

# New Heteropolyacids as Catalysts for the Selective Oxidation of Sulfides to Sulfoxides with Hydrogen Peroxide

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**Abstract:** Pyridinium salts of Keggin-type molybdovanadophosphates proved to be highly active catalysts for the hydrogen peroxide oxidation of sulfides to the corresponding sulfoxide and sulfone derivatives. High conversion and high selectivity for sulfoxide were observed.

**Key words:** sulfides, sulfoxides, oxidation, hydrogen peroxide, Keggin-type molybdovanadophosphate pyridinium salts

The selective oxidation of sulfides to sulfoxides is an important reaction both in industrial processes and in basic research; it has been a challenge for many years, owing to the importance of sulfoxides in organic synthesis.<sup>1</sup> Since the first report on synthesis of sulfoxides published by Maercker at 1865, a number of stoichiometric and catalytic methods has been developed.<sup>2</sup> Various oxidizing reagents used for this purpose include, among others: nitric acid, dinitrogen tetroxide, chromic acid, manganese dioxide, ozone, peracids, selenium dioxide, sodium periodate, hypervalent iodine reagents, sodium perborate,<sup>3</sup> halogens, tetrabutylammonium peroxydisulfate,<sup>4</sup> binuclear manganese complexes–periodic acid,<sup>5</sup> *N*-hydroxyphthalimide–molecular oxygen,<sup>6</sup> camphorsulfonic acid–*t*-butyl hydroperoxide,<sup>7</sup> Fe(NO<sub>3</sub>)<sub>3</sub>–FeBr<sub>3</sub>–molecular oxygen,<sup>8</sup> FeBr<sub>3</sub>–nitric acid and (FeBr<sub>3</sub>)<sub>2</sub>(DMSO)<sub>3</sub>–nitric acid.<sup>9</sup>

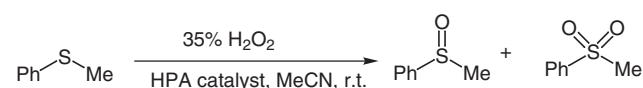
During the last years, useful procedures involving catalysis have been reported; e.g. H<sub>2</sub>WO<sub>4</sub>, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> + [(C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>N]Br,<sup>10</sup> rhenium(V) oxophosphine complexes, methyltrioxorhenium,<sup>11</sup> Sc(OTf)<sub>3</sub>,<sup>12</sup> (salen) Mn(III) and Ti(IV) complexes,<sup>13,14</sup> tellurium dioxide<sup>15</sup> and TPP-Fe(III)Cl–imidazole.<sup>16</sup> These catalysts have been specifically developed for hydrogen peroxide, since this reagent has low cost, safe in storage and operation, and is environmentally friendly.

In this context, heteropolyacid compounds (HPA) with the Keggin structure are polynuclear complexes principally constituted by molybdenum, tungsten or vanadium as polyatoms (M) and phosphorus, silicon or germanium as central atoms or heteroatoms (X). The Keggin structure is

formed by a central tetrahedron XO<sub>4</sub>, surrounded by 12 octahedra MO<sub>6</sub>. They operate either as multi-electron oxidants or as strong acids, with an acid strength higher than that of the classical acids.<sup>17</sup> Currently, there is a considerable interest in exploiting both the structure of catalyst precursor and the multicenter active sites to facilitate catalysis by HPA having Keggin structure.

The catalytic activity of some pyridinium salts of Keggin-type molybdovanadophosphates in the selective oxidation of sulfides to sulfoxides with hydrogen peroxide is here reported. The pyridinium salts of the acids H<sub>4</sub>PMo<sub>11</sub>VO<sub>40</sub>, H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>, H<sub>9</sub>PMo<sub>6</sub>V<sub>6</sub>O<sub>40</sub>, obtained by vanadium substitution in the structure of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, were synthesized and characterized by FT-IR; the change in their acid properties were determined by titration with *n*-butylamine.<sup>18,19</sup>

Catalytic oxidation of methyl phenyl sulfide (Scheme 1) was selected as a test reaction: the sulfide (0.7 mmol), 35% aqueous H<sub>2</sub>O<sub>2</sub> (2.0 or 20.0 molar equiv) and 0.01 molar equivalents of catalyst, were reacted in acetonitrile. Table 1 shows the results obtained for different catalysts under different conditions. High selectivity for the sulfoxide was always obtained.



