Epoxidation of Alkenes and Oxidation of Alcohols with Hydrogen Peroxide Catalyzed by a Fe (Br₈TPPS) Supported on Amberlite IRA-400

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Abstract
Iron (III) meso-tetrakis(p-sulfonatophenyl)-β-octabromoporphyrin supported on Amberlite IRA-400 [Fe(Br₈TPPS)-Ad-400] is a robust and efficient catalyst for oxidation of alkenes and alcohols at room temperature. The catalyst exhibits a high activity and stability in hydrocarbon oxidation by H₂O₂. The method was useful in the oxidation of various primary, secondary-aliphatic, alicyclic and aromatic alcohols. Both activated and non-activated alcohols were converted into their corresponding carbonyls efficiently and selectively. Aqueous hydrogen peroxide as an environmentally benign oxidant is utilized in oxygen transfer. The oxidation reaction using heterogeneous solid catalysts with H₂O₂ as oxidants are environmentally friendly routes to produce extensively useful epoxides which are traditionally obtained from capital-intensive or environmentally polluted processes.

Keywords: Octabromoporphyrin, Epoxidation, Hydrogen peroxide, Catalyst.

Introduction
The epoxidation of olefins are a class of important chemical processes because epoxides are widely used as raw materials for synthesis of variety of chemicals such as alcohols (polyols), glycols, olefinic compounds, lubricants, plasticizer and stabilizer for polymers and their demand is increasing day by day [1-5]. Oxidation reactions with environmentally friendly oxidants such as molecular oxygen and hydrogen peroxide [6, 7] have been intensively studied during recent years. These oxidants are highly attractive since they are cheap and produce no toxic waste products in contrast to many commonly employed oxidants, MCPBA, PhIO, NaOCl, etc, but it is not reactive enough for many applications. Catalysts to promote the epoxidation of alkenes, oxidation of sulfides, etc., by hydrogen peroxide are potentially of
Iron porphyrins with the environmentally friendly oxidant hydrogen peroxide have been recently shown to catalyze olefin epoxidation and alkane hydroxylation [9]. High-valent d0 transition metal complexes, such as Mo (VI), V(V) and Ti (IV), are versatile catalysts for the epoxidation of alkenes [12]. Sharpless and co-workers reported a pyridine ligand-accelerated methyltrioxorhenium (MTO) catalyzed epoxidation of various olefinic compounds using H₂O₂ with excellent yields to epoxides [13].

Traditionally, oxidation of benzyl alcohol is carried out with the help of various hazardous and expensive inorganic oxidants, such as hypochlorite, manganese (IV) oxide, permanganate, chromium (IV) oxide and dichromate. Numerous studies have been reported on the oxidation of benzyl alcohol to benzaldehyde by using different catalysts and oxidants under liquid phase condition. Yang et al. reported the oxidation of benzyl alcohol using iodosylbenzene as oxidant. It showed a very high catalytic activity with 100% conversion and selectivity towards benzaldehyde. The disadvantages of iodosylbenzene are low oxygen atom efficiency and high cost of practical application as compared to H₂O₂. Moreover, other promising catalysts such as palladium and gold supported on metal oxides have also been studied and they exhibited remarkable catalytic activity. However, they are not cost effective [14].

More recently, porous metalloporphyrin networks have proven to be potentially applicable as efficient heterogeneous catalysts after immobilization in organic amorphous polymers, amorphous inorganic matrices, or crystalline inorganic materials such as silica, zeolites, clay from the smectite group (montmorillonite), layered double hydroxides, tubular and fibrous matrices, silica matrix obtained by the sol-gel process, among others [15].

Such immobilization makes the catalysts separable from reaction mixtures and reusable, enhance the catalyst stability towards oxidation and allow preparation of eco-friendly catalysts. Many heterogenized metalloporphyrin catalysts have been reported for oxidation of hydrocarbons [16, 17].

In the present research work, Iron (III) meso-tetrakis(p-sulfonatophenyl)-β-octabromoporphyrin has been synthesized and supported on Amberlite IRA 400 and used as reusable heterogeneous catalysts in the selective oxidation of alcohols and epoxidation of olefins using hydrogen peroxide as an environmentally friendly oxidant.

**Experimental**

**Materials**

Alkenes and alcohols were obtained from Merck and Fluka and purified prior to use by passing through a column containing active alumina to remove peroxidic impurities.
The porphyrin ligand H$_2$TPPS was prepared, brominated and metallated according to literature procedures [18-20].

