

Catalytic Oxidation of Primary Aromatic Amines with Sodium Periodate Catalyzed by Mn(III)salophen Complex Supported on Polystyrene-Bound Imidazole

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The catalytic activity of Mn(III)salophen complex supported on polystyrene-bound imidazole, [Mn(salophen)Cl-PSI], was studied in the oxidation of primary aromatic amines in acetonitrile/water, using sodium periodate as an oxygen source. Amines were oxidized efficiently to their corresponding azo derivatives in the presence of this catalyst. The heterogeneous catalyst showed high stability and reusability in the oxidation reactions and could be reused several times without loss of its activity. The effect of different solvents was studied in the oxidation of *p*-toluidine and CH₃CN/H₂O was chosen as the solvent.

Keywords: Amines, Oxidation, Manganese salophen, Polystyrene, Periodate

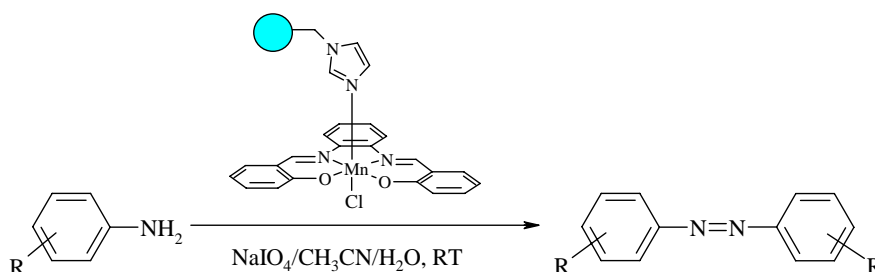
INTRODUCTION

Transition metal complexes with Schiff bases and porphyrin ligands have been successfully used as models for the heme containing Cytochrom P-450 [1]. P-450 enzymes are known to oxidize a very extensive range of endogenous and exogenous organic compounds. These reactions are important in biological systems because they are crucial steps in biosynthesis, cellular biochemistry, metabolism, pharmacology and medicine [2,3]. Various single oxygen atom donors such as NaClO, PhIO, KHSO₅, H₂O₂ and NaIO₄ have been used for oxidation reactions [4-10]. These complexes catalyze the transfer of oxygen atoms to organic substrates and the nature of products depends on several factors such as substrate, oxidant, counter ion, solvent, structure of salen ligands and the kind of axial ligand [11,12]. Metal complexes of salen and salophen ligands have been used as reagents and catalysts in many reactions including olefin epoxidation, nucleic acid modification, electrochemical reduction, alkane hydroxylation, Diels-Alder transformation,

decarboxylation of carboxylic acids, amines oxidation and medicinal studies as models for mimicking the superoxide dismutase [15-17]. 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 salen ligand. The catalytic activity of these biomimetic catalysts decreases in a homogeneous medium, because of the formation of inactive dimeric μ -oxo manganese(IV) species [13,14]. The heterogenization of these complexes on several supports is the subject of intense research in order to facilitate catalyst separation from the reaction mixture, simplify procedures for catalyst recycling and maximizing the site isolation of catalytic centers to minimize the possibility of inactive oxo-bridged dimer formation [18-21].

Recently, we reported the use of supported Manganese(III) salophen/periodate systems in the epoxidation of alkenes and hydroxylation of alkanes [22-24]. This paper describes a catalytic system based on a chloromethylated polystyrene support modified with imidazole (PSI), which could act as an axial ligand for Mn(salophen) by covalent attachment. The catalytic activity and reusability of this catalyst in the

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Scheme 1

oxidation of primary aromatic amines with NaIO_4 were investigated (Scheme 1).

EXPERIMENTAL

Instruments and Reagents

All materials were commercial reagent grade. Chloromethylated polystyrene (4-5% Cl content, 2% cross-linked with divinylbenzene) was purchased from Merck. Amines were obtained from Merck or Fluka and were passed through a column containing active alumina to remove oxidation impurities. $[\text{Mn}(\text{salophen})\text{Cl-PSI}]$ was synthesized according to our previously reported method [22].