**Scheme 1**

When PMo<sub>11</sub>VO<sub>40</sub>H<sub>3</sub>Py is used as a catalyst, the reaction gave rise to highest selectivity. After 30 minutes of reaction at room temperature, 98% of methyl phenyl sulfide conversion was obtained, with a H<sub>2</sub>O<sub>2</sub>/substrate ratio of 2.0, and 98% of selectivity to methyl phenyl sulfoxide. As a comparison in the same conditions, after 15 minutes of reaction and with PMo<sub>12</sub>O<sub>40</sub>Py<sub>3</sub> as a catalyst, methyl phenyl sulfide was 98% oxidized with 90% of selectivity to methyl phenyl sulfoxide (10% sulfone). PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>Py<sub>5</sub> and PMo<sub>10</sub>V<sub>6</sub>O<sub>40</sub>Py<sub>9</sub> catalysts, after 2 hours of reaction and a large excess of H<sub>2</sub>O<sub>2</sub> (H<sub>2</sub>O<sub>2</sub>/substrate ratio = 20), lead to only methyl phenyl sulfone (100%). This result may be explained with the help of previous theoretical

**Table 1** Oxidation with 35% Aqueous H<sub>2</sub>O<sub>2</sub> of Methyl Phenyl Sulfide at Room Temperature in Acetonitrile Catalyzed by Heteropolyacids<sup>a</sup>

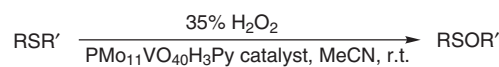
Catalyst	Time (h)	H <sub>2</sub> O <sub>2</sub> (mol equiv)	Conversion (%)	Selectivity (%)	
				Sulfoxide	Sulfone
No Catalyst	16	2	0	–	–
No Catalyst	16	20	0	–	–
PMo <sub>12</sub> O <sub>40</sub> H <sub>3</sub>	0.25	2	20	100	0
PMo <sub>12</sub> O <sub>40</sub> H <sub>3</sub>	2	2	95	97	3
PMo <sub>12</sub> O <sub>40</sub> H <sub>3</sub>	2	20	100	80	20
PMo <sub>12</sub> O <sub>40</sub> H <sub>3</sub>	16	20	100	8	92
PMo <sub>12</sub> O <sub>40</sub> Py <sub>3</sub>	0.25	2	98	90	10
PMo <sub>12</sub> O <sub>40</sub> Py <sub>3</sub>	0.25	2	99	81	19
PMo <sub>12</sub> O <sub>40</sub> Py <sub>3</sub>	2	20	100	–	100
PMo <sub>11</sub> VO <sub>40</sub> H <sub>3</sub> Py	0.25	2	82	99	1
PMo <sub>11</sub> VO <sub>40</sub> H <sub>3</sub> Py	0.5	2	98	98	2
PMo <sub>11</sub> VO <sub>40</sub> H <sub>3</sub> Py	2	20	100	60	40
PMo <sub>11</sub> VO <sub>40</sub> H <sub>3</sub> Py	16	20	100	–	100
PMo <sub>11</sub> VO <sub>40</sub> HPy <sub>3</sub>	0.25	2	2	100	–
PMo <sub>11</sub> VO <sub>40</sub> HPy <sub>3</sub>	2	2	93	95	5
PMo <sub>11</sub> VO <sub>40</sub> HPy <sub>3</sub>	2	20	99	73	27
PMo <sub>11</sub> VO <sub>40</sub> HPy <sub>3</sub>	16	20	100	–	100
PMo <sub>11</sub> VO <sub>40</sub> Py <sub>4</sub>	0.25	2	3	100	–
PMo <sub>11</sub> VO <sub>40</sub> Py <sub>4</sub>	2	2	72	99.5	0.5
PMo <sub>11</sub> VO <sub>40</sub> Py <sub>4</sub>	2	20	96	76	24
PMo <sub>11</sub> VO <sub>40</sub> Py <sub>4</sub>	16	20	100	5	95
PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> Py <sub>5</sub>	0.25	2	75	94	6
PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> Py <sub>5</sub>	2	2	100	71	29
PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> Py <sub>5</sub>	2	20	100	–	100
PMo <sub>10</sub> V <sub>6</sub> O <sub>40</sub> Py <sub>9</sub>	0.25	2	78	92	8
PMo <sub>10</sub> V <sub>6</sub> O <sub>40</sub> Py <sub>9</sub>	2	2	100	71	29
PMo <sub>10</sub> V <sub>6</sub> O <sub>40</sub> Py <sub>9</sub>	2	20	100	–	100

