

Efficient oxidation of sulfides with sodium periodate catalyzed by manganese(III) Schiff base complexes

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Abstract

Efficient oxidation of sulfides was achieved. In the chemical system containing Mn(III)–salophen complex as catalyst, sulfides converted efficiently to the corresponding sulfoxides and sulfones with sodium periodate. The ability of various Schiff base complexes in the oxidation of sulfides was also investigated.

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1. Introduction

The development of efficient catalytic systems for oxidation reactions that mimic the action of cytochrome P-450 dependent monooxygenases has attracted much attention in recent years [1]. Many efficient biomimetic oxidation systems using iron and manganese porphyrins as catalysts, and various single oxygen atom donors, such as PhIO, ClO[−], H₂O₂, ROOH or IO₄[−] have been reported [2–11]. The high efficiency of some of these systems makes them potentially useful for preparative oxidations in organic synthesis. Recently, mono- and binuclear transition metal complexes derived from ligands other than porphyrins have also been employed as catalysts. The use of metal Schiff base complexes, i.e. metal salen and metal salophen to catalyze the oxidation of hydrocarbons by single oxygen atom donors has received much attention. Manganese, chromium, nickel and cobalt Schiff base complexes have been used for these transformations [12–21].

We have chosen the salophen ligand because it is similar to porphyrin and 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.

This catalytic system exhibits a high activity in the oxidation of sulfides with sodium periodate in 1:1 CH₃CN/H₂O mixture in the presence of imidazole as axial ligand (Scheme 1).

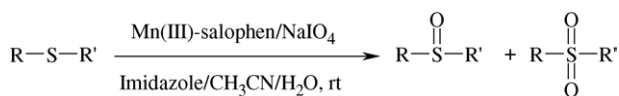
The type of metal ion and Schiff base and the nature of reactive intermediate were also investigated.

2. Results and discussion

2.1. Oxidation of sulfides with different metal Schiff base complexes

In a preliminary approach to the periodate anion activation by metal Schiff base complexes, we decided to investigate the activity of different Schiff base complexes of Fe, Mn, Co and Ni as metal ions. Table 1 summarizes our trials on catalytic oxidation of sulfides with NaIO₄ in the presence of various

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Scheme 1.

metal Schiff base complexes (shown in Fig. 1). We found that the nature of the metal ion has an important role on the catalytic properties of Schiff base complexes. The use of iron, cobalt and nickel complexes gives small amount of oxidized products in the oxidation of diphenyl sulfide. However, the use of manganese(III) complex, Mn–salophen, resulted in a significant amount of oxidized products after 15 min.

Among the 1:1 mixture of methanol, ethanol, acetone, acetonitrile (single phase systems), 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. We found that the addition of small amounts of imidazole as axial ligand considerably improved the efficiency of catalyst which was determined by comparison of turnover numbers in the presence and in the absence of imidazole.

Pure σ -donor amines, with very large $\text{p}K_a$ values, are relatively poor co-catalysts in the oxidation of sulfides. Pyridine and methyl-substituted pyridines, with weak π -donating ability and $\text{p}K_a$ values smaller than those of σ -donor amines, generally show co-catalytic activities similar to those of amines. The observed order of co-catalytic activities, which is 4-*tert*-butylpyridine > pyridine \gg 4-cyanopyridine, seems to be directly related to both the σ - and π -donating abilities of these nitrogen donors. Electron-withdrawing substituents such as CN^- , essentially displays no co-catalytic activity.

2.2. Oxidation of sulfides with sodium periodate catalyzed by Mn(III)–salophen

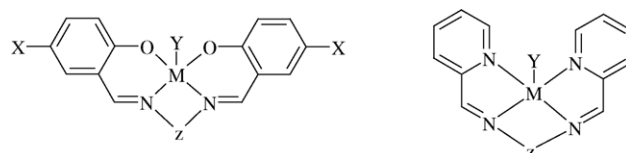
The imidazole-modified Mn–salophen/ NaIO_4 oxidizing system can be applied to oxidation of a wide variety of diaryl, dibenzyl, aryl benzyl, and cyclic sulfides at room temperature in high yields at short times. All experiments

Table 1

Oxidation of diphenyl sulfide by various metal Schiff base complexes with sodium periodate

Schiff base	Conversion (%)	Sulfoxide (%) ^a	Sulfone (%) ^a
1	100	77	18
2	30	18	8
3	8	4	Trace
4	10	6	Trace
5	7	Trace	Trace
6	18	9	5
7	12	6	Trace
8	28	17	6
9	5	Trace	Trace
10	22	13	5
11	12	7	Trace

^a Isolated yields.

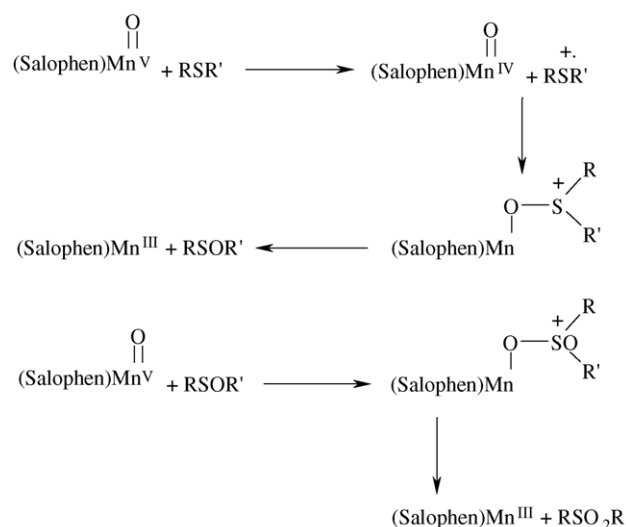


	M	z	X	Y
1	Mn	C_6H_4	H	Cl
2	Mn	C_6H_4	NO_2	Cl
3	Fe	C_6H_4	H	Cl
4	Co	C_6H_4	H	-
5	Ni	C_6H_4	H	-
6	Mn	$(\text{CH}_2)_2$	H	Cl
7	Fe	$(\text{CH}_2)_2$	H	Cl
8	Mn	C_6H_4	H	Cl
9	Fe	C_6H_4	H	Cl
10	Mn	$(\text{CH}_2)_2$	H	Cl
11	Fe	$(\text{CH}_2)_2$	H	Cl