Catalytic Experiments

All reactions took place at room temperature under air in a 25 ml flask equipped with a magnetic stirrer bar. In a typical experiment, a solution of NaIO_4 (2 mmol) in H_2O (3 ml) was added to a mixture of amine (1 mmol), $\text{Mn}(\text{salophen})\text{Cl-PSI}$ (0.096 mmol) in CH_3CN (3 ml). The reaction mixture was stirred at room temperature. The progress of reaction was monitored by TLC. After the reaction was completed, the reaction products were extracted with CH_2Cl_2 (2×10 ml) and purified on a silica-gel plate or a silica-gel column (eluent: $\text{CCl}_4\text{-Et}_2\text{O}$). IR and ^1H NMR spectral data confirmed the identities of the products.

RESULTS AND DISCUSSION

Effect of Solvent on the Oxidation of *p*-Toluidine with NaIO_4 Catalyzed by $\text{Mn}(\text{salophen})\text{-PSI}$

From among the mixtures of acetonitrile, acetone (single

phase systems), dichloromethane, chloroform and carbontetrachloride (two phase systems with Bu_4NBr as phase transfer catalyst) with water, the 1:1 acetonitrile/water mixture was chosen as the reaction medium whose higher catalytic activity was observed. The results are shown in Table 1.

Catalytic Oxidation of Primary Aromatic Amines with NaIO_4 Catalyzed by $\text{Mn}(\text{salophen})\text{-PSI}$

First, to find the optimized conditions, the oxidation of *p*-toluidine with NaIO_4 in the presence of catalytic amounts of $\text{Mn}(\text{salophen})\text{-PSI}$ was investigated. The optimum conditions which were obtained for the oxidation of *p*-toluidine by this catalytic system, were the catalyst, oxidant, and substrate in a molar ratio of 1:2:10, respectively.

Oxidation of various primary aromatic amines was performed under the same reaction conditions which were

Table 1. Effect of Solvent on the Oxidation of *p*-Toluidine Catalyzed by $\text{Mn}(\text{salophen})\text{Cl-PSI}$ at Room Temperature^a

| Row | Solvent | Conversion (%) ^b after 30 min |
|-----|---|--|
| 1 | $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ | 87 |
| 2 | $\text{CH}_3\text{COCH}_3/\text{H}_2\text{O}$ | 51 |
| 3 | $\text{CHCl}_3/\text{H}_2\text{O}$ | 18 |
| 4 | $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ | 20 |
| 5 | $\text{CCl}_4/\text{H}_2\text{O}$ | 15 |

^aReaction conditions: amine (1 mmol), NaIO_4 (2 mmol), catalyst (0.096 mmol), CH_3CN (3 ml), H_2O (3 ml).

^bIsolated yield.

obtained for *p*-toluidine. The obtained results showed that the catalyst was an efficient one for oxidation of amines under agitation with magnetic stirring. As shown in Table 2, the azo derivatives were obtained in 60-87% isolated yields. It is clear that the electron rich amines are more reactive than the electron poor ones.

A blank experiment in the presence of the oxidant using the same experimental conditions as in the absence of the catalyst was also investigated in the oxidation of *p*-toluidine. The results showed that NaIO₄ had poor ability to oxidize the *p*-toluidine at room temperature.

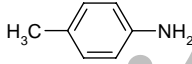
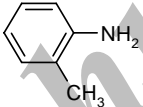
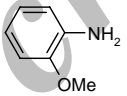
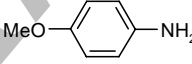
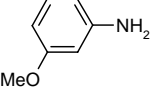
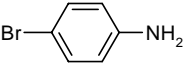
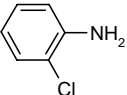
Catalyst Reuse and Stability

The stability of Mn(salophen)-PSI was studied in repeated

oxidation reactions of *p*-toluidine with NaIO₄ under agitation with magnetic stirring. At the end of each reaction, the catalyst was separated from the reaction mixture by filtration, washed with water and acetonitrile and dried carefully before using it in the subsequent runs. After the use of the catalyst for four consecutive times, the azo yield was 87% (Table 3). The filtrates were used for the determination of manganese leaching. The results showed that only small amounts of Mn was detected in the filtrates after the two first runs by atomic absorption spectroscopy.