<sup>a</sup> See experimentals for reaction conditions.

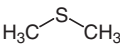
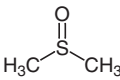
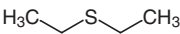
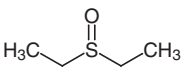
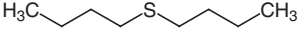
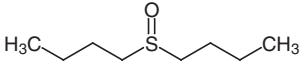
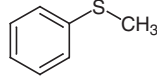
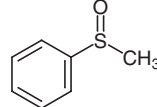
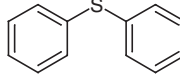
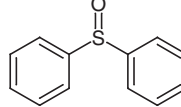
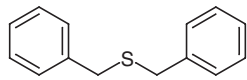
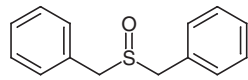

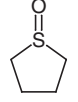
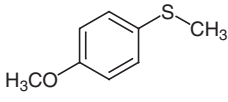
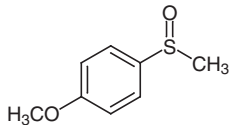
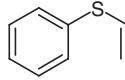
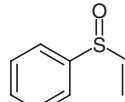
and computational studies:<sup>19</sup> the vanadium atom, present as the V-OH group in classical Keggin-type catalysts, lowers its average oxidation state when present as the VO<sup>(-)</sup>PyH<sup>(+)</sup> species. For PMo<sub>11</sub>VO<sub>40</sub>HPy<sub>3</sub> and PMo<sub>11</sub>VO<sub>40</sub>Py<sub>4</sub> catalysts, the reaction requires more time for completion as compared with PMo<sub>11</sub>VO<sub>40</sub>H<sub>3</sub>Py (Table 1), due to their partial insolubility in the reaction medium.

In order to explore the general applicability of the method for the selective oxidation of sulfides to sulfoxides, various functionalized sulfides were reacted according to this

oxidation protocol (Scheme 2 and Table 2), by using PMo<sub>11</sub>VO<sub>40</sub>H<sub>3</sub>Py as the catalyst. All the reactions were complete within a very short time and the sulfoxides were obtained in excellent yields, as practically unique oxidation products. Importantly, benzaldehyde is not affected under these reaction conditions (Table 2, note).

**Scheme 2**

**Table 2** Oxidation with 35% Aqueous H<sub>2</sub>O<sub>2</sub> of Sulfides to Sulfoxides in Acetonitrile at Room Temperature Catalyzed by PMo<sub>11</sub>VO<sub>40</sub>H<sub>3</sub>Py<sup>a,b</sup>

Entry	Substrate	Product	Time (h)	Yield (%)
1			0.5	98
2			0.5	97
3			0.5	99
4			0.5	96 <sup>c</sup>
5			2	95
6			0.5	94
7			1	92
8			0.5	91
9			0.5	89

<sup>a</sup> See experimentals for reaction conditions.

<sup>b</sup> Double bonds and alcohols are not oxidized if the reaction is carried out at r.t.: styrene, 1-undecene, phenyl allyl ether, benzylic alcohol, 1-decanol and 2-decanol were independently reacted under the same conditions of Table 2: after 20 h, 20 h, 20 h, 20 h, 3 h, and 3 h, respectively, no trace of oxidation products was detected.

