Selective and efficient detoxification of sulfur mustard gas analogues with H_2O_2 using bioinspired Mo and W dithiolene catalysts

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ABSTRACT: Efficient and selective decomposition of chemical warfare agents (CWAs) is immensely important to cope with threats from accidental or intentional releases from stockpiles. One of the most stockpiled CWAs is sulfur mustard (SM) gas. The most effective way to detoxify stockpiled SM is to oxidize the thioether functionality to its benign sulfoxide (SMO) state. However, overoxidation to the corresponding sulfone (SMO_2), itself a potent toxin, should be avoided. Thus, catalysts for SM detoxification must be precisely tuned to promote the sluggish oxidation of SM while avoiding overoxidation of SMO to SMO_2. In this study, Mo and W dithiolene catalysts, $[MO_2(\text{dithiolene})_2]^{2-}$ (M = Mo or W), inspired by the active site structures of oxotransferase enzymes such as DMSO reductase were used as catalysts for oxidation of the SM research analogue, 2-chloroethyl ethyl sulfide (CEES), with aqueous H_2O_2 as a green oxidant. Under optimized conditions, $[WO_2(mnt)_2]^{2-}$ and $[MoO_2(bdt)_2]^{2-}$ (mnt = maleonitriledithiolate, bdt = 1,2-benzenedithiolate) were found to promote selective CEES oxidation to sulfoxide CEESO without overoxidation to sulfone $CEESO_2$ in as little as 5-15 min with catalyst loadings as low as 0.015 mol%. The W catalyst was also found to be reusable without measurable loss of activity. Experimental and computational studies indicate the involvement of η^2-peroxo species, $[M(O)(\eta^2\text{-}O_2)(\text{dithiolene})_2]^{2-}$, as the active oxidants formed *in situ*. Overall, the bioinspired catalysts in this study are shown to be promising candidates for developing convenient, inexpensive, efficient, and selective mustard gas detoxification technologies.

Since its first deployment as a weapon during World War I, sulfur mustard (SM, bis(2-chloroethyl) sulfide) has been recognized as a major chemical warfare agent (CWA), causing severe skin blistering, eye irritation, and respiratory damage.[1] Although production, stockpiling, and use of CWAs including SM has long been banned by international treaty, SM still presents a significant threat because it is a simple molecule that can be synthesized readily by nefarious actors.[2] In fact, deployment of SM by a terrorist organization was reported as recently as 2016.[3] Therefore, it is critical to continue developing improved methods for detoxification of SM stockpiles.[4] Although significant effort has been spent towards optimizing hydrolysis and dehydrochlorination processes, the most promising detoxification strategies for SM disposal involve oxidation of its sulfur center, as the corresponding bis(2-chloroethyl) sulfoxide (SMO) is benign and inert towards biological systems. Because SM undergoes oxidation significantly slower than other aliphatic thioethers,[2] it is necessary to identify highly active sulfur oxidation catalysts. However, overoxidation of SM produces bis(2-chloroethyl) sulfone (SMO_2), which is also a potent toxin.[5] Thus, SM detoxification requires a catalyst precisely tuned to promote the sluggish oxidation of SM to SMO without further oxidation to SMO_2 (Figure 1a). Ideally, such a catalytic process would also employ a green oxidant (i.e., O_2 or H_2O_2) that produces no chemical waste streams.[6] Compounds including strong acids, molecular metal complexes, polyoxometalates (POMs), and metal oxide solids have been explored as catalysts for oxidation of the SM research analogue, 2-chloroethyl ethyl sulfide (CEES).[2] Photoactive porous materials,[6] especially metal-organic frameworks (MOFs),[7] have received significant attention for their ability to catalyze selective CEES oxidation to 2-chloroethyl ethyl sulfoxide (CEESO) under UV or visible light-mediated conditions via $^1O_2$ generation.[8,9] Despite the successes of these photosensitization strategies, it is desirable to develop complementary thermal processes.

