Journal of Molecular Catalysis A: Chemical 180 (2002) 19–24

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Alkene epoxidation catalysed by binuclear manganese complexes

Maria Louloudi*, Chrisavgi Kolokytha, Nick Hadjiliadis

Department of Chemistry, Laboratory of Inorganic and General Chemistry, University of Ioannina, 45110 Ioannina, Greece

Received 19 June 2001; received in revised form 31 August 2001; accepted 8 October 2001

Abstract

Binuclear manganese(II) complexes with macrocyclic ligands have been synthesized by template Schiff base condensation of diethylenetriamine and pentane-2,4-dione or 1,3-diphenyl-propane-1,3-dione. Catalytic epoxidation of simple olefins with hydrogen peroxide and *t*-BHP were studied using the above manganese complexes in the presence of a base. The influence of reaction temperature, the additive methanol and the cocatalyst had been investigated. The major products of the oxidations were the epoxides. The new manganese complexes showed significant catalytic activities for the epoxidation of alkenes using hydrogen peroxide as oxidant and ammonium acetate as cocatalyst. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic epoxidation; Manganese complexes; Schiff base; Hydrogen peroxide

1. Introduction

The epoxidation of olefins is a particular challenging problem in organic chemistry leading to a great interest in new and more efficient catalytic versions for these reactions [1,2]. In this context, biological catalysts such as cytochrome P450 [3] and non-heme iron and manganese enzymes [4,5] have received a great deal of attention. The desire to construct biomimetic oxidation catalysts has prompted an extensive area of research into manganese complexes with various synthetic ligands such as porphyrin [6], Schiff bases [7–9], 2,2′-bipyridine [10] or cyclic triamines [11].

On the other hand, it would be particularly interesting to associate hydrogen peroxide as oxidant, an inexpensive, readily available reagent which should give water as the only byproduct. However, the use of hydrogen peroxide in the presence of manganese complexes leads to several problems related to the easy dismutation of hydrogen peroxide by these complexes. This is presumably why only a few such systems, using hydrogen peroxide, efficient for alkene epoxidation have been explored [11–13]. Recently, it has been shown that peroxide disproportionation is suppressed in acetone favouring alkene epoxidation [14,15].

Herein we describe the template synthesis of two dinuclear manganese(II) complexes by condensation of penta-2,4-dione and 1,3-diphenyl-propan-1,3-dione with diethylenetriamine. It is shown that these complexes catalyse efficiently the epoxidation of several alkenes by hydrogen peroxide, even under mild conditions.

2. Experimental

All substrates were purchased in their highest commercial purity, stored at 5 °C and purified by passage

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* Corresponding author.
E-mail addresses: mlouloud@cc.uoi.gr (M. Louloudi), nhadjil@cc.uoi.gr (N. Hadjiliadis).

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PII: S1381-1169(01)00411-3

through a column of basic alumina prior to use. Hydrogen peroxide was 30% solution in water. *t*-BHP was purchased from Aldrich (~5.0 M solution in decane). Infrared spectra were recorded on a Spectrum GX Perkin-Elmer FT-IR System, UV–Vis spectra were recorded using a UV/VIS/NIR JASCO spectrophotometer, electron paramagnetic spectra were recorded at liquid helium temperatures with a Bruker ER 200D X-band spectrometer equipped with an Oxford Instruments cryostat. GC analysis was performed using a Shimadzu GC-17A gas chromatograph coupled with a GCMS-QP5000 mass spectrometer.

2.1. Synthesis of dimanganese complex of 1,5,8,11,15,18-hexaaza-2,4,12,14-tetramethyl-cyclocosane-1,4,11,14-tetraene (L_1)

To a stirred solution of $MnBr_2$ (2 mmol) in ethanol (10 ml), penta-2,4-dione (2 mmol) and triethylorthoformate (TEOF, 2 ml) were added. The resulting mixture was stirred for 5 min, and then diethylenetriamine was added. The reaction mixture was heated at reflux for 3 h. After slight reduction of the reaction solvents and cooling, the manganese complex is precipitated. Finally, the product, $Mn_2L_1Br_4$ (**1**), was filtered, washed with cold ethanol and ether and recrystallised from an methanol/ethanol mixture. Anal. calcd. for $Mn_2C_{18}H_{34}N_6Br_4{\cdot}2C_2H_5OH$: C, 30.84; N, 9.81; H, 5.37; Mn, 12.85. Found: C, 30.64; N, 9.62; H, 5.07; Mn, 12.50.