**Immobilization of Fe(Br$_8$TPPS) on Amberlite IRA-400**

Fe(Br$_8$TPPS) (0.5 g) was dissolved in a 1:1 mixture of acetone-water and Amberlite IRA-400 (5 g) was added to the solution. The mixture was stirred at 80 °C for 8 hr. The reaction mixture was cooled to room temperature, filtered, washed with water and acetone and dried. The polymer supported porphyrin is insoluble in common organic solvents. The reflectance spectrum clearly indicates a Soret band at 481 nm and a Q band at 569 nm. The IR spectrum of the solid supported iron porphyrin shows ν(S=O) at 1400 and 1170 cm$^{-1}$. The degree of iron porphyrin incorporation into the polymer was determined by neutron activation analysis (NAA), which gave a value of about 0.21% w/w.

**Typical procedure for oxidation reactions catalyzed by Fe(Br$_8$TPPS)-Ad-400**

All of the reactions were carried out at room temperature under air in a 25 mL flask equipped with a magnetic stirring bar. A solution of H$_2$O$_2$ (4 mmol) was added to a mixture of alkene or alcohol (1 mmol), Fe(Br$_8$TPPS)-Ad 400 (11 μmol) and imidazole (0.2 mmol) in CH$_3$CN (10 mL). The progress of reaction was monitored by GLC. The reaction mixture was diluted with CH$_2$Cl$_2$ (20 mL) and filtered. The resin was thoroughly washed with CH$_2$Cl$_2$ and the combined washings and filtrates were purified on silica-gel plates or a silica-gel column. IR and $^1$H-NMR spectral data confirmed the identities of the products.

**Catalyst reuse**

The stability of Fe(Br$_8$TPPS)-Ad 400 was studied in repeated epoxidation reaction. The epoxidation of cyclooctene was chosen as a model substrate for studying the reuse and stability of the catalysts. The reaction was carried out as described above. At the end of the reaction, the catalyst was separated from the reaction mixture by simple filtration and washed with water and acetonitrile and reused. The dried catalyst was consecutively reused four times. After the use of catalyst for four consecutive times, the conversion yield was 77%. The amount of leached Fe (1.0 %) was determined by atomic absorption spectroscopy.

**Results and discussion**

Because hydrogen peroxide is the desired green oxidant of choice and also because of our success in the oxidative transformation of functional group, we wanted to study the much-sought-after oxidation of alcohols and epoxidation of alkenes with hydrogen peroxide under the influence of a suitable catalytic system that is recyclable and hence economical, mild and efficient. Therefore, we
studied the oxidation alcohols and epoxidation of alkenes with hydrogen peroxide (30%) using acetonitril as solvent at room temperature in the presence of Fe(Br$_8$TPPS) supported on Amberlite IRA-400. The use of basic amberlite IRA-400 resin has two advantages. Firstly, it acts as a phase-transfer catalyst (PTC) and secondly, it can very easily be separated out from the reaction mixture as it remains in the solid form [21].

Fe(Br$_8$TPPS) is a sulfonated hindered metalloporphyrin with electron withdrawing substituents at the β-positions of the pyrroles. The electronegative groups on the pyrrole moieties enhance the reactivity of the metal oxo species and immobilization of the metalloporphyrin on ion-exchange resin (Amberlite IRA-400) and avoid μ-oxo formation. The catalyst exhibits a high activity and stability for the oxidation of hydrocarbons with hydrogen peroxide. Scheme 1 shows the reaction conditions:

\[
\text{R-CH}_2\text{OH and R'-CH-R''} 
\quad \text{and} \quad \text{Fe}^{\text{III}} (\text{Br}_8\text{TPPS})-\text{Ad}-\text{400/imidazole/H}_2\text{O}_2 \quad \text{CH}_3\text{CN} 
\quad \text{O} \quad \text{O} 
\quad \text{R'-C-R''} \quad \text{R-CHO and R'-C-R'}
\]

Scheme 1. The reaction conditions of hydrocarbon oxidation by H$_2$O$_2$.