In biological systems, selective oxygen atom transfer (OAT) reactions are catalyzed by oxotransferase enzymes[10–12] whose active sites feature bis(dithiolene) ligation to Mo (and sometimes W)[13,14] via the pyranopterin dithiolate cofactor. Particularly relevant to the SM problem is biological dimethyl sulfoxide reduction, i.e., the microscope reverse of desired SM detoxification, which is catalyzed by the DMSO reductase enzyme whose $Mo(\text{dithiolene})_2$ active site (Figure 1b) is proposed to shuttle between Mo^{IV} and Mo^{VI}=O states during OAT catalysis.[15–17] Accordingly, synthetic oxomolybdenum(VI) compounds have been studied for catalytic OAT reactions including sulfur oxidations.[18–22] A prototypical example, commercially-available $MoO_2(acac)_2$ (acac = acetylacetonate), efficiently catalyzes oxidations of sulfoxides to sulfones[23] and is representative of the challenge of taming the oxidizing power of high-valent Mo and W catalysts to avoid overoxidation of SM to SMO_2. Despite extensive synthetic modeling literature of the DMSO reductase active site and related Mo/W enzymes,[11,24–27] the use of close structural mimics of oxotransferases featuring bis(dithiolene) ligation to Mo or W in catalytic OAT reactions of sulfides has not yet been reported. Here, we report that $[MO_2(\text{dithiolene})_2]^{2-}$ complexes (M = Mo or W, Figure 1c) catalyze oxidation of CEES with unusually high efficiency and with perfect selectivity for formation of CEESO rather

than 2-chloroethyl ethyl sulfone ($CEESO_2$). These catalysts operate at ambient conditions without requiring inert atmosphere, are robust enough for repeated use, and employ a green oxidant, H_2O_2. Thus, these bioinspired catalysts represent excellent candidates for SM detoxification technology development.

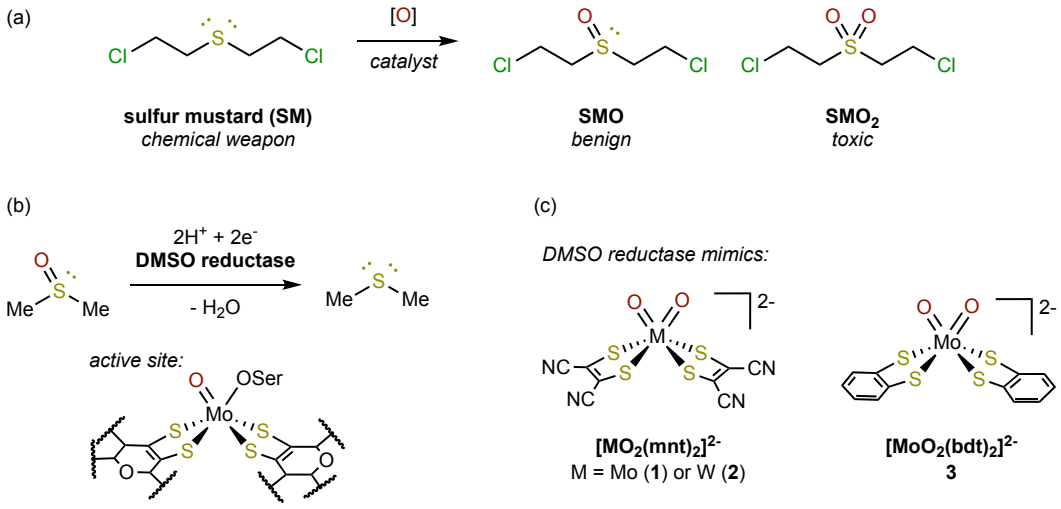
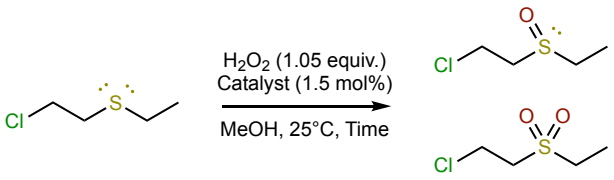


Figure 1. (a) Detoxification of sulfur mustard gas, (b) dimethyl sulfoxide reduction by Mo-dependent DMSO reductase, (c) DMSO reductase mimics used in this study.

