* 158 (2000) 19–35.
- [7] K.P. Bryliakov, I.V. Khavrutskii, E.P. Talsi, O.A. Kholdeeva, *React. Kinet. Catal. Lett.* 171 (2000) 183.
- [8] W. Adam, C. Mock-Knoblauch, C.R. Saha-Möllner, M. Herderich, *J. Am. Chem. Soc.* 122 (2000) 9685.
- [9] H.J. Gerritsen, E.S. Sabisky, *Phys. Rev.* 132 (1963) 1507.
- [10] S.L. Dexheimer, J.W. Gohdes, M.K. Chan, K.S. Hagen, W.H. Armstrong, M.P. Klein, *J. Am. Chem. Soc.* 111 (1989) 8923.
- [11] S. Pal, P. Ghosh, A. Chakravorty, *Inorg. Chem.* 24 (1985) 3704.
- [12] J.T. Groves, M.K. Stern, *J. Am. Chem. Soc.* 110 (1988) 8628.
- [13] J.T. Groves, Y. Watanabe, *Inorg. Chem.* 25 (1986) 4804.
- [14] W. Nam, H.J. Kim, S.H. Kim, R.Y.N. Ho, J.S. Valentine, *Inorg. Chem.* 35 (1996) 1045.
- [15] G.C. Dismukes. In: K. Prassides (Ed.), *Mixed Valency Systems: Applications in Chemistry, Physics and Biology*, Kluwer Academic Publisher, Dordrecht, The Netherlands, 1990.
- [16] B. Mabad, J.-P. Tuchagues, Y.T. Hwang, D.N. Hendrickson, *J. Am. Chem. Soc.* 107 (1985) 2801.
- [17] G.C. Dismukes, J.E. Sheats, J.A. Smegal, *J. Am. Chem. Soc.* 109 (1987) 7202.
- [18] M. Perree-Fauvet, A. Gaudemar, J. Bonvoisin, J.J. Girerd, C. Boucly-Goester, P. Boucly, *Inorg. Chem.* 28 (1989) 3533.
- [19] C.P. Horwitz, P.J. Winslow, J.T. Warden, C.A. Lisek, *Inorg. Chem.* 32 (1993) 82.
- [20] T.J. Collins, S.W. Gordon-Wylie, *J. Am. Chem. Soc.* 111 (1989) 4511.
- [21] T.J. Collins, R.D. Powell, C. Slobodnick, E.S. Uffelman, *J. Am. Chem. Soc.* 112 (1990) 899.
- [22] N. Jin, J.T. Groves, *J. Am. Chem. Soc.* 121 (1999) 2923.
- [23] J.T. Groves, J. Lee, S.S. Marla, *J. Am. Chem. Soc.* 119 (1997) 6269.
- [24] D. Feichtinger, D.A. Plattner, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 5457.
- [25] D.A. Plattner, D. Feichtinger, J. El-Baraoui, O. Weist, *Int. J. Mass Spectrom.* 195/196 (2000) 351.