It is found that addition of a heterocyclic nitrogen base such as imidazole or 1-methylimidazole to this catalytic system improves the activity of the catalyst. In the presence of imidazole, the Fe(Br$_8$TPPS)–Ad-400 system converts different alkenes efficiently to their corresponding epoxide compounds with hydrogen peroxide in CH$_3$CN at room temperature (Table 1). The selectivity to the corresponding epoxide product was between 20 to 100%. Epoxidation of trans-stilbene proceeds in a stereospecific manner with complete retention of configuration. In contrast, epoxidation of cis-stilbene is associated with some loss of stereochemistry, affording 80% cis- and 10% trans-stilbene oxides, respectively. Evidently, this thermodynamically more stable trans-stilbene oxide requires a free rotation about the alkene C-C bond at some intermediate steps, which is more feasible using catalysts with less steric strain [22]. The oxidation potential of the catalyst was further explored by performing oxidation of various alcohols under the same reaction conditions. Fe(Br$_8$TPPS)-Ad-400 catalyst was found to exhibit excellent activity for the oxidation of a variety of alcohols using hydrogen peroxide as oxidant at room temperature in acetonitrile and the results are shown in Table 2. The selectivity to the corresponding carbonyl products was 100%. Even though the best conditions and therefore
the maximum conversions obtainable for individual alcohols were not optimized, the method was found to be useful in the oxidation of various primary, secondary-aliphatic, alicyclic and aromatic alcohols. Both activated and non-activated alcohols were converted to the corresponding carbonyls efficiently and selectively.

**Table 1.** Oxidation of various alkenes catalyzed by Fe(Br₅TPPS)-Ad-400⁴.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Conv. (%)</th>
<th>Product (selectivity, %)</th>
<th>Reaction time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>89</td>
<td>O (100)</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>66</td>
<td>O (100)</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>73</td>
<td>O (38)</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>81</td>
<td>O (76)</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>90</td>
<td>(80)</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>69</td>
<td>(100)</td>
<td>6</td>
</tr>
</tbody>
</table>

a catalyst 11 μmmol, alkene 1.0 mmol, CH₃CN 10 ml, imidazole 0.2 mmol and H₂O₂ 4 mmol at room temperature; b All products were identified by comparison of their physical and spectral data with those of authentic samples or GC-Mass.
Benzyl alcohol was oxidized quantitavely to benzaldehyde (Table 2, entry 1). The oxidation products of 4-choloro benzyl alcohol and 4-bromo benzyl alcohol (Table 2, entries 2 and 3) were corresponding aldehydes. Conversion was increased for the 4-methoxy substituted benzyl alcohol (Table 2, entry 4). The oxidation product of 2-choloro benzyl alcohol (entry 5) was the corresponding carbonyl product. Alicyclic alcohol such as cyclohexanol (Table 2, entry 6), cyclooctanol (entry 7) and 1-indanol (entry 8) were also successfully converted to their respective cyclic ketones.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Conv. (%)</th>
<th>Product (selectivity, %)</th>
<th>Reaction time/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₂OH</td>
<td>98</td>
<td>CHO</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>CH₂OH Cl</td>
<td>81</td>
<td>CHO Cl</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>CH₂OH Br</td>
<td>75</td>
<td>CHO Br</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>CH₂OH MeO</td>
<td>80</td>
<td>CHO MeO</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>CH₂OH Cl</td>
<td>91</td>
<td>CHO Cl</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>OH</td>
<td>90</td>
<td>CO</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>OH</td>
<td>78</td>
<td>CO</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>OH</td>
<td>64</td>
<td>CO</td>
<td>4</td>
</tr>
</tbody>
</table>

*a* catalyst 11 μmol, alcohol 1.0 mmol, CH₃CN 10 ml, imidazole 0.2 mmol and H₂O₂ 4 mmol at room temperature; *b* All products were identified by comparison of their physical and spectral data with those of authentic samples or GC-Mass.
A comparison of Fe(Br₈TPPS)-Ad-400 catalytic system with previously reported systems (Table 3) shows that the conversions (specially primary alcohols) are much higher than in the other systems like vanadium phosphorus oxide catalyst [23], furthermore, over-oxidation of benzyl alcohol or primary alcohols that have been reported by catalyst SiW11Zn [24] was not observed.