Table 1. CEES oxidation with bio-inspired Mo and W dithiolene catalysts.[a]



Entry	Catalyst	Time	Conversion (%)[b]	Sulfoxide selectivity (%)[c]
1	$[MoO_2(mnt)_2]^{2-}$ (**1**)	5 min	100	100
2	$[MoO_2(mnt)_2]^{2-}$ (**1**)	1 h	100	94
3	None	1 h	3	100
4[d]	$[WO_2(mnt)_2]^{2-}$ (**2**)	1 h	0	n/a
5	$[WO_2(mnt)_2]^{2-}$ (**2**)	1 h	100	100
6	$[MoO_2(bdt)_2]^{2-}$ (**3**)	1 h	100	100
7	$[WO_2(mnt)_2]^{2-}$ (**2**)	15 min	100	100
8	$[MoO_2(bdt)_2]^{2-}$ (**3**)	5 min	100	100

[a]Reaction conditions: CEES (2.0 mmol), H_2O_2 (2.1 mmol), Catalyst (1.5 mol%), MeOH (6 mL), room temperature. [b]Determined by GC using mesitylene as an internal standard. [c]Determined by GC. Sulfoxide selectivity = [%sulfoxide / (%sulfoxide + %sulfone)]*100. [d]O_2(g) in place of H_2O_2.

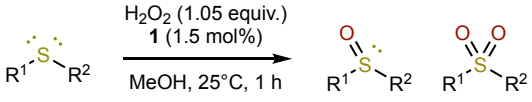
We began our investigation by attempting oxidation of a methanol solution of CEES with aqueous H_2O_2 (1.05 equiv.) at ambient temperature in the presence of $[MoO_2(mnt)_2][N^nBu_4]_2$ (**1**, mnt = maleonitriledithiolate)[28,29] as a catalyst at 1.5 mol% loading. Although only CEESO was observed at 5 min reaction time, some $CEESO_2$ was observed after 1 h (Table 1, entries 1-2). A control experiment without the catalyst showed only trace CEES conversion (entry 3), and no conversion was observed using molecular oxygen in place of H_2O_2 (entry 4). Under the same conditions, changing the catalyst to either $[WO_2(mnt)_2][N^nBu_4]_2$ (**2**)[30] or $[MoO_2(bdt)_2][NEt_4]_2$ (**3**, bdt = 1,2-benzenedithiolate)[25,31,32] resulted in quantitative conversion of CEES to CEESO without any overoxidation to $CEESO_2$ (entries 5-6). Both catalysts **2** and **3** were found to be extremely active (Figure S31), showing complete consumption of CEES within 15 and 5 min, respectively (entries 7-8). These and all subsequent catalytic trials with **1** and **2** were performed on the benchtop without protection from room atmosphere, whereas **3** required an inert N_2 atmosphere. Use of methanol solvent is critical,[33,34] as experiments in other solvents (e.g., CH_3CN or DMF) resulted in slightly lower sulfoxide selectivity. The oxygen-ligated catalyst, $MoO_2(acac)_2$ (acac = acetylacetonate), was found to be highly active but formed some sulfone initially, with sulfoxide selectivity further degrading as the reaction mixture was allowed to sit for longer than 1 h. Therefore, sulfur ligation to the catalytic metal site is critical to control selectivity.

Investigations with other thioether substrates were performed with catalysts **1** and **2**. Whereas **2** consistently gave perfect sulfoxide selectivity (see Supporting Information), sulfone products were observed in some cases for **1** (Table 2). Like CEES (entry 1), diethyl sulfide was oxidized completely within 1 h and showed slightly better sulfoxide selectivity (entry 2). Interestingly, a control experiment with Et_2S in the absence of catalyst resulted in formation of 2-(ethylthio)ethan-1-ol, a product that was completely suppressed in the catalytic trials (Figures S1-S3). For thioanisole, quantitative conversion was observed with 94%

selectivity for methyl phenyl sulfoxide (entry 3). Diphenyl sulfide was found to undergo oxidation sluggishly under these conditions, with 13% sulfide remaining after 1 h (entry 4) and complete conversion requiring 4 h.

