Tin(II) Polyoxometalate as an Efficient Catalyst for the Selective Oxidation of Sulfides to Sulfoxides

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The applicability of the tin(II) polyoxometalate catalyst, ([n-C4H9]4N)5PSnMo2W9O39·9H2O, for sulfoxidation of diaryl, dibenzyl, aryl benzyl, dialkyl, cyclic, and heterocyclic sulfides with 30% hydrogen peroxide was examined under organic halogen-free condition. It is noteworthy that different functional groups including carbon-carbon double bonds, ketones, oximes, aldehydes, ethers, alcohols, and acetals were tolerated under this reaction condition.

Key words: Tin(II) Polyoxometalate, Sulfoxidation, Sulfoxide, Sulfone, Lewis Acid

Introduction

Oxidation of sulfides is the most straightforward method for the synthesis of sulfoxides and sulfones [1 – 3], both of which are important as commodity chemicals and, in some cases, as pharmaceuticals [4]. Although there are a large number of procedures for oxidation of sulfides to sulfoxides [5 – 29], few of these are highly chemoselective and can be stopped at the sulfoxide level [30, 31]. Some of these methods show limitations such as long reaction times, low yields of the products, expensive reagents, poor selectivity, strongly acidic or basic media, acidic work-up, and hazardous or toxic oxidizing agents. Therefore introduction of a clean, mild and efficient method for conversion of sulfides to sulfoxides is still needed.

Aqueous hydrogen peroxide (H2O2) is an ideal oxidant due to its effective oxygen content, low cost, safety in storage and operation, and environmentally friendly character, although a catalyst is necessary to activate this oxidant [23, 32]. As part of our ongoing search for application of polyoxometalates in the oxidation of organic substrates [26, 33], the use of tin(II)-substituted polyoxometalates as catalysts for the oxidation of organic sulfides to sulfoxides (Scheme 1) was demonstrated in the preceding paper. Metal-substituted polyoxometalates, so-called inorganic metalloporphyrins, have attracted much attention as oxidation catalysts because they are thermodynamically stable against oxidative degradation, unlike metalloporphyrins and other metal complexes with organic ligands. These compounds combine the selectivity advantages of homogeneous catalysts with the stability advantages of heterogeneous catalysts. There are more than 50 papers addressing the oxygenation or oxidation of a wide variety of substrates in the presence of polyoxometalate derivatives, and this literature has been recently reviewed [28, 34, 35].

Results and Discussion

In continuation of our interest in the catalytic activities of polyoxometalates [38], here, our studies in the oxidation of aromatic, aliphatic, cyclic and heterocyclic sulfides using H2O2 (30%) as oxidant in the presence of catalytic amounts of tetrabutylammonium salts of Sn(II)-substituted polyoxometalates, [PSnMo2W9O39]5−, are reported. This catalyst is readily available and easily prepared from α-K2PMo2W9O39·19H2O by a slight modification of the previously reported method [33]. The formation of a Keggin structure and the composition of the compounds were confirmed by FTIR, 31P NMR, UV-vis, and elemental analysis. Thermal gravimetric analysis
Table 1. Oxidation of sulfides to sulfoxides with 30% H₂O₂ catalyzed by [(η⁵-C₅H₅)₄N]₅PSnMo₂-W₉O₃₉·9H₂O.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sulfide</th>
<th>Sulfoxide</th>
<th>Time (min)</th>
<th>Yield of sulfoxide (%)</th>
</tr>
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<tr>
<td>1</td>
<td><img src="image1" alt="Sulfide 1" /></td>
<td><img src="image2" alt="Sulfoxide 2a" /></td>
<td>15</td>
<td>95</td>
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<tr>
<td>2</td>
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<td><img src="image4" alt="Sulfoxide 2b" /></td>
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<td>3</td>
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<td><img src="image6" alt="Sulfoxide 2c" /></td>
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<td><img src="image8" alt="Sulfoxide 2d" /></td>
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</tr>
<tr>
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<td><img src="image32" alt="Sulfoxide 2p" /></td>
<td>10</td>
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</tr>
</tbody>
</table>

*Isolated yields, all products were identified by comparison of their spectral data with those of authentic samples.
was performed on the catalyst. The result indicated that the hydration number was 9.

The oxidation reaction was preliminarily investigated for methyl phenyl sulfide. Different solvents such as dichloromethane, chloroform, acetonitrile, acetone, and benzene were examined. It was observed that acetonitrile is the solvent of choice for this purpose. The reaction rates were very slow for the other solvents. The molar ratio of sulfide to catalyst 1 : 0.04 was found to be ideal for complete conversion of sulfides to sulfoxides, while with lesser amounts (for example 1 : 0.03) the reaction remains incomplete. A control experiment confirmed that, at the time cited in Table 1, little oxidation occurred in the absence of catalyst (below 7%). The optimum molar ratio of sulfide to H2O2 30% was found to be 1.0 : 1.2 and when a higher amount of oxidant was employed, a significant increase in the formation of sulfones was observed.

