

Selective oxidation of sulfides to sulfoxides in water using 30% hydrogen peroxide catalyzed with a recoverable VO(acac)₂ exchanged sulfonic acid resin catalyst

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Abstract

Various types of sulfides are selectively oxidized to sulfoxides in good to excellent yields in aqueous media using 30% aqueous hydrogen peroxide as an oxidant in the presence of catalytic amounts of a VO(acac)₂-exchanged strongly acidic polymeric resin catalyst in water at room temperature. The catalyst can be recovered and reused at least five times without loss of activity and selectivity.

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1. Introduction

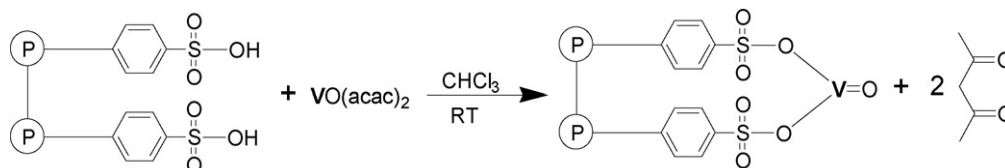
The selective oxidation of sulfides to sulfoxides is an important method in organic synthesis because sulfoxides are useful synthetic intermediates for the construction of various chemically and biologically significant molecules [1]. To date, the most important method of preparation involves the oxidation of sulfides. Various oxidizing agents are used for this purpose [2–15], and unfortunately, most of these reagents are not satisfactory for medium to large-scale operations for several reasons. The first reason is that the low content of the effective oxygen that is available for the oxidation, generation of environmentally unfavorable by-products, and high cost. Another reason is that over oxidation of the sulfoxides to their sulfones during the oxidation of sulfides. Indeed selective oxidation of sulfides to sulfoxides remains a challenging task, and constitutes an active research on its own particularly with the emphasis on ‘green chemistry’. Thus, there is still a need for sulfoxidation procedures that are efficient, more selective, and in particular conform to a class of greener technologies. In this direction, use of aqueous hydrogen peroxide as oxidizing agent is highly preferred because of its high effective oxygen content (as high as 47%)

and cleanliness as it produces only water as by-product [16]. This feature has already stimulated the development of useful procedures for H₂O₂ oxidation [17,18], and recently, Karimi et al. have reported highly efficient synthesis of sulfoxides with a recoverable silica-based tungstate interphase catalyst using hydrogen peroxide as oxidizing agent [19]. With ever-increasing environmental awareness, there is much incentive to develop new processes that are robust, recyclable, and environmentally very benign. In this paper, we disclose a new heterogeneous protocol in aqueous media for the selective oxidation of sulfides to sulfoxides using 30% aqueous hydrogen peroxide as oxidizing agent in the presence of catalytic amounts of a recoverable VO(acac)₂-exchanged polymeric resin catalyst at room temperature.

2. Experimental

All organic reagents and solvents were reagent grade and purchased from commercial vendors. Strongly acidic ion-exchange resin INDION-770 was procured from Ion Exchange India Ltd., and was used as received. All reactions were carried out under nitrogen atmosphere, and monitored by thin layer chromatography (TLC). Column chromatography purifications were performed using silica gel. All solvents were dried and degassed before use. NMR spectra were measured in CDCl₃ on a Bruker 300 MHz and Varian-200 MHz instruments with TMS as an

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Scheme 1. Preparation of catalyst.

internal reference. Atomic emission spectra were recorded on an IRIS Interpid 11 XDL instrument. IR spectra were recorded on a FT-IR (Perkin-Elmer Spectrum 1000) instrument.

2.1. Synthesis of VO(acac)₂

To an aqueous suspension of vanadium pentoxide (5 g, 27.49 mmol) in 20 mL of water taken in a 500 mL beaker, 30% hydrogen peroxide (37.37 mL, 329.88 mmol) was added drop-wise in an ice-cold condition and the mixture was stirred till a clear dark solution was formed. To this solution, distilled acetyl acetone (19.84 mL, 192.5 mmol) was added drop-wise very carefully with continuous stirring. Vigorous effervescence took place after 15 min, and further stirring for a period of 30 min led to a precipitation of a brown colored microcrystalline compound from the reaction mixture. This mixture was then allowed to react at 70 °C for 15 min under vigorous stirring. During this time, the brown precipitate turned olive green with shiny crystalline appearance with the solution also turning green. The solution was concentrated by heating on a steam bath for 30 min and then placed in an ice-water bath for 15 min. The precipitate was filtered through Whatman no. 42 filter paper, washed with acetone, and dried *in vacuo* over fused calcium chloride. Yield: 11.7 g (80%).

