

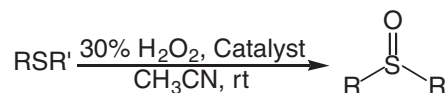
Catalytic Conversion of Sulfides to Sulfoxides by The $[\text{PZnMo}_2\text{W}_9\text{O}_{39}]^{5-}$ Polyoxometalate¹

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Keggin type polyoxometalates can be used as catalysts for the activation of 30% aqueous hydrogen peroxide for the selective transformation of various organic substrates. In this paper, results are presented for the oxidation of sulfides to sulfoxides in high to excellent yields using 30% aqueous H_2O_2 as oxidant and $[\text{PZnMo}_2\text{W}_9\text{O}_{39}]^{5-}$ as catalyst in acetonitrile.



Scheme 1.

Partial oxidation reactions are extensively used in industrial processes to functionalize hydrocarbon substrates, increasing their reactivity so that they can be utilized as intermediates in chemical industry. Preparation of sulfoxide derivatives by efficient methods is of continuous interest in organic chemistry.² The selective oxidation of sulfides to sulfoxides has been a challenge for many years, partly because of the importance of sulfoxides as intermediates in organic synthesis.³

During the last years, very useful procedures involving an oxidant and a catalytic activator have been developed to promote this transformation.²⁻⁴ Conventional oxidants include, among others, NaIO_4 ,^{5a} KMnO_4 ,^{5b} KHSO_5 ,^{5c} NaClO ,^{5d} NaBO_3 ,^{5e} $\text{CF}_3\text{CO}_3\text{H}$,^{5f} dimethyldioxirane,^{5g} $t\text{-C}_4\text{H}_9\text{O}_2\text{H}$ ^{5h} and singlet oxygen⁶ or molecular oxygen.⁷ Because of the low content of effective oxygen, the formation of environmentally unfavorable co-products and high cost, most of these reagents are not satisfactory. Aqueous hydrogen peroxide (H_2O_2) as terminal oxidant due to the effective oxygen content, low cost, safety in storage and operation, and environmentally friendly character, is an ideal oxidant, however, a catalyst is necessary to activate this oxidant.⁸

In continuation of our research on the application of polyoxometalates in oxidation of organic substrates,⁹ we describe our efforts in developing catalytic procedures for oxidation of organic sulfides to sulfoxides using aqueous hydrogen peroxide as oxidant and transition metal-substituted polyoxometalates as catalysts.

The polyoxometalates comprise of a class of d^0 metal complexes of the group VB and VIB elements (excluding Cr) and exhibit both diverse and tunable domains of sizes, shapes, charge densities, acidities, and reversible redox potentials.¹⁰ The catalytic function of the polyoxometalates has attracted much attention and they are used in solution as well as in the solid state. These compounds have awoken interest for catalytic oxidations, as they are inherently stable to oxidation. An especially interesting subclass of the polyoxometalates is Keggin type compounds where one or perhaps more of the metal atom are substituted by lower valent transition metals. These so called transition-metal-substituted polyoxometalates are uniquely synthetically attractive as well as interesting as oxidation catalysts because one may visualize these compounds as having reactive low valent transition metal centers complexed by inorganic oxometalate ligands which also have high capacity for electrons.^{10e,10f}

Various tungsten (W) catalyst systems⁸ were used in addition to CH_3ReO_3 ,¹¹ $\text{Na}_2\text{MoO}_4 + (n\text{-C}_4\text{H}_9)_3\text{PO}$,¹² and titanium

silicate (TS-1).¹³ However, many of these procedures require either chlorohydrocarbon solvents that affect human health and the environment, or anhydrous H_2O_2 in ethanol. We will describe below our results on the use of the zinc-substituted polyoxometalate, $[\text{PZnMo}_2\text{W}_9\text{O}_{39}]^{5-}$, as catalyst for the oxidation of sulfides to sulfoxides using aqueous hydrogen peroxide (30%) as oxidant in acetonitrile (Scheme 1).

