



Chemoselective oxidation of sulfides to sulfoxides with urea hydrogen peroxide (UHP) catalyzed by non-, partially and fully β -brominated *meso*-tetraphenylporphyrinatomanganese(III) acetate



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ABSTRACT

Selective oxidation of sulfides to sulfoxides with urea hydrogen peroxide in the presence of the manganese complex of non-, partially and fully brominated *meso*-tetraphenylporphyrin, (MnTPPBr_x(OAc) ($x = 0, 2, 4, 6$ and 8)) is reported. Although, the maximum conversion was achieved in the case of MnTPPBr₄(OAc), little difference was found between the catalytic activity of MnTPP(OAc), MnTPPBr₂(OAc) and MnTPPBr₄(OAc). MnTPPBr₈(OAc) showed an unusually very low catalytic efficiency compared to the other manganese porphyrins. The presence of small amounts of acetic acid was shown to have significant effect on the total conversion and the oxidative stability of the catalyst.

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Organic sulfoxides are useful and active intermediates in both laboratory and industry, organic synthesis and therefore the chemoselective oxidation of organic sulfides to the corresponding sulfoxides has been the subject of various studies for the past two decades [1–3]. An additional challenge in this respect is to make such processes environmentally friendly, by strategies such as using nontoxic solvents, green oxidants and energy-efficient catalytic methods [2–5]. Metalloporphyrins as model catalysts of cytochrome P450 have been used extensively for biomimetic oxidation of organic compounds [6–10]. On the other hand, in the past two decades great interest has been focused on using clean procedures for oxidation reactions catalyzed by metalloporphyrins [11–13]. In this regard, hydrogen peroxide and its derivatives such as UHP (urea hydrogen peroxide) and polyvinylpyrrolidone-supported hydrogen peroxide (PVP–H₂O₂) as cheap and environmentally friendly oxidants which only produce water and oxygen as side products are attractive oxidants for oxidation of organic compounds [2–5, 11–14]. Also, UHP has the advantage that the vacuum dried reagent may be used as a nearly water-free peroxide source. It is noteworthy that in the oxidation of organic compounds catalyzed by manganese porphyrins, the presence of H₂O leads to the formation of a high-valent Mn-oxo species as the active oxidant [11, 12]. In the oxidation of sulfides, higher oxidizing ability of the high valent manganese oxo species compared to the corresponding manganese(III) species, i.e. (porphyrin)Mn(III)(oxidant)(axial base) is possible to direct the reaction towards the formation of sulfone as the major product [15]. In other words, further oxidation of sulfoxide to sulfone may be prevented by the removal of water from the reaction

mixture. The released urea upon the reaction of UHP with organic substrates is then available to form strong hydrogen bonds with the water molecules formed in the oxidation reaction. Herein, a green and simple method for selective oxidation of sulfides to sulfoxides with UHP catalyzed by (MnTPPBr_x(OAc) ($x = 0, 2, 4, 6$ and 8)), in the presence of imidazole (ImH) in ethanol is reported. Also, the influence of different parameters on the efficiency of the catalysts was investigated.

The free base porphyrins and the manganese complexes were prepared and purified as reported previously [16].

Oxidation of methyl phenyl sulfide with UHP catalyzed by MnTPPBr_x(OAc) ($x = 0, 2, 4, 6$ and 8) gave methyl phenyl sulfoxide as the major product. In a search for suitable reaction conditions to achieve the maximum conversion and highest selectivity for sulfoxide, the effect of different parameters including solvent, temperature, amount of oxidant and ImH and the presence of acetic acid (HOAc) was studied.

Oxidation of methyl phenyl sulfide with UHP was carried out in the presence of MnTPPBr_x(OAc) ($x = 0, 2, 4, 6$ and 8) (Table 1) and the highest conversion was observed in the presence of MnTPPBr₄(OAc). However, little difference was found between the catalytic activity of MnTPPBr_x(OAc) with no, two and four bromine atoms. Also, MnTPPBr₈ showed very low catalytic activity. Along with our previous work [16], the present results confirmed that the partially brominated Mn-porphyrins have a higher catalytic activities compared to the fully β -brominated one.