Such a finding confirmed the strong covalent bonding of the polymer and the metallosalophen, in which the Mn(salophen) catalyst was not leached from the polymer during the oxidation reaction.

Table 2. Oxidation of Primary Aromatic Amines to Azo Derivatives with NaIO₄ Catalyzed by Mn(salophen)Cl-PSI^a

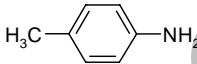
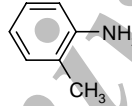
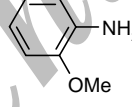
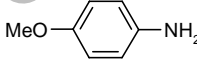
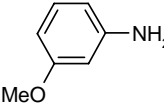
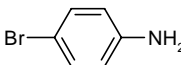
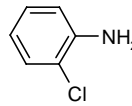
| Row | Amine | Conversion (%) ^b | Time (h) | TOF |
|-----|---|-----------------------------|----------|-------|
| 1 |  | 87 | 0.5 | 18.13 |
| 2 |  | 85 | 0.5 | 17.71 |
| 3 |  | 86 | 1 | 17.92 |
| 4 |  | 77 | 1 | 16.04 |
| 5 |  | 74 | 1 | 15.42 |
| 6 |  | 67 | 1 | 13.96 |
| 7 |  | 60 | 3 | 12.50 |

^aReaction conditions: amine (1 mmol), NaIO₄ (2 mmol), catalyst (0.096 mmol), CH₃CN (3 ml), H₂O (3 ml). ^bBased on aromatic amine.

Table 3. The Results of [Mn(salophen)Cl-PSI] Catalyst Recovery and the Manganese Leached in the Oxidation of *p*-Toluidine with NaIO₄

| Run | Conversion (%) ^a | Time (h) | Mn leached (%) ^b |
|-----|-----------------------------|----------|-----------------------------|
| 1 | 87 | 0.5 | 0.5 |
| 2 | 82 | 0.5 | 0.2 |
| 3 | 80 | 0.5 | 0 |
| 4 | 80 | 0.5 | 0 |

^aIsolated yield. ^bDetermined by atomic absorption spectroscopy.**Table 4.** Oxidation of Primary Aromatic Amines to azo Derivatives with NaIO₄ Catalyzed by Mn(III)salophen and Mn(III)salophen-PSI

| Row | Amine | Conversion (%) /time (h) | |
|-----|---|--------------------------|-------------|
| | | Heterogeneous | Homogeneous |
| 1 |  | 87/0.5 | 88/0.2 |
| 2 |  | 85/0.5 | 83/0.2 |
| 3 |  | 86/1 | 82/0.2 |
| 4 |  | 77/1 | 85/0.2 |
| 5 |  | 74/1 | 83/0.2 |
| 6 |  | 67/1 | 61/0.5 |
| 7 |  | 60/3 | 65/0.5 |

Comparison of Homogeneous Mn(salophen)Cl and Heterogeneous Mn(salophen)Cl-PSI in Amine Oxidation with Sodium Periodate

In order to show the effect of supporting on the catalytic activity of manganese(III) salophen in the amine oxidation with sodium periodate, we repeated all the reactions under the same reaction conditions and the same amounts of the catalyst, substrate, NaIO_4 and imidazole as an axial ligand in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ mixture. The obtained results, which are summarized in Table 4, showed that in the amine oxidation, the turnover frequencies (TOF) for the homogeneous catalyst were higher than the heterogeneous counterpart, but the stability of the heterogeneous catalyst was better than that of the homogeneous catalyst. On the other hand, the heterogeneous catalyst could be recovered several times without loss of its activity.

CONCLUSIONS

In this paper, we demonstrated the use of $[\text{Mn}(\text{salophen})\text{Cl-PSI}]$ catalyst in the oxidation of primary aromatic amines to azo derivatives with NaIO_4 . This catalytic system showed high activity in the oxidation of various primary aromatic amines under mild reaction conditions. Easy preparation and handling of the catalyst, commercial availability of support, mild reaction conditions (room temperature), no need for axial ligand in the catalyst system and facial and effective catalyst recovery and recycling make this catalytic system a useful method for oxidizing of amines.

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