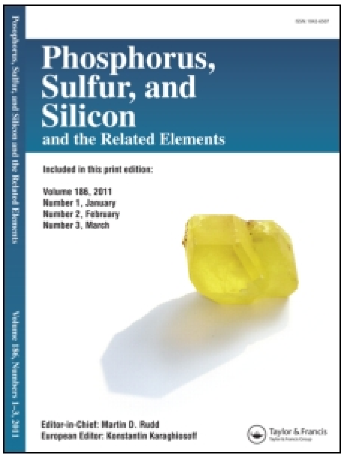

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Selective Oxidation of Sulfides to Sulfones Using H_2O_2 and Anderson-Type Hexamolybdochromate(III) as Catalyst

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SELECTIVE OXIDATION OF SULFIDES TO SULFONES USING H_2O_2 AND ANDERSON-TYPE HEXAMOLYBDOCHROMATE(III) AS CATALYST

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An Anderson-type hexamolybdochromate(III) is found to be an effective catalyst for the selective oxidation of sulfides to their corresponding sulfones. The reaction was carried out in 60% aq. acetonitrile (v/v) using 30% H_2O_2 at 60°C. Various dialkyl, alkyl-aryl, and diaryl sulfides were selectively oxidized, giving high yields of sulfones after a simple workup procedure.

Keywords Hexamolybdochromate (III); homogeneous catalysis; hydrogen peroxide; oxidation; sulfones

INTRODUCTION

Sulfoxides and sulfones play an important role in organic synthetic chemistry.[1–2] Sulfones are valuable intermediates for the formation of chemically and biologically important molecules.[3] Among the various oxidants[4–8] employed for the oxidation of sulfides, hydrogen peroxide is an ideal oxidant, having water as the only byproduct with high oxygen content.[9] In the case of sulfoxide preparation, careful monitoring of the reaction is required to minimize the amount of sulfone as a side product, while oxidation of sulfide to sulfone requires a long reaction time and lengthy treatment with the use of toxic materials and heavy metals. Several catalysts have also been utilized for oxidation of sulfides by aqueous H_2O_2,[10] but most of them have one or more drawbacks such as long reaction time, toxic byproducts, unavailability, and high cost of reagents, as well as selectivity. Polyoxometalates are very good catalysts[11–13] for both gas and liquid phase oxidation reactions. They were successfully utilized[14–17] in various organic transformations. Most of the polyoxometalate catalysis is concentrated on Keggin and Dawson types,[12] and less attention is given to the other type of polyoxometalates such as Anderson-type[18] compounds.

Sodium hexamolybdochromate(III) is an Anderson-type polyoxometalate. Detailed analysis of the structure of catalyst is reported.[19] Among the oxidation states of chromium, chromium(VI) is carcinogenic, while chromium(III) is required for carbohydrate and lipid

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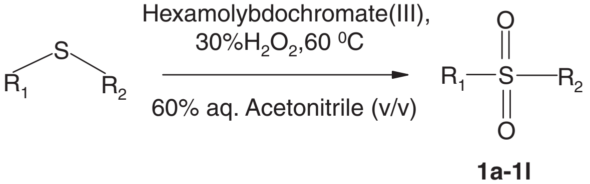
metabolism in mammals.[20] In continuation of our work[21–24] on catalyzed oxidation reactions, we now present a novel catalytic system for oxidation of sulfides to sulfone by using aqueous H_2O_2 and sodium hexamolybdochromate(III) as catalyst, as shown in Scheme 1.



1a-1l

Scheme 1 Oxidation of sulfide to sulfone catalyzed by hexamolybdochromate(III).

