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Biomimetic Alkene Epoxidation and Alkane Hydroxylation with Sodium Periodate Catalyzed by Mn(III)-*salen* Supported on Amberlite IRA-200

Valiollah Mirkhani[1,*], **Majid Moghadam**[1,2], **Shahram Tangestaninejad**[1], and **Bahram Bahramian**[3]

[1] Department of Chemistry, University of Isfahan, Isfahan, Iran
[2] Department of Chemistry, Yasouj University, Yasouj, Iran
[3] Department of Chemistry, Shahrood University, Shahrood, Iran

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Summary. The Mn(III)-*salen*, containing phosphonium groups at the 5,5′-positions of the *salen* ligand supported on Amberlite IRA-200 *via* electrostatic binding was used for the oxidation of alkenes and alkanes with sodium periodate at room temperature in the presence of imidazoles as axial ligands, and the effect of solvent, different axial ligands, and various oxygen donors was investigated. This heterogenized catalyst shows high catalytic activity in alkene epoxidation and alkane hydroxylation. It showed high selectivity in the epoxidation of stilbenes, α-pinene, and (*R*)-(+)-limonene, and exhibits a particular ability to epoxidize linear alkenes. The stability and reusability of this new heterogenized metallo-*salen* complex was also investigated. The catalyst was characterized by FTIR, UV-Vis, SEM, and thermal analysis.

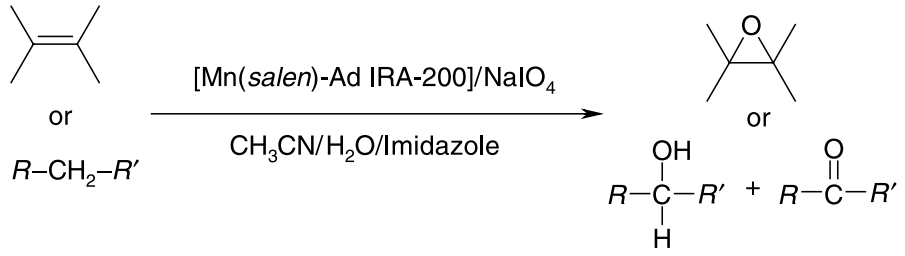
Keywords. Epoxidation; Hydroxylation; Periodate; Manganese(III)-*salen*; Supported catalyst.

Introduction

Cytochrome P-450 enzymes constitute an interesting family of catalysts, which enable the transfer of an oxygen atom to a wide range of organic compounds [1, 2]. Designing of biomimetic models based on metalloporphyrins and *Schiff* base complexes is one of the most important topics in chemistry. Metallo-*salen* complexes such as Mn(III)-*salen*, Cr(III)-*salen*, Ni(II)-*salen*, and Cu(II)-*salen* have been synthesized and used for the epoxidation of olefins [3–6]. Among these reported metallo-*salen* complexes, Manganese(III) *Schiff* base complexes are know to be highly active homogeneous catalysts in the epoxidation of olefins with various oxidants, such as iodosylbenzene, sodium hypochlorite, hydrogen peroxide, and periodate [7–11]. The electronic and steric nature of the metal complex can be tuned by introducing electron-withdrawing and electron-releasing substituents and bulky groups in the ligand. However, the instability of *Schiff* base complexes toward oxidative degradation and difficulties in recovering of these catalysts limit their practical applications in both synthetic and industrial processes. One way to achieve stable *Schiff* base complexes is to immobilize them onto solid supports. Such immobilization offers the combined advantages of homogeneous (mild reaction conditions) and heterogeneous (easy separation) catalysts, and may improve the selectivities and activities because of the support environment.

In our search for new heterogeneous *Schiff* base catalysts [12] we report the attachment of a water-soluble manganese(III)-*salen* complex containing phosphonium groups at the 5,5′-positions of the *salen* ligand on amberlite IRA-200, [Mn(*salen*)-Ad IRA-200], and its catalytic activity in the epoxidation of alkenes and hydroxylation of alkanes with various oxygen atom donors at room temperature (Scheme 1).