Fig. 1. Transition metal Schiff base complexes used in this study.

were carried out with two equivalents of sodium periodate per one equivalent of sulfide. As shown in Table 2, sulfides completely oxidize and the major product is sulfoxide and only up to 25% of sulfone was obtained. In the absence of manganese(III)–salophen catalyst, NaIO_4 shows poor ability to oxidize sulfides at room temperature (3–6% yields). The obtained results in shorter reaction times show that sulfoxides were initially produced and were successively converted to sulfones. Fig. 2a and b show the results for oxidation of dibenzylsulfide and diphenylsulfide, respectively, clearly supporting this pathway (Scheme 2).

Previously, many systems have reported the oxidation of organic sulfides by metal Schiff base complexes, such as Mn, Ti, V, and Cu [22–29]. Titanium (salen) has been used for the oxidation of substituted thioanisole with H_2O_2 , UHP and



Scheme 2.

Table 2
Oxidation of sulfides with NaIO₄ catalyzed by Mn–salophen at room temperature

Row	Sulfide	Conversion (%) ^a	Sulfoxide (%) ^{a,b}	Sulfone (%) ^{a,b}
1		100	77	18
2		100	76	20
3		100	80	15
4		100	78	17
5		100	77	19
6		100	74	22
7		100	83	14
8		100	73	13
9		100	69	28
10		100	70	25
11		100	74	23

^a Isolated yields.

^b All products were identified by comparison of their physical and spectral data with those of authentic samples.

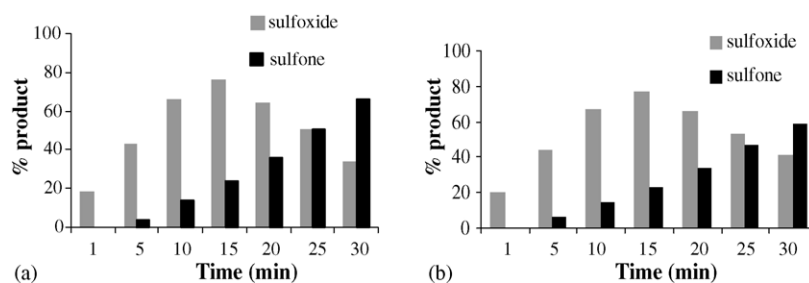


Fig. 2. The obtained results for oxidation of: (a) dibenzylsulfide and (b) diphenylsulfide. The results clearly indicate that, sulfoxide primary is produced and then is oxidized to sulfone dibenzylsulfide and (b) diphenylsulfide. The results clearly indicate that, sulfoxide primary is produced and then is oxidized to sulfone.

ROOH. The yields are high but reaction times are long (24 h). The chiral copper Schiff base complex has been reported for asymmetric oxidation of thioanisole with H_2O_2 or TBHP in long reaction times (24 h). Manganese (salen) complexes can be used for oxidation of *p*-substituted thioanisole with PhIO during 5 h, and the corresponding sulfoxides were obtained in good to high yields. Among the metal Schiff base complexes, homogenous and heterogeneous vanadyl complexes have attracted much attention in the oxidation of organic sulfides. $\text{VO}(\text{acac})_2/\text{H}_2\text{O}_2$ systems (homogenous and polymer bound) convert various thioanisoles to the corresponding sulfoxides in 16 h. Maeda et al. reported the sulfide oxidation of sulfides with vanadyl Schiff base complexes and resin bound oxovanadium(IV) Schiff base complexes. In comparison with the data reported in the oxidation of organic sulfides by various Schiff base complexes, our system shows the following advantages: (i) mild reaction conditions; (ii) shorter reaction times; (iii) non-toxicity and ease of handling of oxidant.

3. Experimental

Schiff base complexes 1–11 (Fig. 1), were prepared as described by Boucher [30] or by the more recently modified methods [12,31,32]. Cyclic sulfides (entries 10, 11) were purchased from Merck chemical company and the others were prepared according to the reported procedure [33]. IR spectra were run on a Philips PU9716 spectrophotometer. ^1H NMR spectra were obtained with a Bruker 80, 200, or 500 spectrometers in CDCl_3 as solvent and TMS as internal standard.

3.1. General procedure for oxidation of sulfides

In a 25 mL flask equipped with a magnetic stirring bar, a solution of sodium periodate (2 mmol in 5 mL H_2O) was added to a mixture of sulfide (1 mmol), Mn–salophen (0.067 mmol) and imidazole (0.067 mmol) in CH_3CN (5 mL). Progress of the reaction was monitored by TLC. After the reaction was completed, the reaction products were extracted with CH_2Cl_2 (20 mL) and were purified by a silica gel plate or a silica gel column (eluent: *n*-hexane-ethyl acetate, 7/2). The identities of products were confirmed by mp, IR and ^1H NMR spectral data.

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