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Electron Transfer–Oxygen Transfer Oxidation of Sulfides Catalyzed by the  
 $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  PolyoxometalateAlexander M. Khenkin,<sup>†</sup> Gregory Leitus,<sup>‡</sup> and Ronny Neumann<sup>\*,†</sup>Department of Organic Chemistry and Chemical Research Support Unit, Weizmann Institute of Science,  
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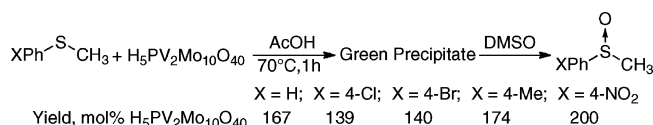
Received June 14, 2010; E-mail: Ronny.Neumann@weizmann.ac.il

**Abstract:** The oxygenation of sulfides to the corresponding sulfoxides catalyzed by  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  and other acidic vanadomolybdates has been shown to proceed by a low-temperature electron transfer–oxygen transfer (ET–OT) mechanism. First, a sulfide reacts with  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  to yield a cation radical–reduced polyoxometalate ion pair,  $\text{R}_2^{+\bullet}, \text{H}_5\text{PV}^{\text{IV}}\text{V}^{\text{V}}\text{Mo}_{10}\text{O}_{40}$ , that was identified by UV–vis spectroscopy (absorptions at 650 and 887 nm for  $\text{PhSMe}^{+\bullet}$  and  $\text{H}_5\text{PV}^{\text{IV}}\text{V}^{\text{V}}\text{Mo}_{10}\text{O}_{40}$ ) and EPR spectroscopy (quintet at  $g = 2.0079$ ,  $A = 1.34$  G for the thianthrene cation radical and the typical eight-line spectrum for  $\text{V}^{\text{IV}}$ ). Next, a precipitate is formed that shows by IR the incipient formation of the sulfoxide and by EPR a  $\text{VO}^{2+}$  moiety supported on the polyoxometalate. Dissolution of this precipitate releases the sulfoxide product. ET–OT oxidation of diethylsulfide yielded crystals containing  $[\text{V}(\text{O})(\text{OSeEt}_2)_x(\text{solvent})_{5-x}]^{2+}$  cations and polyoxometalate anions. Under aerobic conditions, catalytic cycles can be realized with formation of mostly sulfoxide (90%) but also some disulfide (10%) via carbon–sulfide bond cleavage.

During the past decade, we have shown that  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  can catalyze oxygenation reactions of arenes and alkyl arenes,<sup>1</sup> primary alcohols and vicinal diols,<sup>2</sup> and  $\text{CO}^3$  by an outer-sphere electron transfer–oxygen transfer (ET–OT) mechanism,<sup>4</sup> which is a homogeneous low-temperature analogue of the heterogeneous, high-temperature Mars–van Krevelen oxygenation.<sup>5</sup> The salient property of these reactions is that contrary to the general paradigm in organic and bioorganic chemistry that higher-valent oxo species are more reactive than lower-valent ones, in the ET–OT reactions the species containing lower-valent  $\text{V}^{\text{IV}}\text{–O}$  are reactive while the  $\text{V}^{\text{V}}\text{–O}$  species are not; reduction of the polyoxometalate precedes the oxygen transfer. Although the oxygenation of sulfides to sulfoxides with  $\text{H}_2\text{O}_2$  is a relatively facile reaction, similar reactions with  $\text{O}_2$  using metal-based catalysts are not so.<sup>6</sup> With polyoxometalates, mostly synthetic aspects were stressed in the oxidation of sulfides to sulfoxides with TBHP<sup>7</sup> and with  $\text{O}_2$  using both iron- and vanadium-containing polyoxometalates.<sup>8</sup> In this paper, we describe our research on the ET–OT oxidation of sulfides with  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ , including the identification of the electron-transfer step and the “suicidal” formation of sulfoxides that under anaerobic conditions yields  $[\text{V}(\text{O})(\text{OSR}_2)_x(\text{solvent})_{5-x}]^{2+}$ . In the presence of  $\text{O}_2$  and a suitable solvent, mainly sulfoxides but also disulfides are formed.