2.2. Synthesis of dimanganese complex of 1,5,8,11,15,18-hexaaza-2,4,12,14-tetraphenyl-cyclocosane-1,4,11,14-tetraene (L_2)

The $Mn_2L_2Br_4$ (**2**) complex was obtained by a similar procedure allowing 1,3-diphenyl-propan-1,3-dione (2 mmol) to react instead of penta-2,4-dione. The crystalline products separated on cooling and standing. Anal. calcd. for $Mn_2C_{38}H_{42}N_6Br_4{\cdot}2C_2H_5OH$: C, 45.65; N, 7.61; H, 4.89; Mn, 9.96. Found: C, 45.52; N, 7.42; H, 4.51; Mn, 9.55.

2.3. Catalytic reactions

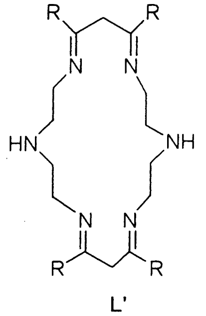
Hydrogen peroxide or *t*-BHP were slowly added to solution of alkene and cocatalyst in a acetone/MeOH (600/250 μl) solvent mixture at room temperature or at 0 °C. As an internal standard, acetophenone or bromobenzene were used. Catalytic reactions were started by adding 1 μmol of manganese complex **1** or **2**. The ratio of catalyst:oxidant:cocatalyst:substrate was equal to 1:2000:1000:1000. The progress of the reaction was monitored by GC–MS, by removing small samples of the reaction mixture. Reactions were usually complete within 2 h. To establish the identity of the products unequivocally, the retention times and spectral data were compared to those of commercially available compounds.

In competitive reactions, the same conditions were used with a ratio of catalyst:hydrogen peroxide: ammonium acetate:alkene 1:alkene 2 equal to 1:2000: 1000:500:500.

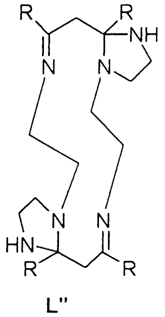
3. Results and discussion

3.1. Synthesis and characterisation of manganese complexes

The synthesis of the manganese(II) Schiff base complexes **1** and **2** consists of the condensation of diethylenetriamine and β-diketones, penta-2,4-dione and 1,3-diphenyl-propan-1,3-dione, respectively, in the presence of manganese(II) as template ions in refluxing EtOH for 3 h. The used molar ratio of diethylenetriamine:β-diketone:manganese(II) salt was 1:1:1. The products of these reactions, as in previous cases [16–18], led to the formation of binuclear manganese(II) complexes with macrocyclic ligands presenting a three N-donor set for each Mn-site. However, chemical and spectral analyses do not allow a distinction to be made between the 14-membered macrocycle L″ and the rather expected 20-membered ring L′.



L′



L″

The infrared spectra of **1** and **2** on KBr disks exhibited a strong band at 1645 and 1642 cm^{-1}, respectively, which are attributable to the coordinated imine band stretching, $\nu_{\mathrm{C=N}}$ [19]. The observation of only a single sharp band at ca. 3330 cm^{-1} in the NH stretching region was taken as evidence for the absence of primary amine groups and the presence of secondary amine groups [20]. The manganese complex **1** in MeOH shows an intense absorption band at 348 nm which is assigned to the π–π^* transition associated with an azomethine linkage, whereas **2** in MeOH shows the corresponding band at 309 nm [21,22]. The EPR spectra of these manganese complexes recorded at 4 K are characterised by a broad derivative centered at $g \sim 2$ accompanied by forbidden ($\Delta m_{\mathrm{s}} = 2$) transitions at $g = 4$ indicating antiferromagnetically coupled $\mathrm{Mn^{II}Mn^{II}}$ dimers [23]. While hyperfine splittings of $^{55}\mathrm{Mn}$ $S = \frac{5}{2}$ nuclei usually dominate the EPR spectra of dimeric manganese(II) complexes and proteins, the hyperfine lines are only partially resolved at the EPR spectra of the present systems.

3.2. Catalytic properties of the manganese complexes

The oxidations were carried out in a mixture of CH_3COCH_3:CH_3OH equal to 0.6:0.25 (v/v) using a molar ratio of catalyst:oxidant:cocatalyst:substrate of 1:2000:1000:1000. To explore the reaction conditions, the epoxidation of cyclooctene was used as a standard reaction. We found that the amount of oxidant, of protic methanol and the nature of cocatalyst [24–26] strongly affected the oxidation catalysed by **1** and **2**. Among 1-methyl-imidazole, pyridine, oxalate buffer and ammonium acetate which have been evaluated as cocatalysts, we found ammonium acetate to be the most efficient for cyclooctene epoxidation with H_2O_2 catalysed by manganese–Schiff base complexes. In all other cases, even without cocatalyst, the obtained yields were found to be below 2%.