Table 3. Comparison of the activity of heterogeneous transition metal catalysts in the oxidation of benzyl alcohol with H₂O₂.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Product</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Selectivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(Br₈TPPS)-Ad-400</td>
<td>Benzaldehyde</td>
<td>4</td>
<td>98</td>
<td>100</td>
<td>This work</td>
</tr>
<tr>
<td>Cr(III)-Schiff base/ MCM-41</td>
<td>Benzaldehyde</td>
<td>4</td>
<td>45</td>
<td>100</td>
<td>[25]</td>
</tr>
<tr>
<td>[Cu(tetraazamacrocycle)]/ NaY a</td>
<td>Benzaldehyde</td>
<td>6</td>
<td>27</td>
<td>96.3</td>
<td>[26]</td>
</tr>
<tr>
<td>Ammonium molybdate</td>
<td>Benzaldehyde</td>
<td>5</td>
<td>77</td>
<td>99</td>
<td>[27]</td>
</tr>
<tr>
<td>alkali-treated ZSM-5 zeolite b</td>
<td>Benzaldehyde</td>
<td>4</td>
<td>53</td>
<td>86</td>
<td>[28]</td>
</tr>
<tr>
<td>[Co((OH)₂-salen)]/ MWNTs c</td>
<td>Benzaldehyde</td>
<td>6</td>
<td>86</td>
<td>100</td>
<td>[29]</td>
</tr>
<tr>
<td>YCu(dimgh)₂ d</td>
<td>Benzaldehyde</td>
<td>8</td>
<td>30</td>
<td>100</td>
<td>[30]</td>
</tr>
<tr>
<td>[(n-C₄H₉)₂N₃]₃H[PW₁₁Ni(H₂O)O₃₉] e</td>
<td>Benzaldehyde</td>
<td>12</td>
<td>96</td>
<td>37</td>
<td>[31]</td>
</tr>
<tr>
<td>Nano-iron oxide (Nano-γ-Fe₂O₃)</td>
<td>Benzaldehyde</td>
<td>12</td>
<td>33</td>
<td>97</td>
<td>[32]</td>
</tr>
<tr>
<td>Vanadium silicate xerogel (V2O₅-SiO₂)</td>
<td>Benzaldehyde</td>
<td>24</td>
<td>18</td>
<td>100</td>
<td>[33]</td>
</tr>
</tbody>
</table>

a [Cu{Me₄(Bzo)₂tetraeneN₄}]-NaY  
b 25ZSM(AT-0.5), where 25 denotes the SiO₂/Al₂O₃ ratio and 0.5 denotes the alkali-treatment time.  
c H₂[(OH)₂-salen] = N,N’-bis(4-hydroxysalicylidene)-ethylene-1,2-diamine, MWNTs = modified multi wall carbon nanotubes.  
d dimgh = dimethylglyoxime synthesized in situ in Y zeolite  
e Nickel-substituted polyoxotungstate

Probable mechanism for epoxidation of olefins

Recent research suggests that complications in the oxidation reaction can have several origins, and competing mechanisms, especially for electronrich porphyrins, can complicate mechanistic interpretations. For instance, direct oxidation of the porphyrin ligands by Fe-oxene intermediates can compete with catalytic oxidation, even if halogenated porphyrins are used. Consequently, reactions of Fe-oxene species with the oxidant to generate free alkoxy radicals may partially explain why Fe porphyrins in catalytic epoxidations can have poor activities [34].

Synthesis of a new porphyrin, Iron (III) meso-tetrakis-(4-sulfonatophenyl)-β-octabromoporphyrin Fe(Br₈TPPS) and catalytic reduction of molecular oxygen to hydrogen peroxide using this porphyrin is described. Based on the experimental results, a proposed mechanism for the oxidation of alcohols by hydrogen peroxide under Fe (III) catalysis can be summarized and is shown in Scheme 2. Although the exact mechanism of this
transformation is still unclear, the catalytic cycle probably involves the formation of an intermediate oxo-Fe(V) complex.

\[ \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} \]

\[ \text{LFe}^{\text{III}} \rightarrow \text{Oxygen Transfer} \rightarrow \text{LFe}^{\text{V}} = \text{O} \]

Scheme 2. Probable mechanism for the oxidation of alcohols and olefins.

**Structural characterization of Carbonyl and Epoxy Compounds**

Cyclooctene oxide (Table 1, entry 1): Colorless oil; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 2.86-2.76 (m, 2H), 2.13-2.06 (m, 2H), 1.55-1.13 (m, 10H); \(^{13}\)C NMR (200 MHz, CDCl\(_3\)) \(\delta\) 57.18, 28.57, 28.30, 27.61.

Cyclohexene oxide (Table 1, entry 2): \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) 3.11 (2H, m), 1.90-1.97 (2H, m), 1.77-1.83 (2H, m), 1.37-1.46 (2H, m), 1.17-1.26 (2H, m); \(^{13}\)C NMR (250 MHz, CDCl\(_3\)) \(\delta\) 19.4 (CH\(_2\)), 24.2 (CH\(_2\)), 55.1 (CH).

Styrene oxide (Table 1, entry 3): \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) 2.79 (dd, \(J=\) 5.5 Hz and 2.6 Hz, 1H), 3.86 (dd, \(J=\) 2.6 Hz and 4.0 Hz, 1H), 7.34 (m, 5H); \(^{13}\)C NMR (250 MHz, CDCl\(_3\)) \(\delta\) 51.3 (CH\(_2\)), 52.5 (CH), 125.6 (CH), 128.3 (CH), 128.9 (CH), 137.7 (C).