* Corresponding author. E-mail: mirkhani@sci.ui.ac.ir



Scheme 1

Results and Discussion

Preparation and Characterization of the Polymer Supported Catalyst, [Mn(salen)-Ad IRA-200]

Mn(III)-*salen* containing the phosphonium groups at the 5,5′-positions of the *salen* ligand was immobilized onto the Amberlite IRA-200, [Mn(*salen*)-Ad IRA-200], *via* electrostatic binding by simple absorption of dicationic manganese(III)-*salen* on Ambelite IRA-200 in aqueous acetone at 80°C. The catalyst loading, which was determined by neutron activation analysis (NAA), is 0.076 mmol per gram of Amberlite. The diffuse reflectance spectra of [Mn(*salen*)-Ad IRA-200] in a $BaSO_4$ matrix clearly indicated that Mn(III)-*salen* complex was immobilized on the Amberlite IRA-200. The FTIR spectrum of the supported catalyst showed signals at 3053 (C_{arom}–H), 1627, 1542, 1463, 1438, 1307, 749, and 509 cm^{-1}, which are assigned to the manganese(III)-*salen* complex, where the Amberlite does not show any peak in this region.

Differential thermal analysis and thermogravimetric analysis were used to characterize the immobilized metal complex. The decomposition behavior of the free complex and the immobilized complex was compared in order to understand the effect of immobilization. The free complex [Mn(III)-*salen*]O*Ac* decomposes during heating to 535°C in several well-defined steps. The immobilized complex showed less defined steps of weight loss and maxima peak. A broad exothermic DTA peak is observed between 235 and 530°C. The free complex showed a weight loss of 33% at temperatures below 400°C. However, for the corresponding immobilized complex, a 6% weight loss appears at temperatures below 400°C. This behavior indicates thermal stability and immobilization of the complex on to the Amberlite. A clear change in morphology of the Amberlite supported complex was also observed by SEM.

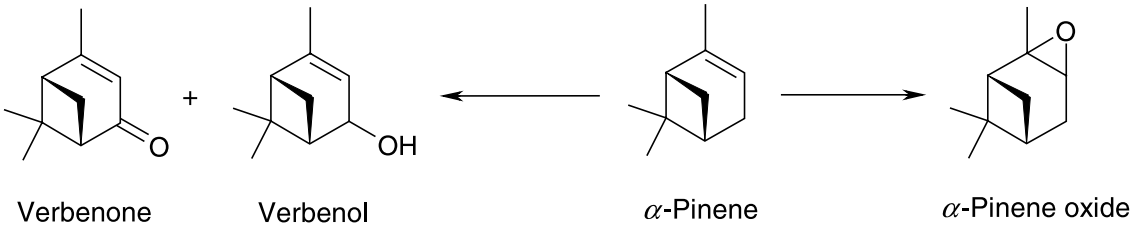
Catalytic Alkene Epoxidation with $NaIO_4$ in the Presence of [Mn(salen)-Ad IRA-200]

The epoxidation of olefins with $NaIO_4$ and [Mn(*salen*)-Ad IRA-200] in the presence of imidazole yielded the corresponding oxidized products in

Table 1. Epoxidation of alkenes with $NaIO_4$ catalyzed by [Mn(*salen*)-Ad IRA-200]

Entry	Alkene	Conversion/%[a]	Epoxide yield/%[a]	Time/min
1	Cyclooctene	97	97	35
2	Cyclohexene	100	95[b]	35
3	Styrene	94	89[c]	35
4	α-Methylstyrene	100	96[d]	35
5	(*R*)-(+)-Limonene	90	75 (1,2-Epoxide) 15 (8,9-Epoxide)	35
6	Indene	95	95	35
7	(*E*)-Stilbene	69	69 (*trans*-Epoxide)[e]	35
8	(*Z*)-Stilbene	78	41 (*cis*-Epoxide)[e] 37 (*trans*-Epoxide)[e]	35
9	1-Heptene	63	63	45
10	1-Dodecene	52	52	50
11	α-Pinene	100	85[f]	35

[a] GLC yield based on the starting alkene; [b] the by-product is 5% allylic ketone; [c] the by-product is 3% benzaldehyde; [d] the by-product is acetophenone; [e] both ^1H NMR and GLC data approved the reported yields; [f] the by-products are 4% verbenone and 11% verbenol



Scheme 2

aqueous acetonitrile at room temperature (Table 1). Cyclooctene was converted to cyclooctene oxide in high yield. In the oxidation of cyclohexene, only trace amount of cyclohexenone was produced. Epoxidation of styrene and α-methylstyrene produced only 5% benzaldehyde and 4% acetophenone as by-products. This catalytic system showed high regioselectivity in the case of (*R*)-(+)-limonene. The ratio among 1,2- and 8,9-epoxides was found to be 5:1. In the case of stilbenes, the (*E*)-stilbene was converted into the *trans*-epoxide in 69% yield, but (*Z*)-stilbene afforded a 41:37 mixture of the *cis*- and *trans*-epoxides. The catalytic system exhibits a particular ability to epoxidize linear alkenes such as 1-heptene and 1-dodecene. In the case of α-pinene, the major product is α-pinene oxide (85%), and allylic oxidation products verbenone and verbenol were produced as minor products (Scheme 2).

