PRF# ACS PRF 58343-UR3
Project Title: Fundamental Investigation of Sulfide Oxidation by New Bisoxido Molybdenum(VI) Catalyst
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The main goals of the PRF-UR were (1) examination of the sulfide oxidation by a new class of molybdenum(VI) dioxo coordination complexes and (2) investigation of the fate of the Mo(VI) dioxo complex upon activation by peroxides. In terms of the PRF objectives, both fundamental questions help develop new metal systems that perform an oxidative transformation critical for sulfur removal from fossil fuels.

The title complex was 2,6-bis(hydroxyl(methyl)amino)-4-morpholino-1,3,5-triazinatodioxo-molybdenum(VI) (1) which has the central Mo(VI) in a distorted trigonal bipyramidal geometry.

Originally made to mimic siderophore metal chelation chemistry, this was the first time this pincer-like complex was used for sulfide oxidation. Complex 1 oxidizes sulfides with peroxy addition. The two types of peroxydes that were investigated were 30% H₂O₂(aq) and Ph₃COOH(s). The later dry peroxyde was used to probe the fate of the alkyl peroxyde by ¹³C NMR. To this end, the first investigation sought to examine if the dioxo molybdenum functionality was converted to an η² peroxy group upon addition of peroxyde which was a key hypothesis in the original PRF proposal. This utilized the resonance Raman spectrum of 1 that showed a 941 cm⁻¹ stretch assigned to a water-labile Mo=O ligation. As seen in prior examples, addition of ¹⁸O-water readily replaced the ¹⁶O of the Mo=¹⁶O group to a Mo=¹⁸O group resulting in a 46 cm⁻¹ displacement of the Mo=¹⁸O stretch to 895 cm⁻¹. This ¹⁸O labeling tracks the fate of the oxygen upon sulfide oxidation with peroxydes.

The bimolecular reaction of trityl hydroperoxide and 1 that yields trityl alcohol, and in prior investigations an ¹⁸O-labeled dioxo Mo(VI)-HMPT complex yielded a trityl alcohol with the ¹⁸O on the product alcohol (Eqn 1) and the active η² peroxy species.

\[
\begin{align*}
\text{Mo} & \hspace{1cm} + \hspace{1cm} H\_2O\_2Ph \hspace{1cm} \rightarrow \hspace{1cm} \text{Mo} \hspace{1cm} + \hspace{1cm} H\_2C\_2O\_2Ph \\
\text{H}_2C_2O_2Ph & \hspace{1cm} \rightarrow \hspace{1cm} \text{Mo} \hspace{1cm} + \hspace{1cm} \text{H}_2O \hspace{1cm} \rightarrow \hspace{1cm} \text{H}_2C_2O_2Ph
\end{align*}
\]

Such a transformation was not seen with 1 which suggested an alternate peroxyde active species than the one proposed in Eqn 1. Alternate possibilities include an η¹ alkyl peroxyde (derived from Ph₃COOH used in sulfide oxidation) or an η¹ hydroperoxy (H₂O₂(aq)) species. Resonance Raman of the Equation 1 reaction also revealed new stretches at 560 and 640 cm⁻¹ that could be attributed to peroxyde functionalities when treated with Ph₃COOH(s) or H₂O₂. That ¹⁸O-labeled 1 treated with dry Ph₃COOH yielded no noticeable displacement in these new peroxy 560 and 640 cm⁻¹ stretches indicate activation of 1 retains the Mo=O functionality. This information along with sulfide oxidation results (vide infra) puts together a possible η¹ mechanism for sulfide oxidation by alkyl peroxydes with 1.

In connection with sulfide results, complex 1 catalytically oxidizes thioanisole mainly to the corresponding sulfoxide at 5% catalyst loading. (Eqn 2)

\[
\begin{align*}
\text{PhSCH}_3 & \hspace{1cm} + \hspace{1cm} \text{H}_2\text{O}_2\text{Ph} \hspace{1cm} \rightarrow \hspace{1cm} \text{PhSOCH}_3 \hspace{1cm} + \hspace{1cm} \text{H}_2\text{O} \hspace{1cm} \rightarrow \hspace{1cm} \text{PhSOCH}_3
\end{align*}
\]

An array of kinetics measurements gave a rate law that was first order in thioanisole and 1 with no consistent dependency in [H₂O₂]. Temperature dependence measurements provided an Eyring relationship that yielded thermodynamic parameters set in the table below.