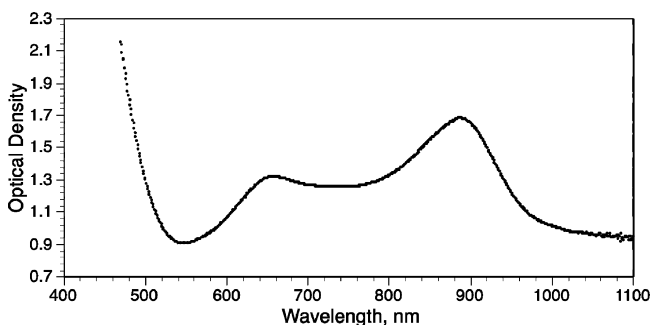
Reactions of  $\text{ArSMe}$  (85 mM) and  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  (30 mM) in acetic acid at 70 °C for 1 h under Ar gave a green precipitate (Scheme 1). Isolation of the solids and their dissolution in DMSO showed the 100% selective formation of  $\text{ArS}(\text{O})\text{Me}$  in 140–200% yields based on  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ .

**Scheme 1.** Oxygenation of  $\text{ArSMe}$  to  $\text{ArS}(\text{O})\text{Me}$  with  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  under Anaerobic Conditions



Reaction of  $\text{PhSMe}$  (85 mM) and  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  (30 mM, ~50% enrichment),<sup>1</sup> yielded  $\text{PhS}^{18}\text{O}\text{Me}$  that was 41%  $^{18}\text{O}$ -labeled. Oxidation of  $\text{PhSMe}$  (85 mM) in the presence of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_5\text{PV}_2\text{W}_{10}\text{O}_{40}$ , or  $(n\text{-BuN})_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  (30 mM) showed no formation of  $\text{PhS}(\text{O})\text{Me}$ , although with  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  the polyoxometalate was reduced, as evidenced by the formation of a green reduced species. With other acidic vanadomolybdates, such as  $\text{H}_5\text{SiVMo}_{11}\text{O}_{40}$ ,  $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ , and  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ ,  $\text{PhS}(\text{O})\text{Me}$  was also formed [Table S1 in the Supporting Information (SI)]. In aerobic reactions,  $\text{PhSMe}$  (850 mM) was reacted in the presence of  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  (10 mM) at 70 °C under 1 bar  $\text{O}_2$  for 15 h in  $\text{CH}_3\text{NO}_2$ . A conversion of 57% with 48 turnovers was observed, with both  $\text{PhS}(\text{O})\text{Me}$  (90%) and  $\text{PhSSPh}$  (10%) obtained as products. The formation of the latter is probably from the cation radical intermediate.<sup>9</sup>

The reaction of  $\text{PhSMe}$  (42 mM) with  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  (1.5 mM) at room temperature (RT) instead of 70 °C under Ar led to a green solution exhibiting a visible spectrum with  $\lambda_{\text{max}} = 650$  and 887 nm, as shown in Figure 1. This spectrum is hypothesized to arise from a strongly red-shifted ion pair complex between  $\text{PhSMe}^{+\bullet}$  and the reduced  $\text{H}_5\text{PV}^{\text{IV}}\text{V}^{\text{V}}\text{Mo}_{10}\text{O}_{40}$ . Previously,  $\text{PhSMe}^{+\bullet}$  was shown to absorb at  $\lambda_{\text{max}} = 530$  nm,<sup>9</sup> but similar UV–vis spectra of sulfide-based cation radicals were reported when measured under acidic conditions;<sup>10</sup> the documented maximum for  $\text{H}_5\text{PV}^{\text{IV}}\text{V}^{\text{V}}\text{Mo}_{10}\text{O}_{40}$  is at ~700 nm.<sup>11</sup>

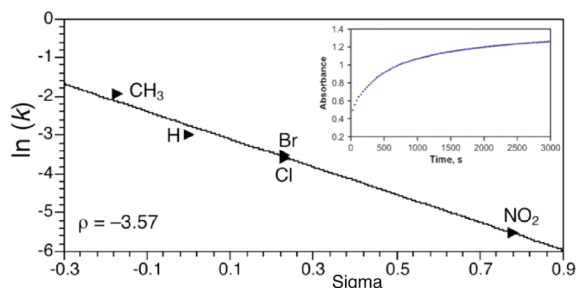


**Figure 1.** Visible spectrum of  $\text{H}_5\text{PV}^{\text{IV}}\text{V}^{\text{V}}\text{Mo}_{10}\text{O}_{40}\text{–PhSMe}^{+\bullet}$ . A strong UV peak at ~300 nm is not shown.