2.2. Synthesis of VO(acac)₂ supported on strongly acidic INDION-770 resin

To a solution of VO(acac)₂ (0.5 g) in chloroform (20 mL), strongly acidic INDION-770 resin (5 g) was added and the mixture was stirred at ambient temperature for 12 h under nitrogen atmosphere. The solid catalyst was filtered, washed several times with chloroform, and finally dried *in vacuo*. Measurement of increase in the mass the mass of the resultant VO(acac)₂-resin indicates that 420 mg of VO(acac)₂ is supported. The quantity of vanadium present was estimated to be 0.283 mmol/g of resin by atomic absorption spectroscopy.

2.3. Typical procedure for the oxidation of methyl phenyl sulfide

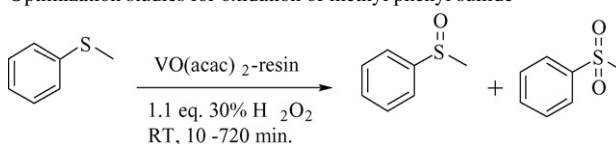
A round bottom flask (10 mL capacity) was charged with methyl phenyl sulfide (124 mg, 1 mmol), water (2 mL), and catalyst (200 mg; 6 mol.%). Aqueous 30% hydrogen peroxide solution (1.1 mmol) was added and the reaction mixture was stirred for 10 min at ambient temperature. After completion of the reaction (followed by TLC), the catalyst was filtered off and washed with water, and product methyl phenyl sulfoxide

was extracted by using dichloromethane (3 mL × 10 mL), dried over anhydrous sodium sulfate and evaporated *in vacuo* to afford the crude product. The crude product was purified by column chromatography on silica gel (10% EtOAc in hexane) to afford analytically pure methyl phenyl sulfoxide (130 mg; 93%). The products were characterized by comparing the ¹H-NMR spectra with those reported in the literature [20]. The products were also characterized by EI-mass spectroscopy.

3. Results and discussion

As shown in Scheme 1, the VO(acac)₂-exchanged polymeric resin catalyst was synthesized by treating strongly acidic cation exchange resin (Sulfonic acid H⁺ form; INDION-770) with VO(acac)₂ in chloroform at room temperature for 12 h. Then, the beads of polymer resin acquired dark blue color indicating formation of the metal complex on the surface of the polymeric material. FT-IR was used to study the structure of the catalyst. The result from this study has strongly indicated that the acetyl acetone functionality is no longer present in the immobilized catalyst. Thus, most probable structure of the catalyst on the polymer surface involves bonding of sulfonyl anions to the V(IV) center so as to form the corresponding sulfonyl complex as shown in Scheme 1. The quantity of vanadium present in the

Table 1
Optimization studies for oxidation of methyl phenyl sulfide^a



Entry	Time (min)	Solvent	Conversion (%) ^{a,b}	Sulfoxide (%) ^b	Sulfone (%) ^b
1	360	CH ₂ Cl ₂	54	67	33
2	60	CH ₂ Cl ₂	80 ^c	75	25
3	720	CHCl ₃	39	36	64
4	10	CH ₃ CN	92	95	5
5	10	CH ₃ OH	84	92	9
6	10	H ₂ O	98	100	0
7	10	H ₂ O	97 ^d	100	0
8	10	H ₂ O	94 ^e	100	0
9	120	H ₂ O	50 ^c	70	30
10	120	H ₂ O	No reaction ^f	–	–

^a Reaction conditions: substrate (1 mmol), catalyst (6 mol.%), and 30% H₂O₂ (1.1 mmol) were stirred at room temperature in respective solvent (2 mL).

^b Determined from ¹H-NMR spectra of the crude product.

^c Reaction was carried out using VO(acac)₂.

^d Recovered catalyst was used (recycling experiments): 1 recycle.

^e Fifth recycle.