The Effect of Different Oxidants on the Epoxidation of Cyclooctene by [Mn(salen)-Ad IRA-200]

In the catalytic epoxidation of alkenes the choice of oxygen donor and solvent is of crucial importance. In order to design the best catalytic system, the ability of different oxidants, such as NaOCl, $NaIO_4$, Bu_4NIO_4, H_2O_2, $KHSO_5$, *tert-Bu*OOH, and urea-H_2O_2, was examined in the epoxidation of cyclooctene at room temperature. As shown in Table 2, NaOCl, H_2O_2, *tert-Bu*OOH, and urea-H_2O_2, either in acetonitrile or dichloromethane, are less efficient than $NaIO_4$ to oxidize cyclooctene. Oxone ($KHSO_5$), which is a strong, cheap, and versatile oxidizing agent was not used further on because of disadvantages, such as need of buffered media and bleaching of the metal catalyst during oxidation reactions.

Sodium periodate was used as the oxygen source because of the following advantages: (i) it gives good oxidation conversion; (ii) it is inert in the absence of catalyst; and (iii) it is readily soluble in CH_3CN/H_2O.

The Effect of Different Solvents on the Epoxidation of Cyclooctene Catalyzed by [Mn(salen)-Ad IRA-200]

In order to choose the reaction media, mixtures of methanol, ethanol, acetone, and acetonitrile with water and wet chloroform, carbontetrachloride, and dichloromethane were tested in the epoxidation of cyclooctene. The obtained results are shown in Table 3. The aqueous acetonitrile was chosen as the reaction medium because higher epoxidation yields were observed. The higher catalytic activity in acetonitrile

Table 2. The effect of different oxidants on the epoxidation of cyclooctene catalyzed by [Mn(*salen*)-Ad IRA-200] at room temperature after 30 min[a]

Oxidant	Solvent	Epoxidation yield/%
$NaIO_4$	CH_3CN/H_2O	97
Oxone ($KHSO_5$)	CH_3CN/H_2O	87
H_2O_2	CH_3CN	61
H_2O_2/urea	CH_3CN	25
NaOCl	CH_3CN	32
*tert-Bu*OOH	CH_3CN	15
Bu_4NIO_4	CH_3CN	38

[a] Cyclooctene (0.5 mmol), oxidant (1 mmol), imidazole (0.14 mmol), catalyst (0.018 mmol), CH_3CN (5 cm^3), H_2O (2.5 cm^3)

Table 3. The effect of solvent on the epoxidation of cyclooctene with $NaIO_4$ catalyzed by [Mn(*salen*)-Ad IRA-200] at room temperature after 30 min[a]

Solvent	Epoxidation yield/%
CH_3CN/H_2O	97
CH_3COCH_3/H_2O	68
CH_3OH/H_2O	56
CH_3CH_2OH/H_2O	44
Wet $CHCl_3$	38
Wet CH_2Cl_2	35
Wet CCl_4	15

[a] Cyclooctene (0.5 mmol), $NaIO_4$ (1 mmol), imidazole (0.14 mmol), catalyst (0.018 mmol), CH_3CN (5 cm^3), H_2O (2.5 cm^3)

is attributed to the polarity of the solvent and the solubility of $NaIO_4$ in the solvent.

The Effect of Different Axial Ligands on the Epoxidation of Cyclooctene with $NaIO_4$ Catalyzed by [Mn(salen)-Ad IRA-200]