RESULTS AND DISCUSSION

To study the catalytic oxidation of sulfides mediated by $Na_3[CrMo_6O_{24}H_6]\cdot 8H_2O$, methyl phenyl sulfide was chosen as a model compound, and the reaction conditions were optimized. At room temperature, the reaction is slow and requires 2 h for complete conversion into sulfone. The reaction proceeds smoothly at 60°C and requires only 10 min for completion. Under these conditions, the presence of sulfoxide was not observed. Other catalytic derivatives such as molybdenum oxide and ammonium molybdate have been used previously for oxidation of sulfides.[25] These methods only afford sulfoxide as a major product. Oxidation of sulfides directly into sulfones is the advantage of the method presented in this article. The present method is compared with previous reports; Table I indicates the advantages of the present catalytic system over previous methods.

Since the solvent has a pronounced effect on the reaction, it was carried out in various solvents and the results are shown in Table II. Among the various solvents used, aqueous acetonitrile (60% v/v) was found to be the most effective solvent, giving a high yield with comparatively low reaction time. In pure aqueous medium, there was no reaction even after 12 h. In the absence of the catalyst, the reaction did not afford sulfone even after 3 h. The yield and rate of the reaction were also found to be dependent on the concentration of the catalyst and oxidant. As the catalyst was decreased from 2 mol% to 0.5 mol%, the yield of product sulfone decreased, and the reaction time also increased considerably. The effect of catalyst variation on the reaction rate and yield are tabulated in Table III.

Table I Comparison of the present system with previous systems

Sr. No.	Catalytic system	Time	(%) Yield	Ref.
1	MoO_2Cl_2/H_2O_2 sulfide (4 mmol), 30% H_2O_2 (4 eq.), MoO_2Cl_2(15 mol%) in 10 mL CH_3CN at RT.	45 min	95	8
2	Titanium catalyst TiO_2_400 (37.4 mg), sulfide (0.4 mmol), H_2O_2 (1.2 mmol) in 4 mL CH_3CN at 80°C	3 h	96	26
3	Silica sulfuric acid/ H_2O_2 SSA(0.2 g), sulfide (1 mmol), 30% H_2O_2(3 eq.), in 5 mL CH_3CN at RT	45 min	96	27
4	Present system $Na_3[CrMo_6H_6O_{24}]$ (2 mol%), sulfide (1 mmol), 30% H_2O_2(2 eq.) in 10 mL 60% CH_3CN (v/v) at 60°C	10 min	94	—

Table II Reaction in various solvents[a]

Solvent	Time (min)	Yield (%)[b]
Acetonitrile	10	94
Methanol	20	85
Ethanol	45	75
Water	720	—

[a] Reaction conditions: sulfide (1 mmol), 2 mol% hexamolybdochromate(III), H_2O_2 (2 equivalent) at 60°C in 60% aq. acetonitrile(v/v).

[b] Isolated yield.

To study the scope of the reaction, a series of sulfides having dialkyl, diaryl, and alkyl-aryl groups were chosen. Sulfides including furfuryl methyl sulfide (**1i**) were selectively converted into sulfones in high yields as shown in Table IV. It is clear from Table IV that dialkyl sulfides (**1j–1l**) afford sulfones in less time in comparison with diaryl (**1g**) and alkyl-aryl (entries **1a–1f**, **1h**) sulfides. It is seen that the substrates containing an electron-donating group are more reactive than the substrates having electron-withdrawing groups due to the deactivating effect in the oxidation procedure by diaryl and electron-withdrawing groups. Since the uncatalyzed reaction is slow under the experimental conditions and the rate of the reaction depends on both the catalyst and oxidant concentrations, the catalyzed reaction proceeds with the interaction of the catalyst and the oxidant. We have reported earlier[21] that the oxidation of sulfide takes place via complex formation between Cr(III) and sulfides. In the present study, the catalyst is a heteropolyoxometalate in which the hetero atom, Cr(III), is buried within the six molybdate octahedrons, which does not favor the formation of a complex between the catalyst and the substrate, thus making it an inert redox catalyst. Therefore, the initiation of the reaction occurs by the oxidation of the catalyst to its higher oxidation state by hydrogen peroxide, which then affects the oxidation of the substrate. In order to get further support for the proposed mechanism, the interaction between the catalyst and oxidant was examined separately under the reaction conditions. The violet solution of hexamolybdochromate(III) turns green when treated with H_2O_2, and the green solution was evaporated to get the crystals of oxidized form of the catalyst, hexamolybdochromate(V). The FT-IR spectra of both oxidized and unoxidized hexamolybdochromate(III) were recorded as KBr pellets. The comparison of both the spectra indicates that the polyoxometalate characteristic $M–O_c–M$ peak at 643 cm^{-1} was found to be split into two peaks in the oxidized form due to a change in the oxidation state[29] of chromium. There was also a new peak at 829 cm^{-1}, characteristic of $Cr^V = O$ in the