The catalytic reactions were also performed at 0 °C, i.e., under conditions where H_2O_2 decomposition is expected to be suppressed [14,15]. In this experiment, we found that at low temperature (273 K), the epoxidation reaction of *cis*-stilbene and isoprene is slightly favoured, while it doubles the formation of hex-1-ene oxide. In contrary, low temperature strongly disfavours limonene epoxidation, while the epoxidations of cyclooctene, cyclohexene and styrene are rather disfavoured. These results show that in the present case temperature did not affect all of the studied reactions in the same way. This is in clear contrast to previously reported cases where the oxidant cooling at 273 K clearly prevented H_2O_2 disproportionation leading to high epoxidation yields [14,15].

As shown in Table 1, the manganese–Schiff base complexes/CH_3COONH_4/H_2O_2 system led to the epoxidation of various alkenes with significant to very good yields (47–88%). In certain cases, the yields exceed any other yield reported in the literature. For example, even in the case of the electron-poor hex-1-ene, the obtained epoxidation yield approaches the value of 30%, which is slightly higher compared to those of De Vos–Bein system [14]. Depending upon the temperature and the nature of catalyst, the yields for cyclooctene, cyclohexene, hex-1-ene, styrene, *cis*-stilbene, isoprene and limonene epoxidation vary from 53.6 to 67.4, 61.2 to 87.9, 9.5 to 29.9, 36.1 to 49.6, 53.5 to 67.7, 63.0 to 81.4 and 8.7 to 46.7%, respectively (Table 1). The obtained data for cyclohexene epoxidation can be directly compared to those of the same reaction catalysed by manganese porphyrins or manganese cyclic triamine [6,14,24]. On the other hand, it should be underlined that isoprene epoxidation catalysed by the present system gave an 81.4% yield, which is even higher than the yield obtained by the classical Mn(TDCPP)Cl/imidazole/H_2O_2 system explored by Mansuy and co workers [6]. In all cases, the epoxide is by far the favoured product. Products from possible cleavage of the double bond in styrene, or from allylic oxidation in alkenes have not been detected. In control experiments replacing our catalysts with $Mn(OAc)_3{\cdot}3H_2O$, strong peroxide decomposition and no epoxide formation was found. Cyclohexene oxide or styrene oxide were found to be stable under the reaction conditions. Retention of alkene configuration is not absolute, since from *cis*-stilbene, for instance, a 75:25 and 70:30 mixture of *cis*- and *trans*-epoxides are obtained catalysed by **1** and **2**, respectively.

Replacing H_2O_2 by *t*-BHP, in all cases the obtained total epoxidation yields are very low, below to 20% (Table 2). It is noticed that in hex-1-ene epoxidation, the obtained low yield is comparable to that of H_2O_2 used as oxidant.

Table 1
Influence of temperature on epoxidations with H_2O_2, catalysed by **1** and **2**[a]

Substrate	Products	T (K)	Yield[b] (%)		Total yield[b] (%)	
			1	**2**	**1**	**2**
Cyclooctene	Epoxide	r.t.			53.6	67.4
		273			54.4	57.0
Cyclohexene	Epoxide	r.t.			87.9	85.3
		273			79.8	61.2
Hex-1-ene	Epoxide	r.t.			9.5	13.6
		273			22.8	29.9
Styrene	Epoxide	r.t.			40.2	47.6
		273			36.1	49.6
cis-Stilbene	*cis*-Epoxide	r.t.	40.3	38.0	53.5	54.8
	trans-Epoxide		13.2	16.8		
	cis-Epoxide	273	48.9	40.8	67.7	59.4
	trans-Epoxide		18.8	18.6		
Isoprene[c]	1,2-Epoxide	r.t.	39.2	32.9	74.2	63.0
	3,4-Epoxide		35.0	30.1		
	1,2-Epoxide	273	42.1	40.2	81.4	73.2
	3,4-Epoxide		39.3	33.0		
Limonene	*cis*-1,2-Epoxide	r.t.	22.4	21.9	45.2	46.7
	trans-1,2-Epoxide		16.6	16.6		
	8,9-Epoxides		6.2	7.9		
	cis-1,2-Epoxide	273	6.5	3.6	14.2	8.7
	trans-1,2-Epoxide		5.4	3.0		
	8,9-Epoxides		2.3	2.1		

[a] Conditions—ratio of catalyst:oxidant:CH_3COONH_4:substrate = 1:2000:1000:1000; equivalent of catalyst = 1 μmol in 0.85 ml CH_3COCH_3:CH_3OH (0.6:0.25) under aerobic conditions. Reactions were usually complete within 2 h; r.t.: room temperature.

[b] Yields based on starting substrate.

[c] Reaction time 12 h.