Because allylic sulfoxides are valuable building blocks that participate in the Mislow-Evans rearrangement,[35] we probed the compatibility of the bioinspired catalysts with allylic sulfides. Phenyl allyl sulfide was efficiently oxidized under the catalytic conditions to phenyl allyl sulfoxide (Table 2, entry 5). Surprisingly, allyl ethyl sulfide converted to thiane 1-oxide under these conditions (entry 6). Unlike the background reactivity observed for Et_2S, here only trace reactivity was observed in the absence of catalyst (Figures S18-S20). Probing the mechanism and generality of this unusual cyclization reaction (Scheme 1) will be subjects of future studies in our laboratory.

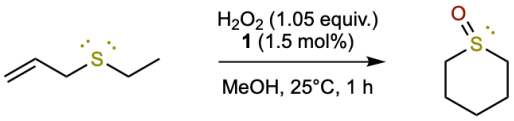
Table 2. Oxidation of other thioethers.[a]



Entry	R^1	R^2	Conversion (%)[b]	Sulfoxide selectivity (%)[c]
1	CH_2CH_2Cl	Et	100	94
2	Et	Et	100	100
3	Ph	Me	100	94
4	Ph	Ph	87	98
5	Ph	$CH_2CH{=}CH_2$	95	98
6	CH_3CH_2	$CH_2CH{=}CH_2$	100	100[d]

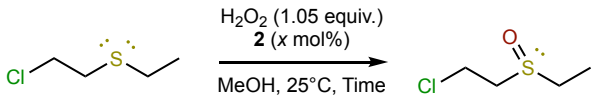
[a]Reaction conditions: Thioether (2.0 mmol), H_2O_2 (2.1 mmol), **1** (1.5 mol%), MeOH (6 mL), room temperature, 1 h. [b]Determined by GC using mesitylene as an internal standard. [c]Determined by GC. Sulfoxide selectivity = [%sulfoxide / (%sulfoxide + %sulfone)]*100. [d]Thiane 1-oxide was the major product, see Scheme 1.

Scheme 1. Catalytic oxidation and cyclization of allyl ethyl sulfide.



Next, we experimented with oxidation of CEES using different catalyst loadings of **2** (Table 3). For catalyst loadings ranging from 3.0 mol% to 0.15 mol%, quantitative oxidation of CEES with perfect CEESO selectivity was achieved within 15 min (entries 1-4). Good catalytic activity was maintained even with 0.015 mol% catalyst loading, but completion of the reaction required 90 min in this case (entry 5). Overall, these experiments indicate that catalyst **2** can achieve turnover numbers of >6.6 x 10^3 and turnover frequencies of >4.4 x 10^3 h^{-1}, making this system competitive with leading POM catalysts[36–38] in terms of CEES oxidation efficiency while still avoiding overoxidation.

Table 3. CEES oxidation with different catalyst loadings.[a]



Entry	Catalyst loading (mol%)	Time (min)[b]
1	3.0	15
2	1.5	15
3	0.75	15
4	0.15	15
5	0.015	90

[a]Reaction conditions: CEES (2.0 mmol), H_2O_2 (2.1 mmol), **2** (*x* mol%), MeOH (6 mL), room temperature, 15 min. [b]Time to reach quantitative conversion of CEES as determined by GC using mesitylene as an internal standard. No $CEESO_2$ sulfone was observed in any of the trials.

We also conducted experiments to establish catalyst reusability. Using 1.5 mol% catalyst loading of **2**, results were monitored over 4 consecutive injections of CEES into the same reaction mixture. For all 4 injections, full conversion of CEES to CEESO was observed (Figure 2). Given that no loss of catalytic activity was evident, it can be concluded that **2** is sufficiently robust for repeated uses.