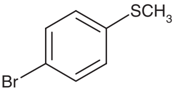
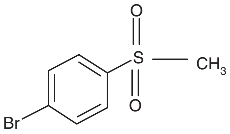
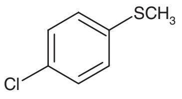
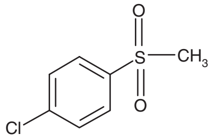
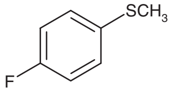
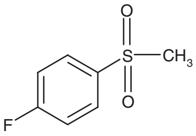
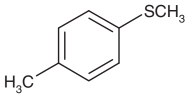
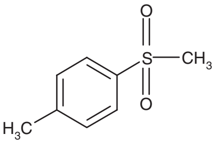
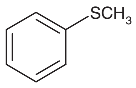
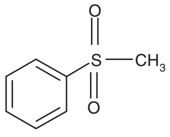
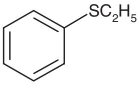
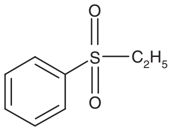
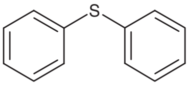
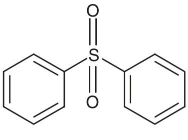
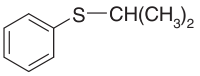
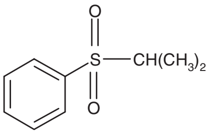
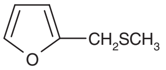
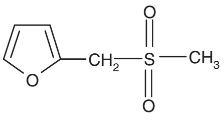
Table III Effect of catalyst on oxidation reaction[a]

Entry	Catalyst (mol%)	Time (min)	Yield (%)[b]
1	2	10	94
2	1	35	85
3	0.8	40	82
4	0.5	60	85

[a] Reaction conditions: sulfide (1 mmol), H_2O_2 (2 equivalent) at 60°C in 60% aq. acetonitrile (v/v).

[b] Pure isolated yield.

Table IV Selective oxidation of sulfides to sulfones catalyzed by hexamolybdochromate(III)[a]

Entry	Sulfide	Sulfone	Time (min)	Yield (%)[b]	M.P. °C (Rep.)
1a			30	88	102 (101–102)[27]
1b			26	90	97 (95–97)[27]
1c			20	90	76 (76–79)[28]
1d			20	95	85 (88)[27]
1e			10	94	85 (86–88)[27]
1f			10	91	43 (42–43)[28]
1g			10	94	126 (128–130)[27]
1h			15	85	oil
1i			25	74	69
1j	$(CH_3)_2S$	$(CH_3)_2SO_2$	6	92	109 (108–110)[28]
1k	$(CH_3CH_2)_2S$	$(CH_3CH_2)_2SO_2$	6	88	73 (73–75)[27]
1l	$(CH_3CH_2)_3)_2S$	$(CH_3CH_2)_3)S_2$	8	92	45 (46)[27]

[a] Reaction conditions: sulfide (1 mmol), H_2O_2 (2 equivalent) at 60°C and 2 mol% hexamolybdochromate(III) at 60°C in 60% acetonitrile(v/v).

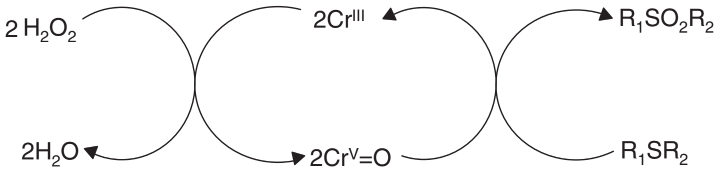
[b] Pure isolated yield.