The reaction was performed in dichloromethane, methanol, ethanol and the mixture of dichloromethane and the non-chlorinated solvents (Table 2). Although the highest conversion was achieved in mixture of CH₂Cl₂:MeOH or methanol, ethanol is a more convenient solvent for

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Table 1Oxidation of methyl phenyl sulfide with UHP catalyzed by MnTPPBr_x(OAc) (x = 0, 2, 4, 6 and 8) in the presence of ImH in CH₃OH:CH₂Cl₂ (9:1) at room temperature.^a

Catalyst	Conversion%	Sulfoxide%	Sulfone%	Sulfoxide selectivity%
None	Trace	–	–	–
MnTPP(OAc)	44	44	–	100
MnTPPBr ₂ (OAc)	46	44	2	96
MnTPPBr ₄ (OAc)	48	48	–	100
MnTPPBr ₆ (OAc)	20	20	–	100
MnTPPBr ₈ (OAc)	5	5	–	100

^a The molar ratios for catalyst:ImH:sulfide:UHP are 1:10:20:60. Reaction time: 5 min.**Table 2**Effect of various solvents (in different molar ratios) on the oxidation of methyl phenyl sulfide in the presence of ImH and MnTPPBr₄ at room temperature.^a

Entry	Time	Solvent	Conversion%	Sulfoxide%	Sulfone%	Selectivity (sulfoxide)%
1	5	CH ₂ Cl ₂	3.6	3.6	–	100
2	5	CH ₂ Cl ₂ :MeOH (1:1)	26.6	26.6	–	100
3	5	CH ₂ Cl ₂ :MeOH (9:1)	21.0	21.0	–	100
4	5	CH ₂ Cl ₂ :MeOH (1:9)	34.7	34.7	–	100
5	5	MeOH	33.0	33.0	–	100
6	15	CH ₂ Cl ₂ :ethanol (1:9)	12.0	12.0	–	100
7	20	Ethanol	5.4	5.4	–	100

^a The molar ratios for MnTPPBr₄:ImH:MePhS:UHP are 1:10:20:40.**Table 3**The effect of various conditions on the oxidation of methyl phenyl sulfide catalyzed by MnTPPBr₄ in the presence of ImH in ethanol.^a

Entry	Time (min)	Temperature	HAC/cat	ImH/cat	UHP/cat	Conversion%	Sulfoxide%	Sulfone%	Sulfoxide selectivity%
1	20	25	–	10	40	5.4	5.4	–	100
2	20	25	–	10	60	6.2	6.2	–	100
3	5	25	–	30	60	19.0	19.0	–	100
4	10	25	–	30	60	26.7	24.2	2.5	90
5	10	25	45	30	60	96.2	39.1	57.1	41
6	5	25	45	30	40	56.7	46.7	10.0	82
7	5	25	30	30	40	67.6	54.2	13.4	80
8	5	25	15	30	40	42.2	37.4	4.7	87
9	5	25	55	30	40	40.0	40.0	0	100
10	5	0	30	30	40	42.5	35.9	6.8	85
11	10	0	30	30	60	80.4	61.6	18.8	77
12	10	0	45	30	60	90.8	55.1	35.7	60
13	10	0	55	30	60	73.6	40.3	33.3	55

^a See the footnotes of Table 1.

environmentally friendly conversion of sulfides to sulfoxides [17–19] and therefore in further optimization of the catalytic system ethanol was used as solvent (Table 3). UHP is very insoluble in dichloromethane, due to the strong hydrogen bonds between H₂O₂ and urea. Solvents such as methanol or ethanol increase the solubility of UHP and consequently hydrogen peroxide.

The selective oxidation of sulfides to sulfoxides has been an important challenge in synthetic organic chemistry [1–3,20]. Accordingly, the optimum conditions for the formation of sulfoxide as the major product have been investigated. The results for the oxidation of methyl phenyl sulfide in various conditions are summarized in Table 3. As the results show, in the absence of HOAc, very low conversions

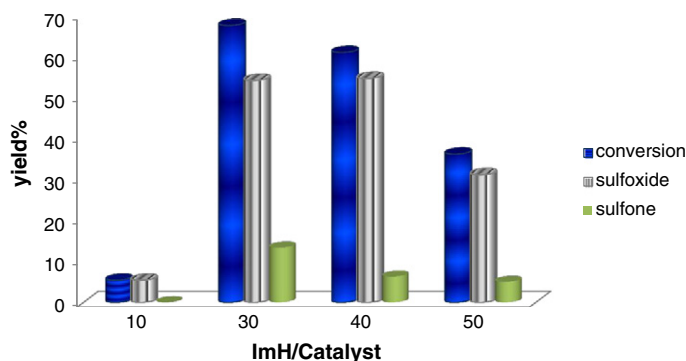


Fig. 1. Effect of molar ratio of the ImH:MnTPPBr₄ on the oxidation of methyl phenyl sulfide with UHP in ethanol and 10 μl HOAc at room temperature. The molar ratios for MnTPPBr₄:ImH:MePhS:UHP are 1:X:20:40.

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