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Electron Transfer−Oxygen Transfer Oxygenation of Sulfides Catalyzed by the $H_5PV_2Mo_{10}O_{40}$ Polyoxometalate

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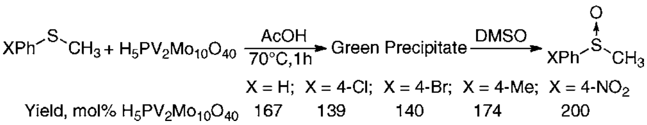
Abstract: The oxygenation of sulfides to the corresponding sulfoxides catalyzed by $H_5PV_2Mo_{10}O_{40}$ and other acidic vanadomolybdates has been shown to proceed by a low-temperature electron transfer−oxygen transfer (ET−OT) mechanism. First, a sulfide reacts with $H_5PV_2Mo_{10}O_{40}$ to yield a cation radical−reduced polyoxometalate ion pair, $R_2^{+\bullet}$,$H_5PV^{IV}V^{V}Mo_{10}O_{40}$, that was identified by UV−vis spectroscopy (absorptions at 650 and 887 nm for $PhSMe^{+\bullet}$ and $H_5PV^{IV}V^{V}Mo_{10}O_{40}$) and EPR spectroscopy (quintet at $g = 2.0079$, $A = 1.34$ G for the thianthrene cation radical and the typical eight-line spectrum for V^{IV}). Next, a precipitate is formed that shows by IR the incipient formation of the sulfoxide and by EPR a VO^{2+} moiety supported on the polyoxometalate. Dissolution of this precipitate releases the sulfoxide product. ET−OT oxidation of diethylsulfide yielded crystals containing $[V(O)(OSEt_2)_x(solv)_{5-x}]^{2+}$ 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 $H_5PV_2Mo_{10}O_{40}$ can catalyze oxygenation reactions of arenes and alkyl arenes,[1] primary alcohols and vicinal diols,[2] and CO[3] by an outer-sphere electron transfer−oxygen transfer (ET−OT) mechanism,[4] which is a homogeneous low-temperature analogue of the heterogeneous, high-temperature Mars−van Krevelen oxygenation.[5] 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 V^{IV}−O are reactive while the V^{V}−O species are not; reduction of the polyoxometalate precedes the oxygen transfer. Although the oxygenation of sulfides to sulfoxides with H_2O_2 is a relatively facile reaction, similar reactions with O_2 using metal-based catalysts are not so.[6] With polyoxometalates, mostly synthetic aspects were stressed in the oxidation of sulfides to sulfoxides with TBHP[7] and with O_2 using both iron- and vanadium-containing poloxometalates.[8] In this paper, we describe our research on the ET−OT oxidation of sulfides with $H_5PV_2Mo_{10}O_{40}$, including the identification of the electron-transfer step and the "suicidal" formation of sulfoxides that under anaerobic conditions yields $[V(O)(OSR_2)_x(solv)_{5-x}]^{2+}$. In the presence of O_2 and a suitable solvent, mainly sulfoxides but also disulfides are formed.

Reactions of ArSMe (85 mM) and $H_5PV_2Mo_{10}O_{40}$ (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 ArS(O)Me in 140−200% yields based on $H_5PV_2Mo_{10}O_{40}$.

Scheme 1. Oxygenation of ArSMe to ArS(O)Me with $H_5PV_2Mo_{10}O_{40}$ under Anaerobic Conditions



Reaction of PhSMe (85 mM) and $H_5PV_2Mo_{10}{}^{18}O_{40}$ (30 mM, ∼50% enrichment),[1] yielded $PhS(^{18}O)Me$ that was 41% ^{18}O-labeled. Oxidation of PhSMe (85 mM) in the presence of $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_5PV_2W_{10}O_{40}$, or $(n\text{-BuN})_5PV_2Mo_{10}O_{40}$ (30 mM) showed no formation of PhS(O)Me, although with $H_3PMo_{12}O_{40}$ the polyoxometalate was reduced, as evidenced by the formation of a green reduced species. With other acidic vanadomolybdates, such as $H_5SiVMo_{11}O_{40}$, $H_4PVMo_{11}O_{40}$, and $H_5PV_2Mo_{10}O_{40}$, PhS(O)Me was also formed [Table S1 in the Supporting Information (SI)]. In aerobic reactions, PhSMe (850 mM) was reacted in the presence of $H_5PV_2Mo_{10}O_{40}$ (10 mM) at 70 °C under 1 bar O_2 for 15 h in CH_3NO_2. A conversion of 57% with 48 turnovers was observed, with both PhS(O)Me (90%) and PhSSPh (10%) obtained as products. The formation of the latter is probably from the cation radical intermediate.[9]