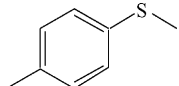
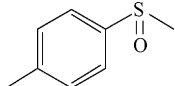
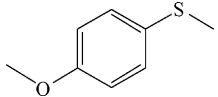
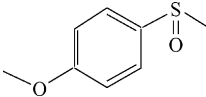
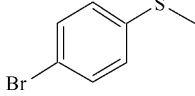
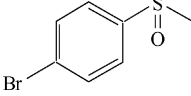
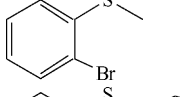
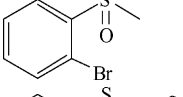
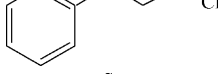
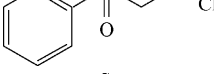
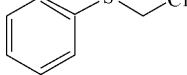
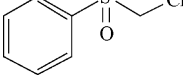
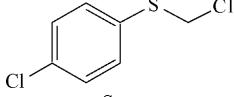
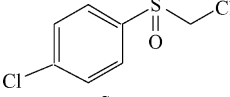
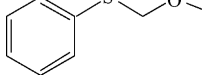
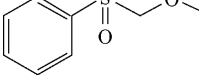
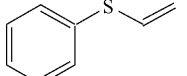
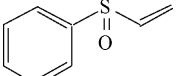
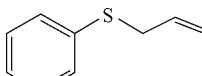
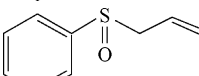
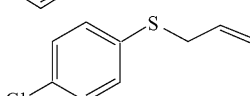
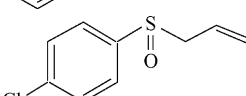
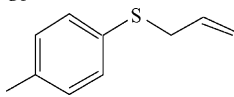
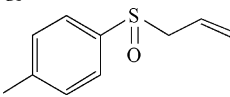
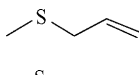
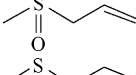
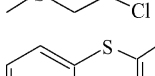
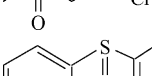

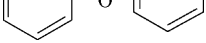
^f No catalyst was used.

heterogeneous complex was estimated to be 0.283 mmol/g of resin by atomic absorption spectroscopy.

The oxidation of methyl phenyl sulfide, as a standard substrate, was first studied in the presence of the VO(acac)₂-exchanged polymeric resin catalyst using 30% aqueous hydrogen peroxide at ambient temperature in a variety of sol-

vents (Table 1). The course of the oxidation reaction is strongly influenced by the nature of the solvent used for the reaction. For example, in chlorinated solvents such as dichloromethane and chloroform the oxidation reaction occurred in a sluggish manner with poor conversion (Table 1; entries 1 and 3). In contrast, in polar organic solvents such as acetonitrile and methanol,

Table 2
VO(acac)₂-exchanged polymer resin catalyzed selective oxidation of sulfides to sulfoxides with 30% H₂O₂ in water^a

Entry	Substrate ^{b,c}	Time (min)	Sulfoxide	Yield ^d
1		20		95
2		05		89
3		10		95
4		10		97
5		40		95
6		40		92
7		130		87
8		160		98
9		160		92
10		160		89
11		160		78
12		160		82
13		140		79
14		25		97
15		720		74

^a Reaction conditions: substrate (1 mmol), resin catalyst (6 mol.%), and 30% H₂O₂ (1.1 mmol) were stirred at room temperature in water as solvent (2 mL).

^b Entries 5–8: reactions were carried out using 9:1 water:methanol as solvent (2 mL).

^c Entries 14 and 15 was carried out in methanol (2 mL) as solvent.

^d Determined from ¹H-NMR spectra of the crude product.

the oxidation reaction proceeded rather fast, and gave mixture of sulfoxides and sulfones with good selectivity toward sulfoxides (Table 1; entries 4 and 5). Formation of sulfones was fully suppressed when highly polar water is used as solvent for the reaction as this reaction gave exclusively sulfoxides (Table 1; entry 6). Thus water is the best solvent for the reaction. This solvent dependence could be attributed to swelling of the polymeric catalyst in polar solvents, thus, enabling greater accessibility of vanadium sites to the substrates for the oxidation reaction [21]. The controlled reaction conducted under identical conditions devoid of catalyst in water showed no oxidized product formation within the stipulated reaction time (Table 1; entry 10).