A wide variety of diaryl, dialkyl, dibenzyl, aryl benzyl, alkyl aryl, cyclic, and heterocyclic sulfides were then reacted using this remarkably simple procedure, and the results are presented in Table 1. It is evident from the results, as summarized in Table 1, that catalytic reactions yield sulfoxides as the major products with selectivities of 90–95%, and only trace amounts of sulfone were observed for some of the sulfides (below 5% for Table 1, entries 1, 4, 7, 8, 10, 14). The results presented in Table 1 also show that the oxidation of dialkyl sulfides to the corresponding sulfoxides is easier than that of alkyl aryl sulfides (Table 1, entries 12–14). We noted that as expected, the susceptibility of sulfides to H2O2 is highly dependent on the substituents. However, with unsaturated sulfides the sulfoxides are formed without any concomitant epoxidation of double bonds. The mechanism of thioether oxidation with H2O2 in the presence of heteropolytungstates was studied by Kholdeeva et al. [29].

Competitive oxidation of sulfides in the presence of oxime, ether, aldehyde, alcohol and acetal functions was monitored (Table 2). These observations clearly suggest that this method can be applied for the chemoselective oxidation of sulfides in the presence of the above-mentioned groups in multifunctional molecules.

### Conclusion

The results presented in this paper demonstrate that this catalytic system is an efficient, rapid, clean, sim-
ple, mild, and inexpensive protocol for selective oxidation of a variety of structurally diverse sulfides to their corresponding Sulfoxides, with very easy workup. Moreover, the excellent chemoselectivity of this catalyst towards the sulfur group makes it a good choice for use in the oxidation of functional sulfides.

Experimental Section

The sulfides 1c, 1k, 1l, 1n, 1o, 1p were purchased from the Merck chemical company. The other sulfides were prepared according to the described procedure [36]. The yields refer to isolated pure products. Melting points were determined using a digital Gallenkamp apparatus and are uncorrected. IR spectra were run on a Philips PU 9716 spectrophotometer and FTIR spectra were performed using a Bomem MB 104 spectrophotometer. Thermogravimetric analyses (TGA) were performed under nitrogen flow using a Perkin-Elmer TGA 7 instrument. The tungsten content in the catalyst was measured by inductively coupled plasma (ICP atomic emission spectroscopy) on a Spectro Cinos CCD spectrometer. 1H NMR spectra were recorded on Bruker Avance 200 or 500 MHz NMR spectrometers with CDCl3 as the solvent and TMS as the internal standard. 31P NMR spectra were recorded on a Bruker Avance 400 DSA 400 NMR spectrometer using 85% H3PO4 as a reference.

Preparation of the catalyst

The synthesis of [(n-C6H13)2N]3PSnMo2W9O39 · 9H2O starts with the preparation of α-K2PMo7W6O39 · 19H2O from β-Na8HPW9O43 · 2H2O and sodium molybdate [33, 37]. To a solution of α-K2PMo7W6O39 · 19H2O (3.5 g, 1.2 mmol) in 25 ml of water, SnCl2 (0.3 g) was added in excess. After 2 h of stirring, tetrabutylammonium bromide was added until a violet powder of [(n-C6H13)2N]3PSnMo2W9O39 · 9H2O precipitated. The powder was filtered and dried in a vacuum desiccator. FTIR (KBr): v = 803, 890, 971, 1072 cm−1. – 31P NMR: δ = −12.12, −13.83, −14.08. – UV/vis: λ = 266 nm. – C50H108Mo2N3O38PSnW9 (3993.0): calcld. C 23.94, Mo 4.78, N 1.75, P 0.77, Sn 2.96, W 41.26; found C 24.56, Mo 4.90, N 1.90, P 0.82, Sn 3.15, W 40.57. Thermal gravimetric analysis (TGA) indicated 9 molecules of H2O.

General procedure for the oxidation of sulfides

To a stirred solution of the sulfide (1 mmol) in acetonitrile (3 ml) in the presence of [(n-C6H13)2N]3PSnMo2W9O39 · 9H2O (0.04 mmol), hydrogen peroxide 30% (1.2 mmol) was added at r.t. The progress of the reaction was monitored by TLC (eluents: toluene-hexane/ethyl acetate). After the time reported in Table 1, the sulfoxide was purified by flash chromatography over silica gel and fully characterized.

Spectroscopic data of products:

**Methyl phenyl sulfoxide (2a).** M. p. 30 – 31 °C. – IR (KBr): v = 1025 cm−1. – 1H NMR (200 MHz): δ = 2.73 (s, 3H), 7.48 – 7.56 (m, 3H), 7.64 – 7.67 (m, 2H).

**Benzyl phenyl sulfoxide (2b).** M. p. 122 – 123 °C. – IR (KBr): v = 1034 cm−1. – 1H NMR (500 MHz, CDCl3): δ = 4.04 (d, J = 12.6 Hz, 1H), 4.14 (d, J = 12.6, 1H), 7.02 – 7.03 (m, 2H), 7.28 – 7.36 (m, 3H), 7.41 – 7.52 (m, 5H).