All products characterized by ^1H NMR and mass spectrometry.

FT-IR of the oxidized form of hexamolybdochromate.

$$Cr^{III}Mo_6O_{24}H_6(H_2O) + H_2O_2 \rightarrow (Cr^V = O)Mo_6O_{24}H_6 + 2H_2O \quad (1)$$

On the basis of FT-IR spectral examination of both the unoxidized and oxidized form of hexamolybdochromate, the formation of Cr^V can be shown as in Equation (1), and the $Cr^V = O$ formed acts as an oxidant in the present study. The proposed mechanism is shown in Scheme 2.



Scheme 2 A plausible catalytic cycle.

Initially H_2O_2 reacts with Cr^{III} and forms $Cr^V = O$. This $Cr^V = O$ oxidizes sulfide to sulfone. The conditions used in the system allowed the use of organic solvents to be reduced as much as possible. The catalyst used is easy to prepare and is very effective with H_2O_2. The method is more advantageous than previous reports due to its green approach.

CONCLUSION

In summary, the reaction is one-step, rapid, mild, and environmentally benign, giving high yields of sulfone after a simple workup procedure. The sulfides having various substituents were selectively oxidized to their respective sulfones. The catalytic role of hexamolybdochromate is briefly described.

EXPERIMENTAL

All the products are known compounds and were identified by comparison of their physical and spectral data with previous reports in the literature.[10,27] ^1H NMR was recorded on Bruker Avance 300 MHz spectrometer. Mass spectra were recorded on Shimadzu GCMS-QP2010. Melting points were determined in an open capillary and are uncorrected. Sulfides were purchased from Lancaster. Acetonitrile and dichloromethane were purchased from SD Fine Chemicals (Mumbai, India) and used without further purification. All yields refer to isolated yields.

Catalyst Preparation

The catalyst sodium hexamolybdochromate(III) was prepared by the previously reported method.[19] The pH of a solution containing $Na_2MoO_4.2H_2O$ (14.5 g in 30 mL of water) was adjusted to 4.5 with concentrated HNO_3. A second solution was made by dissolving $Cr(NO_3)_3$ $.9H_2O$ (4.0 g in 5 mL of water). The solutions were mixed together, and the mixture was boiled for 1 min and filtered while hot. The filtrate was set aside for crystallization, and crystals started to appear in 1 h. the solution was allowed to stand for

2 weeks before the precipitate was filtered off and washed several times with cold water. Reddish-purple crystals were obtained.

Catalyst Characterization

The complex $Na_3[CrMo_6O_{24}H_6]\cdot 8H_2O$ was studied by AAS analysis. 100 mg of recrystallized sample was dissolved in doubly glass-distilled water. 5 mL of this stock solution was diluted to 100 mL and used for AAS analysis of Cr and Mo metals using Perkin-Elmer Analyst-300. The complex $Na_3[CrMo_6O_{24}H_6]\cdot 8H_2O$ shows (Theoretical): Na—5.6303% (5.6052%), Cr—4.2227% (4.2242%), and Mo–46.217% (46.2109%).

General Procedure for Oxidation of Sulfide

In a typical experiment, methyl phenyl sulfide (1 mmol, 0.124 g) and 30% H_2O_2 (2 mmol, 0.22 mL) were taken in 10 mL 60% acetonitrile (v/v) in a round bottom flask. The catalyst $Na_3[CrMo_6H_6O_{24}]$ (2 mol%) was added. The reaction mixture was stirred at 60°C. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was treated with dichloromethane (2 × 25 mL). The organic layer was dried by anhydrous $MgSO_4$ and concentrated to obtain the required product, methyl phenyl sulfone. It was further purified by column chromatography (silica gel, using hexane:ethyl acetate 90:10, v/v). (94% yield, mp = 75°C).

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