Indene oxide (Table 1, entry 4): Colourless oil, v\(_{\text{max(neat)}}\)/cm\(^{-1}\) 3027, 2917, 1482, 1464,

1390, 1372, 1232, 1183, 1142, 829,758, 745, 723; ¹H NMR (250 MHz, CDCl₃) δ 2.97 (1 H, dd, J = 2.7 and 18.1 Hz), 3.21 (1 H, d, J = 17.6 Hz), 4.13 (1 H, t, J = 3.0 Hz), 4.26 (1 H, dd, J = 1.1 and 2.8 Hz), 7.14-7.29 (3 H, m), 7.49 (1 H, dd, J = 1.7 and 6.6 Hz); ¹³C NMR (250 MHz, CDCl₃) δ 34.6, 57.6, 59.1, 125.2, 126.1, 126.3, 128.6, 141.0, 143.6.

trans-Stilbene oxide (Table 1, entry 5): Colourless solid, ν max (nujol)/cm⁻¹ 1601, 1492, 1284, 1176, 1157, 1094, 1072, 1025; ¹H NMR (250 MHz, CDCl₃) δ 3.84 (2 H, s), 7.28-7.37 (10 H m); ¹³C NMR (250 MHz, CDCl₃) δ 63.3, 126.0, 128.6, 129.3, 137.6.

cis-Stilbene epoxide (Table 1, entry 5): ¹H NMR (250 MHz, CDCl₃) δ 7.20-7.05 (m, 10H), 4.35 (s, 2H), ¹³C NMR (250 MHz, CDCl₃) δ 134.33, 127.76, 127.48, 126.84, 59.74.

Benzaldehyde (Table 2, entry 1): Colorless liquid, ¹H NMR (250 MHz, CDCl₃) δ 9.99 (s, 1H), 7.87-7.43 (m, 5H); ¹³C NMR (250 MHz, CDCl₃) δ 192.2, 136.5, 134.4, 129.7, 128.9; IR (neat) 1695 cm⁻¹.

4-Chlorobenzaldehyde (Table 2, entry 2): Colorless solid, ¹H NMR (250 MHz, CDCl₃) δ 9.95 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H); ¹³C NMR (250 MHz, CDCl₃) δ 190.7, 140.9, 137.8, 130.9, 129.4; IR (KBr) 1705 cm⁻¹.

4-Methoxybenzaldehyde (Table 2, entry 4): Colorless liquid, ¹H NMR (CDCl₃) δ 9.84 (s, 1H), 7.80 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H); ¹³C NMR (CDCl₃) δ 190.6, 164.6, 131.9, 130.0, 114.3, 55.5; IR (neat) 1682 cm⁻¹.

2-Chlorobenzaldehyde (Table 2, entry 5): ¹H NMR (CDCl₃) δ 10.44 (s, 1H), 7.89 (d, 1H), 7.44-7.60 (m, 3H); ¹³C NMR (CDCl₃) δ 189.2, 137.5, 135.2, 134.1, 131.1, 130.8, 127.7.

Cyclohexanone (Table 2, entry 6): Colorless liquid, ¹H NMR (CDCl₃) δ 2.33 (t, J = 6.8 Hz, 4H), 1.89-1.83 (m, 4H), 1.75-1.66 (m, 2H); ¹³C NMR (CDCl₃) δ 211.7, 41.9, 27.1, 25.0.

Cyclooctanone (Table 2, entry 7): Colorless liquid, ¹H NMR (CDCl₃) δ 2.41 (t, J = 6.8 Hz, 4H), 1.88 (m, 4H), 1.72-1.24 (m, 4H); ¹³C NMR (CDCl₃) δ 218.09, 41.95, 27.23, 25.69, 24.76.

1-Indanone (Table 2, entry 8): ¹H NMR (CDCl₃) δ 2.64 (t, 2H), 3.1 (t, 2H), 7.32-7.71 (m, 4H); ¹³C NMR (CDCl₃) δ 206.99, 155.08, 136.96, 134.5, 127.17, 126.61, 123.58, 36.12, 25.71.
Conclusion
Fe(Br₈TPPS)–Ad-400 catalyst could be easily recycled and reused without noticeable loss of activity. Furthermore, the advantages such as availability and environment-friendly non-toxicity of the reagent, and an excellent conversion could make this method a useful addition to the present methodologies in organic synthesis.

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References
(2008).