To better understand the efficiency of our catalyst system, we have studied the oxidation of methyl phenyl sulfide under homogeneous conditions in the presence of VO(acac)₂ and aqueous 30% hydrogen peroxide. Both in aqueous media and dichloromethane, the VO(acac)₂ catalyst afforded the desired products in poor yields (Table 1; entries 2 and 9). In contrast, the heterogeneous VO(acac)₂-exchanged resin catalyst selectively affords sulfoxides in excellent yields. Thus, the heterogeneous VO(acac)₂-exchanged resin catalyst is the best catalyst in terms of both catalytic activity and selectivity for sulfoxidation reaction. To study the recyclability of the VO(acac)₂-exchanged resin catalyst, the oxidation of methyl phenyl sulfide was examined in water (Table 1; entries 7 and 8). After completion of the reaction, the catalyst was filtered and washed well with dichloromethane and water and reused in the sulfoxidation reaction. The catalyst was found to be effective and gave quantitative yields up to five times. No significant leaching of the metal ions from the polymeric resin matrix was observed as indicated by atomic absorption analysis of spent catalysts. Thus the catalyst is reusable without significant loss of catalytic activity and selectivity.

To study the scope of the procedure, a series of sulfides having varied R groups containing aromatic and aliphatic attached to the sulfur atom was subjected to the oxidation in water using the VO(acac)₂-exchanged polymeric resin catalyst and 30% aqueous hydrogen peroxide as an oxidant and the results are present in Table 2. A series of substrates, diaryl, aryl-alkyl, alkyl-allyl, aryl-vinyl and dialkyl sulfides was oxidized to the corresponding sulfoxides in high yields. Of these substrates, aryl-alkyl and dialkyl sulfides were very reactive as these substrates were oxidized to their corresponding sulfoxides within 25 min in aqueous media (entries 1–4, and 14). In contrast, both aryl-vinyl and aryl-allyl sulfides were only moderately reactive as it took longer reaction times for providing the corresponding sulfoxides in aqueous media with good yields (entries 9–13). As anticipated, the oxidation of diphenylsulfide took a much longer reaction time (720 min) to give corresponding sulfoxide in moderate yields (entry 15). The oxidation of diphenylsulfide, and 2-chloroethylmethylsulfide proceeded much slower in water; however, their oxidation reaction was reasonably faster when methanol was used as solvent (see foot note c in Table 2: entries 14 and 15). For substrates such as (2-chloro-ethylsulfanyl)benzene, chloromethylsulfanylbenzene, methoxymethylsulfanylbenzene,

1-chloro-4-chloro-methylsulfanylbenzene, the oxidation reaction proceeded very slowly in water quite possibly due to poor dispersion of the sulfide in the aqueous media (entries 5–8). For this reason, their oxidation reactions were carried out using a 9:1 mixture of water and methanol with 30% aqueous hydrogen peroxide as oxidant (entries 5–8). The additive methanol has substantially increased the speed of the reaction, and gave excellent yields for the corresponding sulfoxides.

A good functional group tolerance was observed under our experimental conditions. For example, in the case of allylic and vinylic sulfides, no overoxidation to the sulfones or epoxidation of the double bond was observed, and only the corresponding sulfoxides products were obtained in excellent yields (entries 9–13). A similar functional group tolerance was also observed for substrates containing reactive chloro functional group in the moiety for the oxidation reaction (entries 5–8). These substrates selectively underwent oxidation at the sulfur atom without undergoing further structural changes in their functional groups as suggested by ¹H-NMR and EI-mass spectroscopic analyses of the products.

Being guided by the published reports on the peroxo-chemistry of titanium [22] and vanadium [23], it is believed that the catalyst interacts with peroxide to form a peroxometal intermediate, thereby activating the bound peroxide for the oxidation reaction. The ease of transfer of electrophilic oxygen from the peroxometal species to the nucleophilic sulfide facilitates the formation of sulfoxides with the eventual regeneration of the catalyst.

4. Conclusion

The oxidation of sulfides to sulfoxides in aqueous media is conducted using the VO(acac)₂-exchanged polymeric resin catalyst in the presence of 30% aqueous hydrogen peroxide at ambient temperature. A variety of substrates with diverse structural features undergo oxidation to the corresponding sulfoxides with excellent yields. It is important to note that the catalyst is reused five times without significant loss of activity and selectivity. From an environmental standpoint, this procedure provides a simple method for the formation of sulfoxides from sulfides, which is a potentially competitive and an economically viable process.

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