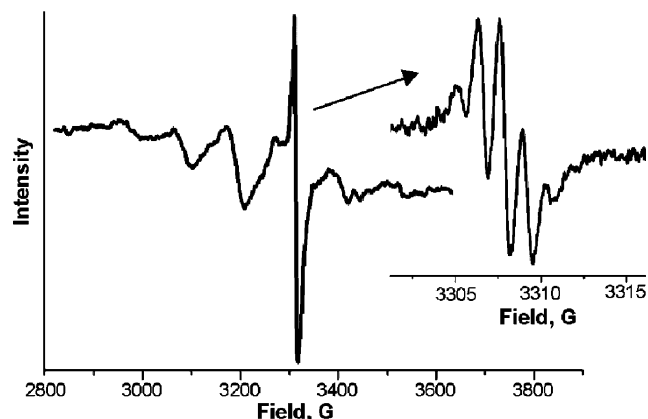
The kinetic behavior of  $\text{H}_5\text{PV}^{\text{IV}}\text{V}^{\text{V}}\text{Mo}_{10}\text{O}_{40}\text{–ArSMe}^{+\bullet}$  formation with various substrates showed a good Hammett correlation with

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**Figure 2.** Hammett plot for the electron-transfer reaction between ArSMe and  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ . Reaction conditions: 42 mM ArSMe, 1.5 mM  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ , 2 mL of AcOH, RT, Ar. The value of  $r^2$  was 0.984. Inset: time profile for the reaction of PhSMe with  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ .



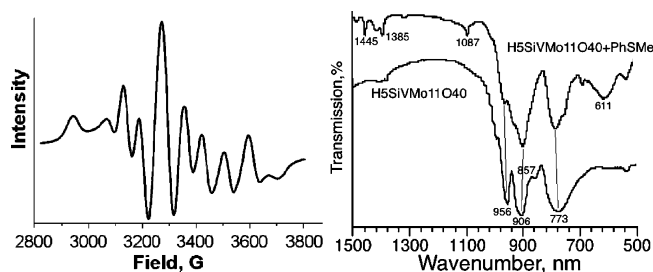
**Figure 3.** EPR spectrum resulting from the reaction of thianthrene and  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ .

$\rho = -3.6$  (Figure 2), as expected for the formation of a one-electron-oxidized species in this step.<sup>12</sup>

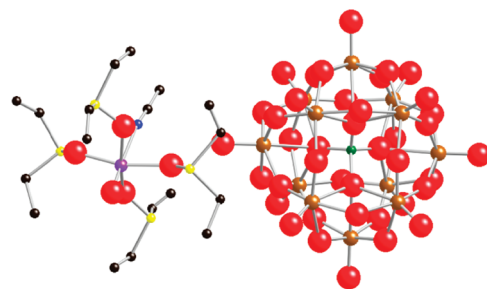
To solidify the hypothesis of the formation of  $\text{H}_5\text{PV}^{\text{V}}\text{V}^{\text{IV}}\text{Mo}_{10}\text{O}_{40}\text{--PhSMe}^+$ , we sought to observe such a species in solution using thianthrene, since it is known to form a stable radical cation with a known EPR spectrum.<sup>12</sup> In Figure 3 one is able to observe both a rather weak eight-line signal attributable to  $\text{V}^{\text{IV}}$  in  $\text{H}_5\text{PV}^{\text{V}}\text{V}^{\text{IV}}\text{Mo}_{10}\text{O}_{40}$  and a signal at  $g = 2.0079$ ,  $A = 1.34$  G due to the thianthrene cation radical. This spectrum consists of five lines in an integral ratio of 1:4:6:4:1.<sup>13</sup> A similar EPR spectrum was observed with diphenyl sulfide (see the SI).