**Diphenyl sulfoxide (2c).** M. p. 72 – 73 °C. – IR (KBr): v = 1038 cm−1. – 1H NMR (200 MHz, CDCl3): δ = 7.41 – 7.50 (m, 6H), 7.61 – 7.66 (m, 4H).

**Dibenzyl sulfoxide (2d).** M. p. 132 – 133 °C. – IR (KBr): v = 1026 cm−1. – 1H NMR (500 MHz, CDCl3): δ = 3.91 (d, J = 13.0 Hz, 2H), 3.98 (d, J = 13.0 Hz, 2H), 7.31 – 7.41 (m, 10H).

**4-Bromobenzyl-4-methylphenyl sulfoxide (2e).** M. p. 159 – 161 °C. – IR (KBr): v = 1030 cm−1. – 1H NMR (500 MHz, CDCl3): δ = 2.46 (s, 3H), 3.99 (s, 2H), 6.88 (d, J = 8.2 Hz, 2H), 7.27 – 7.31 (m, 4H), 7.42 (d, J = 8.2, 2H).

**Benzimidazol-2-yl benzyl sulfoxide (2f).** M. p. 154 – 156 °C. – IR (KBr): v = 1023 cm−1. – 1H NMR (200 MHz, CDCl3): δ = 4.72 (s, 2H), 7.02 – 7.31 (m, 5H), 7.42 – 8.03 (m, 4H).

**Benzimidazol-2-yl 4-nitrobenzyl sulfoxide (2g).** M. p. 182 – 183 °C. – IR (KBr): v = 1025 cm−1. – 1H NMR (200 MHz, CDCl3): δ = 4.83 (s, 2H), 7.08 – 7.37 (m, 4H), 7.47 – 8.12 (m, 4H).

**n-Butyl phenyl sulfoxide (2h).** Oil. – IR (KBr): v = 1018 cm−1. – 1H NMR (200 MHz, CDCl3): δ = 0.91 (t, J = 7.0 Hz, 3H), 1.15 – 1.53 (m, 4H), 2.88 (t, J = 7.0 Hz, 2H), 7.36 – 7.49 (m, 3H), 7.89 – 7.92 (m, 2H).

**3-Bromobenzyl phenyl sulfoxide (2i).** M. p. 178 – 179 °C. – IR (KBr): v = 1028 cm−1. – 1H NMR (200 MHz, CDCl3): δ = 3.98 (d, J = 12.70 Hz, 1H), 4.04 (d, J = 12.70 Hz, 1H), 6.85 (m, 4H), 7.44 (m, 5H).

**2-Chlorobenzyl 4-chlorophenyl sulfoxide (2j).** M. p. 73 – 74 °C. – IR (KBr): v = 1040 cm−1. – 1H NMR (500 MHz, CDCl3): δ = 4.20 (d, J = 12.56 Hz, 1H), 4.30 (d, J = 12.56, 1H), 7.16 (d, J = 7.05 Hz, 2H), 7.25 (d, J = 7.04, 2H), 7.41 (d, J = 8.5, 2H), 7.47 (d, J = 8.5, 2H).

**Dibenzo-phenylene S-oxide (2k).** M. p. 182 – 183 °C. – IR (KBr): v = 1038 cm−1. – 1H NMR (500 MHz, CDCl3): δ = 7.53 – 7.70 (m, 4H), 7.83 – 8.04 (m, 4H).

**Thioanthen-9-one 10-oxide (2l).** M. p. 201 – 203 °C. – IR (KBr): v = 1058, 1670 cm−1. – 1H NMR (500 MHz, CDCl3): δ = 7.71 – 7.83 (m, 4H), 8.13 – 8.38 (m, 4H).

**Allyl phenyl sulfoxide (2m).** Oil. – IR (KBr): v = 1043, 1660 cm−1. – 1H NMR (500 MHz, CDCl3): δ = 3.56 (d, J = 6.5 Hz, 2H), 4.89 (d, J = 6.5, 1H), 5.03 (d, J = 10.0 Hz, 1H), 5.55 – 5.64 (m, 1H), 7.38 – 7.59 (m, 5H).
Diallyl sulfoxide (2n). Oil. – IR (KBr): υ = 1035, 1620 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ = 3.57 (d, \(J = 7.1\) Hz, 4H), 5.24 – 5.38 (m, 4H), 5.72 – 5.96 (m, 2H).

Dibutyl sulfoxide (2o). M.p. 34 – 35 °C. – IR (KBr): υ = 1022 cm\(^{-1}\). \(^1\)H NMR (200 MHz, CDCl\(_3\)): δ = 0.92 (t, \(J = 7.2\), 6H), 1.41 – 1.56 (m, 4H), 1.70 – 1.80 (m, 4H), 2.58 – 2.73 (m, 4H).

Dipropyl sulfoxide (2p). Oil. – IR (KBr): υ = 1020 cm\(^{-1}\). \(^1\)H NMR (200 MHz, CDCl\(_3\)): δ = 1.10 (t, \(J = 7.2\), 6H), 1.81 – 1.98 (m, 4H), 2.50 – 2.74 (m, 4H).

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