Table 2
Alkene epoxidations with *t*-BHP at room temperature, catalysed by **1** and **2**[a]

Substrate	Total yield[b] (%)	
	1	**2**
Cyclooctene	10.3	11.9
Hex-1-ene	9.0	5.0
Styrene	4.9	4.8
cis-Stilbene	17.6	12.1
Isoprene[c]	8.6	7.6
Limonene	7.6	11.2

[a] Conditions—ratio of catalyst:oxidant:CH_3COONH_4:substrate = 1:2000:1000:1000; equivalent of catalyst = 1 μmol in 0.85 ml CH_3COCH_3:CH_3OH (0.6:0.25) under aerobic conditions. Reactions were usually complete within 2 h.

[b] Yields based on starting substrate.

[c] Reaction time 12 h.

Competitive reactions show alkene reactivity to increase with the electron density of the double bond, e.g., hex-1-ene < cyclohexene < 1-methylcyclohexene (Table 3), indicating the electrophilic nature of oxygen transfer from manganese-oxo intermediate to the olefinic double bond. However, additional effects of alkene shape are obvious: first, the more electron-rich, methylated 1,2-double bond of isoprene is just slightly preferred than the more exposed 3,4-double bond. However, it is noticed that with both the Mn-catalysts, the ratios of the two epoxides formed upon oxidation of isoprene were identical. Secondly, the electron-rich trisubstituted double bond of limonene in 1,2-position gives several times more epoxides than the more accessible but less electron-rich double bond in 8,9-position. The

Table 3
Chemo- and regio-selectivity in alkene epoxidation with H_2O_2 at room temperature, catalysed by **1** and **2**[a]

Alkene **1**	Alkene **2**	Epoxide **1**/epoxide **2**[b]	
		1	**2**
Styrene	*trans*-Methylstyrene	1.0	1.1
Styrene	*cis*-Stilbene	2.4	2.5
Cyclooctene	Styrene	1.5	1.2
Cyclooctene	Cyclohexene	0.6	0.6
Cyclohexene	Hex-1-ene	10.0	12.3
Cyclohexene	1-Methylcyclohexene	0.7	0.7
Limonene[c]		6.2	4.9
Isoprene[d]		1.1	1.1

[a] Conditions—ratio of catalyst:oxidant:CH_3COONH_4:substrate = 1:2000:1000:1000; equivalent of catalyst = 1 μmol in 0.85 ml CH_3COCH_3:CH_3OH (0.6:0.25) under aerobic conditions. Reactions were usually complete within 2 h.

[b] Yields based on starting substrate.

[c] 1,2-Epoxide vs. 8,9-epoxide.

[d] 1,2-Epoxide vs. 3,4-epoxide.

ratio between the 1,2- and 8,9-epoxides was found to be also dependent on the catalyst structure. It varied from 6.2 for the less hindered catalyst **1** to 4.9 for **2**. The control of the regio-selectivity of limonene epoxidation has also been examined by using hindered metalloporphyrins with lower access of the metal-oxo species to the more electron-rich, but more hindered 1,2-double bond. The reactivity of other substrate types was briefly investigated and the results are listed in Table 3.

This catalytic system in our case shows numerous similarities to the manganese porphyrin catalysts and to the De Vos–Bein system [6,14]. Many trends in chemo- and regio-selectivity are the same in both cases and high yields are also obtained on substrate basis. In manganese porphyrin catalysis, imidazole or ammonium acetate is required to allow an efficient H_2O_2 use [6,24], while in De Vos–Bein system [14], the catalytic reaction is independent of the cocatalyst. In our case, it is found that ammonium acetate is exclusively required for the efficient epoxidation of alkenes.

It has been shown previously that manganese complexes in the presence of cocatalyst are prone to catalyse the dismutation of H_2O_2 [27]. In our case, the observed dependence of the epoxide yields on reaction parameters such as solvent, nature of cocatalyst and temperature probably is due to competition between the substrate and hydrogen peroxide for reaction with the oxo-manganese intermediate. Alternatively, an interplay between competitive epoxidation, dismutation or solvation of the partners in the catalytic reaction should be not excluded.

4. Conclusions

In conclusion, we have demonstrated that the new Schiff base manganese complexes are promising catalysts in catalytic epoxidation procedures using hydrogen peroxide as oxidant. The presence of ammonium acetate is always necessary to incorporate H_2O_2 and to obtain efficient reactions. In an acetone–methanol mixture at ambient temperature these manganese complexes are able to catalyse the efficient epoxidation of various alkenes with H_2O_2 as oxidant. The main advantages of the new catalytic system are the facile synthesis and possibility for ligand modification as well as the environmental friendly catalytic process used. Further studies towards the elucidation of the mechanism and introduction of chirality in the ligand are in progress.

Acknowledgements

We thank the postgraduate program ‘Bioinorganic Chemistry’ coordinated by Prof. N. Hadjiliadis at the Department of Chemistry at the University of Ioannina for a fellowship and financial support.

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