From Scheme 1, a question arises regarding the identification of the green precipitate. The EPR spectrum (Figure 4 left) is very similar to the published spectrum of a  $\text{VO}^{2+}$  species supported on a polyoxometalate with an axially symmetric  $g$  tensor of  $\text{V}(\text{IV})$  with hyperfine splitting due to interaction of an unpaired electron with the nuclear spin of  $^{51}\text{V}$  ( $I = 7/2$ ).<sup>14</sup> Though the peak intensity was strong, there was no signal attributable to  $\text{PhSMe}^+$ , suggesting that  $\text{PhS}(\text{O})\text{Me}$  was present in the precipitate. The S–O vibrations of sulfoxides are typically at  $1050\text{--}1100\text{ cm}^{-1}$ , but the P–O bond of  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  absorbs at these wavenumbers.<sup>15</sup> As stated above,  $\text{H}_5\text{SiVMo}_{11}\text{O}_{40}$  also reacted anaerobically with PhSMe to form  $\text{PhS}(\text{O})\text{Me}$  via a green precipitate. Indeed, in that case the S–O vibration was observed at  $1087\text{ cm}^{-1}$  (Figure 4 right).

Attempts to grow crystals from the reactions with PhSMe failed, but the reaction of EtSet with  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  at RT did yield single crystals after 60 days in MeCN.<sup>16</sup> The X-ray structure (Figure 5) shows that  $\text{VO}^{2+}$  was removed from  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  and that two cationic species,  $[\text{V}(\text{O})(\text{OSeEt}_2)_4(\text{MeCN})]^{2+}$  and  $[\text{V}(\text{O})(\text{OSeEt}_2)_2(\text{OH}_2)_3]^{2+}$ , were formed. The oxygenation reaction is apparently “suicidal” in acetic acid, although in other solvents, such as



**Figure 4.** (left) EPR spectrum of the precipitate from the reaction of PhSMe and  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ . (right) IR spectra of (bottom)  $\text{H}_5\text{SiVMo}_{11}\text{O}_{40}$  and (top) the precipitate from PhSMe and  $\text{H}_5\text{SiVMo}_{11}\text{O}_{40}$ .

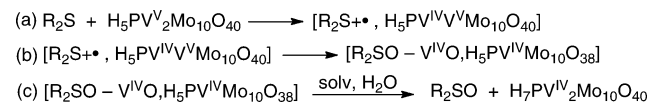


**Figure 5.** Ball-and-stick structure of  $[\text{V}(\text{O})(\text{OSeEt}_2)_4(\text{MeCN})]^{2+}\text{--}[\text{V}(\text{O})(\text{OSeEt}_2)_2(\text{OH}_2)_3]^{2+}\text{--}[\text{PMo}_{12}\text{O}_{40}]^{3-}\cdot 2\text{H}_2\text{O}\cdot \text{MeCN}$ . Only one cation and anion are shown. P, green; Mo, brown; O, red; V, purple; N, blue; C, black; S, yellow.

nitromethane, these compounds do not precipitate and there is turnover in the presence of  $\text{O}_2$  (see above) with re-formation of  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  ( $^{31}\text{P}$  NMR). The removal of  $\text{VO}^{2+}$  from the vicinal isomers of  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  upon reduction was observed by EPR spectroscopy and has been discussed elsewhere,<sup>17</sup> as was the likely identity of oxygen atom involved in the OT step.<sup>3</sup>

On the basis of the evidence presented, a sequence of reactions that are involved in the ET–OT oxidation of sulfides can be suggested (Scheme 2). An outer-sphere ET reaction between  $\text{R}_2\text{S}$  and  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  leads to an ion pair (step a). This is followed by an OT reaction to yield  $\text{R}_2\text{SO}$  with removal of  $\text{VO}^{2+}$  from the Keggin structure (step b), which is postulated to be the green precipitate. In the presence of a suitable solvent (e.g.,  $\text{CH}_3\text{NO}_2$ ), the sulfoxide is liberated with the likely formation of the reduced  $\text{H}_7\text{PV}^{\text{IV}}_2\text{Mo}_{10}\text{O}_{40}$  (step c).

#### Scheme 2. Proposed Pathway for ET–OT Oxidation of Sulfides



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**Supporting Information Available:** Complete experimental section, additional spectra and explanations, and a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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