It is well known that the catalytic ability of manganese *Schiff* bases is improved by the use of a nitrogen base as co-catalyst [13, 14]. Epoxidation of cyclooctene with the [Mn(*salen*)-Ad IRA-200]/$NaIO_4$ catalytic system in the presence of imidazole produced the oxide product in high yield, whereas the formation of epoxide under the same reaction conditions and in the absence of imidazole was only 29%. We also investigated the effect of different axial ligands upon the epoxidation of cyclooctene. Pure α-donor amines, with very high pK_b values are relatively poor co-catalysts in the epoxidation of cyclooctene (Table 4). Pyridine and methyl-substituted pyridines with weak π-donating ability and pK_b values much smaller than those of σ-donor amines generally show co-catalytic activities similar to those of amines. The observed order of co-catalytic activities, 4-*tert*-butyl-pyridine > pyridine $\gg$ 4-cyanopyridine, seems to be directly related to both the σ- and π-donor abilities of those nitrogen donors. Electron-withdrawing substituents, such as CN^-, essentially display no co-catalytic activity. However, substituted pyridines having electron-releasing methyl groups, such as 4-*tert*-butylpyridine, showed 82% conversion in the epoxidation of cyclooctene, which is higher than for the unsubstituted pyridine. Addition of Ph_3PO and *DMF* as donor ligands have no significant influence on the epoxide yields. Among nitrogen bases, which are used as axial ligands, imidazole and methyl-substituted imidazoles exhibited higher activity toward the epoxidation of cyclooctene with sodium periodate. Strong π-donors *Im*H and *MeIm*Hs are generally better co-catalysts than all the nitrogen donors presented in Table 3. The strong coordination of imidazole should result in an increase of electron density on metal and thus allows a facile cleavage of the O–IO_3 bond of $NaIO_4$.

Table 4. The effect of different axial ligands on the epoxidation of cyclooctene catalyzed by [Mn(*salen*)-Ad IRA-200]/$NaIO_4$ system after 30 min[a]

Axial ligand	Epoxidation yield/%
No axial base	29
Triethylamine	30
Diethylamine	33
Piperidine	54
Pyridine	51
4-Cyanopyridine	25
2-Methylpyridine	55
4-Methylpyridine	58
4-*tert*-Butylpyridine	82
Imidazole	97
2-Methylimidazole	92
4(5)-Methylimidazole	93
2-Ethylimidazole	79
Pyrazine	69
Quinaldine	32
Morpholine	41
Triphenylphosphine oxide	34
DMF	30

[a] Cyclooctene (0.5 mmol), $NaIO_4$ (1 mmol), axial ligand (0.14 mmol), catalyst (0.018 mmol), CH_3CN (5 cm^3), H_2O (2.5 cm^3)

Alkane Hydroxylation with $NaIO_4$ in the Presence of [Mn(salen)-Ad IRA-200]

Selective partial alkene oxidation is a particularly challenging problem in organic chemistry. The cat-

Table 5. Hydroxylation of alkanes with $NaIO_4$ catalyzed by [Mn(*salen*)-Ad IRA-200]

Entry	Alkane	Conversion/%[a]	Ketone yield/%[a]	Alcohol yield/%[a]	Time/min
1	Cyclooctane	66	38	36	55
2	Cyclohexane	55	45	10	60
3	1,2,3,4-Tetrahydronaphthalene	91[b]	91	–	55
4	Ethylbenzene	42[c]	42	–	60
5	Adamantane	70	12	58	55
6	Propylbenzene	41[d]	41	–	60
7	Fluorene	81	81	–	55

[a] GLC yield based on starting alkane; [b] only the α-position was oxidized; [c] the product is acetophenone; [d] the product is ethyl phenyl ketone

alytic hydroxylation of alkanes and arylalkanes with sodium periodate was performed in the presence of [Mn(*salen*)-Ad IRA-200] under the same conditions described for alkene epoxidation (Table 5). The obtained results showed that in this catalytic system cyclooctane, cyclohexane, and adamantane produced a mixture of alcohol and ketone, whereas 1,2,3,4-tetrahydronaphthalene, ethylbenzene, propylbenzene, and fluorene only were converted to the corresponding ketones. The regioselectivity observed for the oxidation of adamantane showed a significant preference for position 1 over position 2. This can be attributed to the unique microenvironment constituted by the *Schiff* base macrocycle and support matrix. In the case of 1,2,3,4-tetrahydronaphthalene, only the α-position was oxidized and α-tetralon was obtained in high yield. Oxidation of alkylaromatics, such as ethylbenzene and propylbenzene led to producing acetophenone and ethyl phenyl ketone.

Catalyst Reuse and Stability

To assess long-term stability and reusability of [Mn(*salen*)-Ad IRA-200], cyclooctene was used as a model substrate, and recycling experiments were carried out with a single sample of the catalyst. After each experiment, the catalyst was removed by simple filtration, washed with water and acetonitrile, and reused. The resulting yields are listed in Table 6. The loss of activity observed in the reused catalyst may be attributed to the degradation of the *salen* complex during the reaction [16]. The filtrates were used for determination of manganese leaching. The amounts of manganese leached after each run was determined by atomic absorption spectroscopy (Table 6). The nature of the recovered catalyst was followed by IR and UV-Vis spectra. The results indicated that the catalyst after reusing several times, showed no change in its IR and UV-Vis spectra.