<sup>c</sup> Benzaldehyde remains unaffected either if present in this reaction mixture or alone in an independent experiment: 0.7 mmol of PhCHO were stirred for 5 h under the same conditions: no PhCOOH was observed. After 20 h, but operating at 70 °C, 10% PhCOOH was obtained.

In conclusion, we have found a new, convenient and selective procedure for oxidizing sulfides to sulfoxides, with 35% aqueous H<sub>2</sub>O<sub>2</sub> and a catalytic amount of pyridinium salt of heteropolyacids. The yields were excellent. Reagents and catalysts are cheap and easily available. The oxidation is carried out at room temperature and requires a short reaction time. Further studies on the oxidations of other organic substrates and other polyoxometallates are currently in progress.

#### Catalyst Preparation

The heteropoly compounds were prepared by a hydrothermal synthesis method.<sup>18</sup>

**PMo<sub>11</sub>VO<sub>40</sub>H<sub>4</sub>**: a stoichiometric mixture of 0.98 g of phosphoric acid, 0.91 g of vanadium pentoxide and 14.4 g of molybdenum trioxide was suspended in distilled water. The mixture was stirred for a given time at 80–90 °C. After cooling to r.t. and removal of insoluble molybdates and vanadates, the heteropolyacid solution was evaporated and dried: orange crystals of PMo<sub>11</sub>VO<sub>40</sub>H<sub>4</sub> were obtained.

Mixed proton-pyridinium and pyridinium counter cations (containing x pyridinium cations per heteropolyanion, 1 < x < 9) were prepared from H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, H<sub>4</sub>PMo<sub>11</sub>VO<sub>40</sub>, H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> and H<sub>9</sub>PMo<sub>6</sub>V<sub>6</sub>O<sub>40</sub>. For H<sub>4</sub>PMo<sub>11</sub>VO<sub>40</sub> acid, the salts are designated as PMo<sub>11</sub>VO<sub>40</sub>H<sub>4-x</sub>Py<sub>x</sub> and PMo<sub>11</sub>VO<sub>40</sub>Py<sub>4</sub>, respectively. Molybdo-

vanadophosphate pyridinium salts were prepared by addition of the corresponding molar equivalent of pyridine to the aqueous solution of heteropolyacid. The pyridine was added slowly to the solution of heteropolyacid and the mixture was stirred for a few minutes at 80 °C. The resulting precipitates were filtered and dried at r.t.

#### General Procedure for the Oxidation of Sulfides to Sulfoxides

**Table 1:** The oxidation of methyl phenyl sulfide was typically carried out by stirring a solution of 0.7 mmol of the substrate and 1% molar equiv of the catalyst in 5 mL of MeCN, at 20 °C, with 35% aq H<sub>2</sub>O<sub>2</sub>. During the reaction, about 20 µL of the reaction mixture was taken and diluted in a mixture of H<sub>2</sub>O–CH<sub>2</sub>Cl<sub>2</sub> (2 mL); the CH<sub>2</sub>Cl<sub>2</sub> layer was shaken with anhyd Na<sub>2</sub>SO<sub>4</sub> and filtered. CG/MS analyses were performed on HP 5971 mass detector coupled to a HP gas chromatograph fitted with a 30 m × 0.25 mm DB5 capillary column. The percentages of each compound in the reaction mixture were directly estimated from the corresponding chromatographic peak areas.

**Table 2:** To a stirred solution of the sulfide (0.7 mmol) and PMo<sub>11</sub>VO<sub>40</sub>H<sub>3</sub>Py (0.01 mmol), in MeCN (5 mL), 2.0 mmol of 35% aq H<sub>2</sub>O<sub>2</sub> were added at r.t. The solvent was evaporated and the substrate was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried with anhyd Na<sub>2</sub>SO<sub>4</sub>; filtration and evaporation afforded the corresponding pure crude sulfoxides. The solid sulfoxides were purified by re-crystallization to afford the pure products.

All the compounds were identified via comparison with authentic samples and mass spectra analysis and their purity was established by GLC.

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