

Tris[(2-oxazolinyl)phenolato]manganese(III) as catalyst for mild and efficient oxidation of sulfides to sulfones with Oxone[®]†

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Tris[(2-oxazolinyl)phenolato]manganese(III), Mn(phox)₃, catalysed oxidation of dialkyl, diaryl, dibenzyl, and alkyl aryl sulfides to the corresponding sulfones is carried out by Oxone[®] in biphasic conditions (CH₂Cl₂/H₂O), in the presence of tetra *n*-butylammonium bromide as phase transfer agent at room temperature in very short reaction times (5 min.) with quantitative yields.

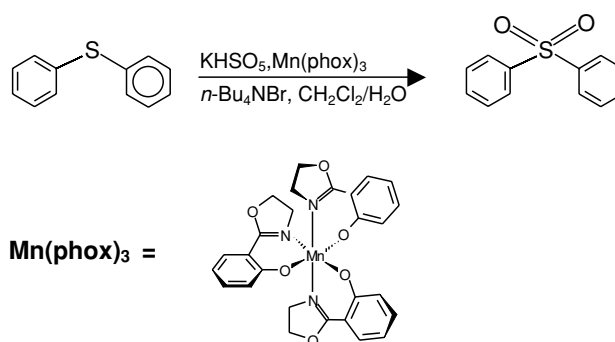
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Oxone[®], 2KHSO₅·KHSO₄·K₂SO₄, has been used widely as an oxidant for the oxidation of various organic compounds such as alkanes, olefins, alcohols,¹ and sulfides.² Its combinations with manganese-porphyrins were used as catalysts in olefin epoxidation.³ Recently, we have reported procedures for the nitration of phenols, *N*-nitrosation of amines and the oxidation of urazoles to their corresponding triazolidines using Oxone[®] as oxidant.⁴

Various transition metal complexes such as manganese, iron, and titanium complexes have been used as catalysts in sulfide oxidation.⁵ In the course of our interest in extending the application of Mn-complexes to the catalytic oxidation of organic compounds,⁶ we found that *mer*-tris[(2-oxazolinyl)phenolato]manganese(III), Mn(phox)₃, previously used in catalytic epoxidation of styrene with H₂O₂,⁷ was a very efficient catalyst for oxidation of sulfides. We now wish to report that the treatment of sulfides with Oxone[®] using Mn(phox)₃ as a catalyst in a biphasic solvent system (CH₂Cl₂/H₂O) with tetra *n*-butylammonium bromide, *n*-Bu₄NBr, as phase transfer agent, provides a simple and very efficient way to oxidise various organic sulfides to the corresponding sulfones with very short reaction times (5 min) at room temperature, and with a simple experimental procedure (Scheme 1).

In a typical experiment a solution of Oxone[®] (0.5 mmol, containing 1 mmol of the oxidizing component of Oxone[®], *i.e.* potassium peroxymonosulfate, KHSO₅) in H₂O (5 ml) at room temperature was added to a solution of a sulfide (0.25 mmol), tetra *n*-butylammonium bromide (0.1 mmol), and Mn(phox)₃, (0.0075 mmol) in CH₂Cl₂ (1 ml). The biphasic mixture was stirred vigorously. Formation of the product and consumption of the substrate was monitored by gas-liquid chromatography (GLC). The identity of products was determined by IR and ¹H NMR spectral data⁸ and by comparison with authentic samples in GC.⁹ The isolated yield was also determined for the diphenyl sulfide oxidation reaction.¹⁰

In contrast to the reported results for the epoxidation of styrene with H₂O₂ catalysed by *tris*[(2-oxazolinyl)phenolato]manganese(III)⁷, and some other manganese-complex catalysed oxidations such as Mn-porphyrins^{6,11} and Mn-salens¹² complexes the reactivity of the present catalytic system is not influenced by the presence of added axial ligands such as imidazole and pyridine. The phase transfer agent (PTA), tetra *n*-butylammonium bromide, has an



Scheme 1

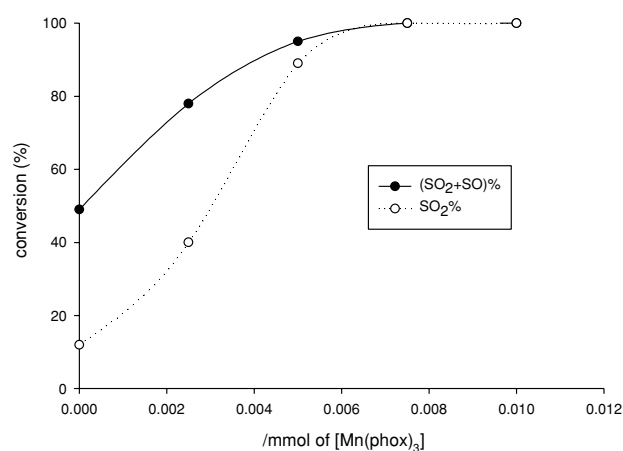


Fig. 1 Influence of the catalyst concentration on conversion and sulfone selectivity in methyl phenyl sulfide oxidation by the Mn(phox)₃/Oxone/*n*-Bu₄NBr oxidation system. Reaction conditions: the reactions were run for 5 min at room temperature; solvents: CH₂Cl₂ (1 ml), H₂O (5ml); Mn(phox)₃ (0, 0.0025, 0.0050, 0.0075 or 0.01 mmol); tetra *n*-butylammonium bromide (0.1 mmol), methyl phenyl sulfide (0.25 mmol); and Oxone[®] (0.5 mmol).