Table 6. The results obtained from catalyst reuse and stability in the oxidation of cyclooctene with sodium periodate by [Mn(*salen*)-Ad IRA-200]

Run	Epoxide yield/%[a]	Time/min	Mn leached/%[b]
1	97	30	5
2	79	30	3
3	60	30	1

[a] GC yield; [b] determined by atomic absorption spectroscopy

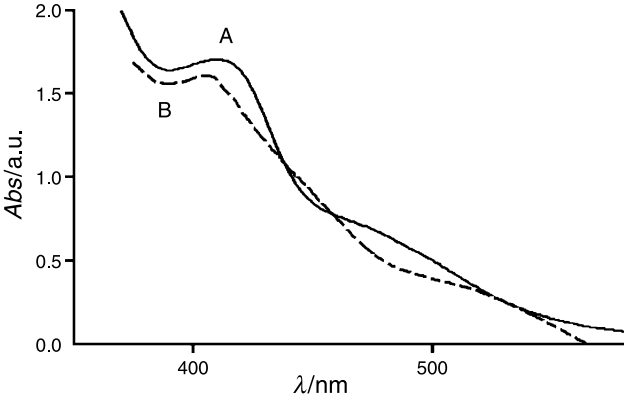


Fig. 1. The UV-Vis spectra of A) non-supported solid Mn(III)-(*salen*)O*Ac* and B) Mn(*salen*)-Ad IRA-200

Experimental

All chemicals were used as received from Merck, Aldrich, and Fluka. Amberlite IRA-200 was purchased form Fluka. Alkenes and alkanes were purified prior to use by passing through a column containing active alumina to remove peroxidic impurities.

Preparation of the Complex

The *Schiff* base ligand was prepared by the standard procedure of refluxing ethanolic solutions of the corresponding diamine and salicylaldehyde derivative in a 1:2 molar ratio according to Refs. [16, 17]. Thus, salicylaldehyde was chloromethylated and reacted with triphenylphosphine, to give 2-hydroxy-5-(triphenylphosphinomethyl)benzaldehyde chloride, which in the condensation with ethylenediamine in a 1:2 molar ratio gave *N*,*N*′-bis{[5-(triphenylphosphonium)methyl]salicylidene}-1,2-ethanediamine chloride. Finally, the ligand was complexed with manganese acetate to give [Mn(III)-*salen*]O*Ac*.

Immobilization of Schiff Base Complex on Amberlite IRA-200

To a solution of 0.5 g of the complex in 100 cm^3 of a 1:1 acetone:water mixture was added 5 g Amberlite IRA-200 and stirred at 80°C for 24 h. After cooling to room temperature, the brown solids were washed with H_2O until no metallo-*salen* could be detected in the filtrates by UV-Vis analysis. The catalyst was dried under vacuum prior to use.

The content of manganese(III)-*salen* on the Amberlite IRA-200 support was calculated from the manganese content in heterogenized catalyst as determined by NAA. Diffuse reflectance spectra were recorded on a Shimadzu UV-265 instrument using optical grade $BaSO_4$ as the reference. Themogravimetric analysis of the catalyst was carried out on a Mettler TA4000 instrument.

FTIR spectra were obtained for KBr pellets in the range 400–4000 cm^{-1} with a Nicolet Impact 400D spectrometer. Scanning electron micrographs of the catalyst and resin were taken on a SEM Philips XL 30 instrument. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m.

General Procedure for Catalytic Epoxidation of Alkenes and Hydroxylation of Alkanes

All of the reactions were carried out at room temperature under air in a 25 cm^3 flask equipped with a magnetic stirring bar. A solution of 1 mmol $NaIO_4$ in 2.5 cm^3 H_2O was added to a mixture of 0.5 mmol alkene or alkane, 0.018 mmol catalyst, and 0.14 mmol imidazole in 5 cm^3 CH_3CN. The progress of the reaction was monitored by GC. The reaction mixture was diluted with 10 cm^3 CH_2Cl_2 and filtered. The resin was thoroughly washed with CH_2Cl_2 and the combined washings and filtrates were purified on silica-gel plates or a silica-gel column. IR and ^1H NMR spectral data confirmed the identities of the product.

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