In this paper, we wish to report our studies in the oxidation of aromatic and aliphatic sulfides using H_2O_2 (30%) as oxidant in the presence of catalytic amount of tetrabutylammonium salts of transition-metal-substituted polyoxometalates ($[\text{P}(\text{M}^{n+})\text{Mo}_2\text{W}_9\text{O}_{39}]^{7-}$, $\text{M} = \text{Mn}^{2+}$, Co^{2+} , Zn^{2+} , Fe^{3+}). These catalysts are readily available and easily prepared from $\alpha\text{-K}_7\text{PMo}_2\text{W}_9\text{O}_{39}$ by a slight modification of the previously reported method.⁹ The formation of Keggin structure and composition of the compounds were confirmed by IR, NMR and elemental analysis. Thermal gravimetric analysis was performed on all of the catalysts (between 40 and 240 °C). The results indicated that the hydration numbers were between 3 to 6.

From initial studies carried out with methyl phenyl sulfide, we found the best reaction condition. Initially using the methyl phenyl sulfide, 30% H_2O_2 and catalytic amount of various transition metal substituted polyoxometalate salts in acetonitrile, we searched the optimum conditions of reaction.¹⁴ The reactions were conducted at ambient temperature with magnetic stirring. The oxidation was efficiently achieved under this condition (Table 1, Entry 1), and the presence of the catalyst was crucial to obtain full conversion of the sulfide. After studied the various amount of the catalyst, we found the 0.05 equivalent from Zn(II) substituted polyoxometalate catalyst was the best. Lower catalytic activity was observed with other, substituted catalysts (about 20–30%). We chose the CH_3CN as solvent and lower catalytic activities were observed with other solvents such as CH_2Cl_2 , CHCl_3 , CH_3OH , $n\text{-C}_6\text{H}_6$ and $\text{C}_2\text{H}_6\text{O}$. The optimum amount of H_2O_2 30% in this system was found 1.2 mmol and when the higher amount of oxidant was employed, a significant increase in the sulfone was observed.

For methyl phenyl sulfide, separate experiments showed that at the time cited in Table 1, there is little reaction without catalyst (below 7%). From the results as summarized in Table 1, one must divide substrates into classes: aromatic and aliphatic sulfides. Catalytic reactions and substrate/oxidant ratios of 1/1.2 yield sulfoxide as major product with selectivities of 80–92%, and a trace amount of sulfone was observed for some of sulfides (below 5% for Table 1, Entries 2, 13, 14).

Table 1. Oxidation of sulfides to sulfoxides with 30% H₂O₂ catalyzed by [PZnMo₂W₉O₃₉]⁵⁻ via Scheme 1

Entry	Sulfide	Time/min	Yield of Sulfoxide ^{a,b} /%
1		30	92
2		20	80
3		30	90
4		180	90
5		150	87
6		240	90
7		210	90
8		30	92
9		30	87
10		60	88
11		60	85
12		60	88
13		30	85
14		30	87

^aAll of the products were characterized by comparison of their physical and spectral data with those of authentic samples.

^bYields refer to isolated products.

In the case of phenyl methyl sulfide, full oxidation of the starting material was obtained (yield of sulfoxide 92%). The oxidation of benzyl phenyl sulfide results in the formation of benzyl phenyl sulfoxide in 85% yields (Table 1, Entry 11). Allyl methyl thioether (Table 1, Entry 8) was selected for study a molecule having two functional groups for oxidation, namely carbon-carbon double bond and the sulfur atom. However, no oxidation products of the carbon-carbon double bond were observed with [PZnMo₂W₉O₃₉]⁵⁻ as catalyst. The oxidation of dibutyl sulfide occurs to give the sulfoxide in 87% yield. We noted that, as expected, the susceptibility of sulfides to H₂O₂ is highly dependent on the substitution.

In conclusion this catalytic system efficiently promotes the oxidation of aliphatic and aromatic sulfides with 30% hydrogen peroxide and [PZnMo₂W₉O₃₉]⁵⁻ as catalyst in acetonitrile with high to excellent yields. This system is a mild, simple, clean, and cheap method for oxidation of sulfides to sulfoxides.

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References and Notes

- This paper dedicated to: Prof. Mohammad Hosein Habibi and Prof. Shahram Tangestaninejad.
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- Typical experimental procedure: To a stirred solution of sulfide (1 mmol) in acetonitrile (3 mL) in the presence of [PZnMo₂W₉O₃₉]⁵⁻ (0.05 mmol), was added at room temperature 1.2 mmol of 30% H₂O₂. The progress of reaction monitored by TLC. After the time reported in the table, the sulfoxide were purified by flash chromatography over silica gel and fully characterized.