essential role in the selectivity and reactivity of the catalytic reaction. In the absence of PTA less than 6% methyl phenyl sulfide is converted into the corresponding sulfoxide (4%), and sulfone (2%). Conversion and sulfone selectivity increased progressively when the reactions were performed with a PTA/catalyst ratio increasing from 0 to 10. For example, while under 3/1 molar ratio of PTA/ Mn(phox)₃ the oxidation of methyl phenyl sulfide gave a 1:1.5 mixture of corresponding sulfoxide and sulfone, respectively, in 63%

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

Table 1 Oxidation of various sulfides by the Mn(phox)₃/Oxone/*n*-Bu₄NBr catalytic system^a

Entry	Substrate	Product	Yield(%) ^b
1			100(48) ^c
2			100(9) ^c (97) ^d
3			100
4			100
5			98(100) ^c

^aReaction conditions: the reactions were run for 5 min. at room temperature; solvents: CH₂Cl₂ (1 ml), H₂O (5ml); Mn(phox)₃ (0.0075 mmol); tetra *n*-butylammonium bromide (0.1 mmol); methyl phenyl sulfide (0.25 mmol); and Oxone[®] (0.5 mmol).

^bGC yield based on sulfide.

^cThe conversion in the absence of the catalyst.

^dIsolated yield.

^eThe oxidation of dioctyl sulfide was completed after 10 min.

overall yield, complete selectivity in sulfone formation in 100% conversion was observed with the 10/1 molar ratio.

The influence of catalyst concentration has been studied in the methyl phenyl sulfide oxidation (Fig. 1). The reactions were carried out at room temperature during 5 min. in the same conditions as the typical procedure with five different amounts of the catalyst (0, 0.0025, 0.0050, 0.0075, and 0.01 mmol). Fig. 1 shows the conversion of the sulfide for these five different catalyst/sulfide ratios (0–4%). In addition to the role of the catalyst in increasing the efficiency of Oxone[®] oxidation of sulfides (Table 1, entries 1, and 2), the important effect observed on increasing the catalyst/sulfide ratio is the increase of the reaction rate and sulfone selectivity. The catalytic activity of Mn(phox)₃ in the oxidation of sulfides with Oxone[®] was examined using methyl phenyl sulfide as the model substrate. It was found the mole ratio 1: 13: 33: 67 of the catalyst; tetra *n*-butylammonium bromide; methyl phenyl sulfide; Oxone[®], respectively, is the optimum molar ratio for complete selective oxidation of the sulfide to the corresponding sulfone. Reducing the temperature of the oxidation process from room temperature to 0 °C has no effect on the efficiency of the oxidation system.

To demonstrate the scope of the method, oxidation of different kinds of sulfide including alkyl aryl, diaryl, dialkyl, and dibenzyl sulfides has been investigated. The results which are given in Table 1, show that the method is generally applicable to wide range of sulfides and gives the corresponding sulfones in quantitative yields. In general, the oxidations are completed within 5 min. (except for the dioctyl sulfide oxidation that is completed after 10 min.). Reduction of the sulfone yield from 100 to 52% when the oxidation of methyl phenyl sulfide was carried out in the presence of 0.2 mmol of 2,6-di-*tert*-butyl-*p*-cresol as an inhibitor may indicate that a radical intermediate is produced in the described catalytic process. This is in a good agreement with the reported method for the oxidation of sulfide with the MnO₂–HCl oxidation system.¹³

In summary, this work has developed a very fast and efficient method for the selective oxidation of diaryl, dialkyl,

dibenzyl, and alkyl aryl sulfides to the corresponding sulfones using Oxone[®] as a inexpensive and commercially available oxidant in the presence of a catalytic amount of tris[(2-oxazoliny)phenolato]manganese(III), Mn(phox)₃. The advantages of this protocol such as mild reaction conditions, complete selectivity in sulfone formation, very short reaction times, and excellent yields of the products are noteworthy and make this method an attractive and useful contribution to present methodologies.

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- 9 The organic sulfides, diphenyl sulfoxide and diphenyl sulfone were purchased from Merck. The other products were prepared according to well known procedures.¹⁴
- 10 After completion of the oxidation reaction of diphenyl sulfide (5 min), 20 mL CH₂Cl₂ was added to the biphasic mixture. The organic phase was separated, dried over Na₂SO₄ and evaporated *in vacuo*. The residue was chromatographed on silica gel eluting with diethyl ether/hexane (1/1). Diphenyl sulfone was obtained in 97% yield (m.p. 122–124 °C, Lit.^{2e} 124 °C)
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