The reaction of PhSMe (42 mM) with $H_5PV_2Mo_{10}O_{40}$ (1.5 mM) at room temperature (RT) instead of 70 °C under Ar led to a green solution exhibiting a visible spectrum with $\lambda_{max} = 650$ and 887 nm, as shown in Figure 1. This spectrum is hypothesized to arise from a strongly red-shifted ion pair complex between $PhSMe^{+\bullet}$ and the reduced $H_5PV^{V}V^{IV}Mo_{10}O_{40}$. Previously, $PhSMe^{+\bullet}$ was shown to absorb at $\lambda_{max} = 530$ nm,[9] but similar UV−vis spectra of sulfide-based cation radicals were reported when measured under acidic conditions;[10] the documented maximum for $H_5PV^{V}V^{IV}Mo_{10}O_{40}$ is at ∼700 nm.[11]

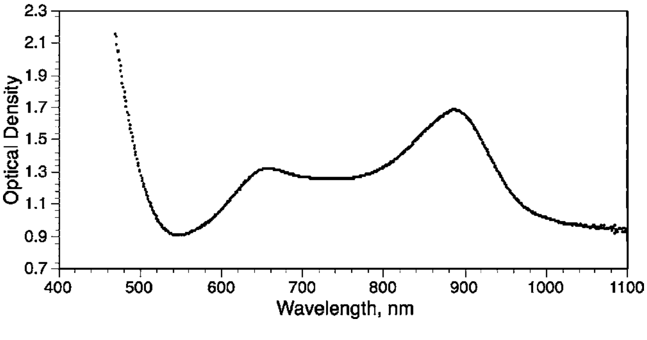


Figure 1. Visible spectrum of $H_5PV^{V}V^{IV}Mo_{10}O_{40}$−$PhSMe^{+\bullet}$. A strong UV peak at ∼300 is not shown.

The kinetic behavior of $H_5PV^{V}V^{IV}Mo_{10}O_{40}$−$ArSMe^{+\bullet}$ formation with various substrates showed a good Hammett correlation with

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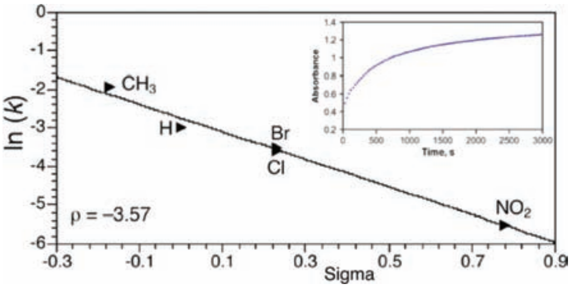


Figure 2. Hammett plot for the electron-transfer reaction between ArSMe and $H_5PV_2Mo_{10}O_{40}$. Reaction conditions: 42 mM ArSMe, 1.5 mM $H_5PV_2Mo_{10}O_{40}$, 2 mL of AcOH, RT, Ar. The value of r^2 was 0.984. Inset: time profile for the reaction of PhSMe with $H_5PV_2Mo_{10}O_{40}$.

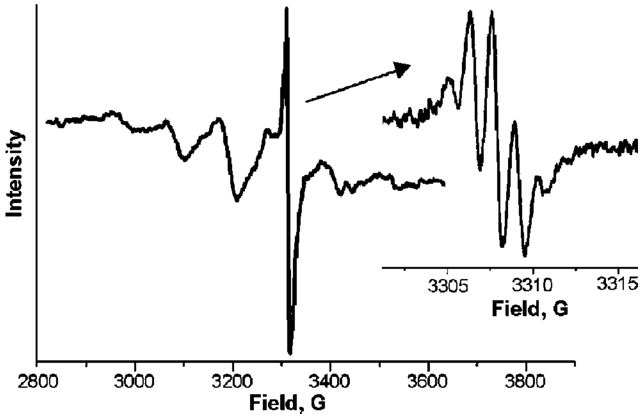


Figure 3. EPR spectrum resulting from the reaction of thianthrene and $H_5PV_2Mo_{10}O_{40}$.

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

To solidify the hypothesis of the formation of $H_5PV^VV^{IV}$-$Mo_{10}O_{40}$−$PhSMe^{+\bullet}$, 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.[12] In Figure 3 one is able to observe both a rather weak eight-line signal attributable to V^{IV} in $H_5PV^VV^{IV}Mo_{10}O_{40}$ 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.[13] 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 VO^{2+} species supported on a polyoxometalate with an axially symmetric **g** tensor of V(IV) with hyperfine splitting due to interaction of an unpaired electron with the nuclear spin of ^{51}V ($I = {}^7/_2$).[14] Though the peak intensity was strong, there was no signal attributable to $PhSMe^{+\bullet}$, suggesting that PhS(O)Me was present in the precipitate. The S−O vibrations of sulfoxides are typically at 1050−1100 cm^{-1}, but the P−O bond of $H_5PV_2Mo_{10}O_{40}$ absorbs at these wavenumbers.[15] As stated above, $H_5SiVMo_{11}O_{40}$ also reacted anaerobically with PhSMe to form PhS(O)Me via a green precipitate. Indeed, in that case the S−O vibration was observed at 1087 cm^{-1} (Figure 4 right).