<table>
<thead>
<tr>
<th></th>
<th>Ea (kJ/mol)</th>
<th>ΔS\textsuperscript{1} J/mol*K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>63.0 ±5.2</td>
<td>-117 ±1.7</td>
</tr>
<tr>
<td>2</td>
<td>56.5 ±1.6</td>
<td>-124</td>
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These energy of activation for thioanisole oxidation is slightly higher than a similar transformation by oxodiperoxo(2-carboxypyridinato-molybdenum(VI)) \( \text{MoO(O)}_2 \). A \( \Delta S^\ddagger \) of -117 J/mol-K for 1 is consistent with a bimolecular rate determining step. It should be noted that thioanisole oxidation by 2 did not require peroxide and presumes an \( \eta^2 \) active species that takes the sulfide to the sulfoxide. When para substituted thioanisoles were oxidized by 1, a linear free energy relationship (LFER) was found with a slope (reaction order) of -0.92 ± 0.17 (Figure 1).

This compares well with other sulfide oxidation reactions by different molybdenum(VI) complexes such as the diperoxo-molybdate dimer \([\text{MoO(O)}_2]_2[\mu-\text{O}]\)^2. The negative slope of the LFER for derivatized thioanisole oxidation by 1 is consistent with prior findings by both molybdenum and tungsten peroxo complexes and suggest the sulfur is the nucleophile that attacks the metal peroxo functionality.

An additional key result involved the absence of \( ^{18}\text{O} \) in the sulfoxide product (Eqn 2) when \(^{18}\text{O}\)-labeled 1 was incubated with dry Ph$_3$COOH or urea hydrogen peroxide. The aforementioned results of the reaction of \(^{18}\text{O}\)-labeled 1 with Ph$_3$COOH (i.e. no \(^{18}\text{O}\) in the product Ph$_3$COH) does not support a \( \eta^2 \)-peroxo species which is further underscored with the absence of \(^{18}\text{O}\) in the sulfoxide product when \(^{18}\text{O}\)-labeled 1 is used. This leads towards an \( \eta^1 \)-alkyl peroxo functionality that delivers the \( \alpha \)-oxygen to the sulfur in sulfide oxidation. A similar oxidative pathway has been postulated in olefin epoxidation by vanadium and molybdenum catalysts; there was an absence of \(^{18}\text{O}\) incorporation in the epoxide and alcohol product. When these results are taken together it suggests the following possible sulfide oxidation pathway (Eqn 3) that goes through \( \eta^1 \)-alkyl or hydroperoxo intermediate (3) formed in the reaction of 1 with ROOH. As delineated in the PRF proposal these experimental results will be correlated with computational (density functional theory) work to study the hypothetical route set in Equation 3.

(3)

Current efforts for this project have a direct broader impact on the PI in terms of broadening his research work towards computational chemistry. The PI is at heart an experimentalist, and the PRF goals of computational modeling opens a new career facet that interfaces experimental and computational chemistry. Specifically, Equation 3 will be the subject of further computational investigation as well as sulfide oxidation by \( \eta^2 \)-peroxo complex 2.

Two undergraduate students were funded by this award through summer stipends. One graduated in May 2019 and will be applying for chemistry employment. The overarching environmental goal of this PRF project (sulfide removal) has directed his attention towards an environmental chemistry line of work. A second student was supported from this PRF award through a summer (2019) stipend and he continues this work as a “senior” thesis. Technically he is a junior and as a double math-chemistry major he will continue the sulfide oxidation project as a thesis project in his junior year; he will then embark on a math thesis next year in his last year in college. A third student will work on this project for her senior thesis (2019-2020) using complex 2 to study the sulfide oxidation; she was not funded by this PRF award last summer as she had an internal scholarship that supported summer research.