Attempts to grow crystals from the reactions with PhSMe failed, but the reaction of EtSEt with $H_5PV_2Mo_{10}O_{40}$ at RT did yield single crystals after 60 days in MeCN.[16] The X-ray structure (Figure 5) shows that VO^{2+} was removed from $H_5PV_2Mo_{10}O_{40}$ and that two cationic species, $[V(O)(OSEt_2)_4(MeCN)]^{2+}$ and $[V(O)(OSEt_2)_2(OH_2)_3]^{2+}$, were formed. The oxygenation reaction is apparently “suicidal” in acetic acid, although in other solvents, such as nitromethane, these compounds do not precipitate and there is turnover in the presence of O_2 (see above) with re-formation of $H_5PV_2Mo_{10}O_{40}$ (^{31}P NMR). The removal of VO^{2+} from the vicinal isomers of $H_5PV_2Mo_{10}O_{40}$ upon reduction was observed by EPR spectroscopy and has been discussed elsewhere,[17] as was the likely identity of oxygen atom involved in the OT step.[3]

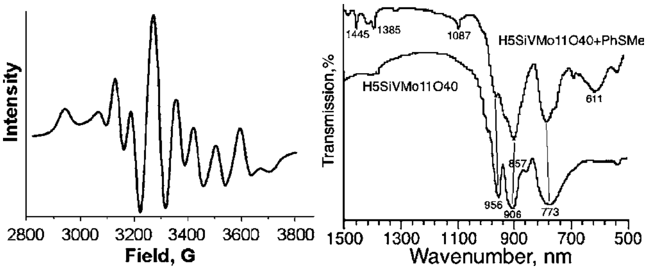


Figure 4. (left) EPR spectrum of the precipitate from the reaction of PhSMe and $H_5PV_2Mo_{10}O_{40}$. (right) IR spectra of (bottom) $H_5SiVMo_{11}O_{40}$ and (top) the precipitate from PhSMe and $H_5SiVMo_{11}O_{40}$.

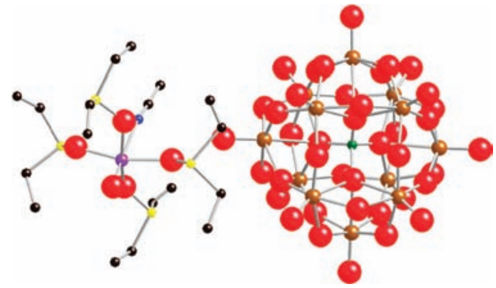
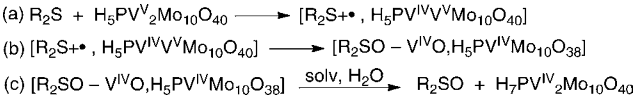


Figure 5. Ball-and-stick structure of $[V(O)(OSEt_2)_4(MeCN)]^{2+}{}_2$-$[V(O)(OSEt_2)_2(OH_2)_3]^{2+}[PMo_{12}O_{40}]^{3-}{}_2\cdot 2H_2O\cdot MeCN$. Only one cation and anion are shown. P, green; Mo, brown; O, red; V, purple; N, blue; C, black; S, yellow.

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 R_2S and $H_5PV_2Mo_{10}O_{40}$ leads to an ion pair (step a). This is followed by an OT reaction to yield R_2SO with removal of 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., CH_3NO_2), the sulfoxide is liberated with the likely formation of the reduced $H_7PV^{IV}{}_2Mo_{10}O_{40}$ (step c).

Scheme 2. Proposed Pathway for ET−OT Oxidation of Sulfides



$$\text{(a) } R_2S + H_5PV^V{}_2Mo_{10}O_{40} \longrightarrow [R_2S^{+\bullet}, H_5PV^{IV}V^VMo_{10}O_{40}]$$

$$\text{(b) } [R_2S^{+\bullet}, H_5PV^{IV}V^VMo_{10}O_{40}] \longrightarrow [R_2SO - V^{IV}O, H_5PV^{IV}Mo_{10}O_{38}]$$

$$\text{(c) } [R_2SO - V^{IV}O, H_5PV^{IV}Mo_{10}O_{38}] \xrightarrow{\text{solv, } H_2O} R_2SO + H_7PV^{IV}{}_2Mo_{10}O_{40}$$

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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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