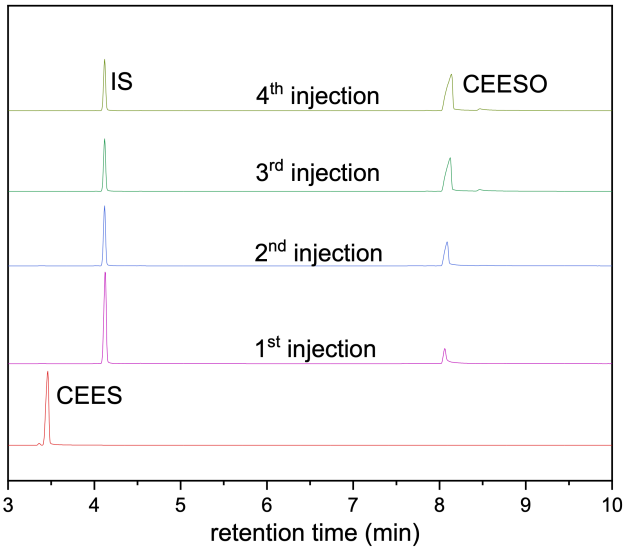


Figure 2. Reusability of catalyst **2** (1.5 mol%) over 4 consecutive CEES injections into the same reaction mixture (GC traces with mesitylene internal standard).

Based on the accepted catalytic mechanisms for the DMSO reductase enzyme family,[10–12,15] one might expect the

bioinspired Mo and W dithiolene catalysts to employ the dioxo intermediate, $[MO_2(dithiolene)_2]^{2-}$, as the active oxidant to convert CEES to CEESO, producing $[MO(dithiolene)_2]^{2-}$ as the immediate byproduct that would undergo reoxidation by H_2O_2. However, literature precedents with synthetic model complexes indicate either that $[MO_2(dithiolene)_2]^{2-}$ intermediates should react sluggishly with thioethers[25] or that the microscopic reverse, sulfoxide reduction by $[MO(dithiolene)_2]^{2-}$, should be thermodynamically favored.[26] In accord with the previous literature, no OAT reactivity was observed in an attempted stoichiometric reaction between CEES and **2**. Additionally, our computational modeling using DFT calculations indicates that OAT from $[MO_2(mnt)_2]^{2-}$ to Me_2S to produce $[MO(mnt)_2]^{2-}$ and DMSO is thermodynamically unfavorable with reaction free energies of ΔG = +6 and +26 kcal mol^{-1} for M = Mo (**1**) and W (**2**), respectively (Figure S34).

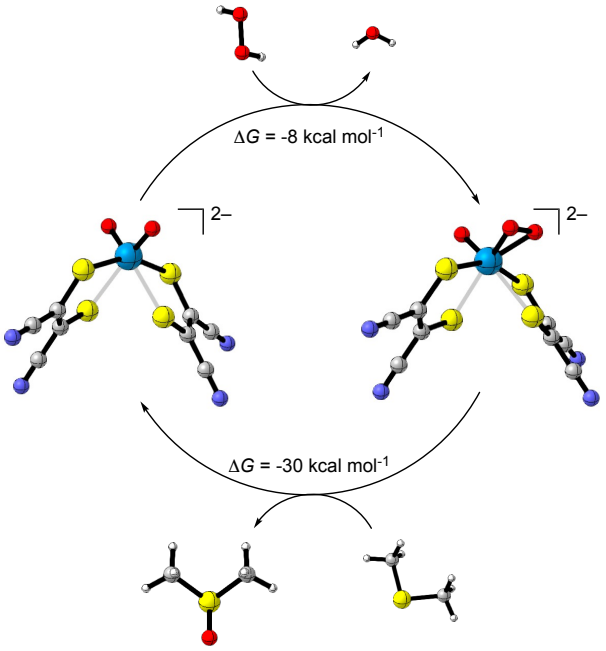


Figure 3. Proposed mechanism for Me_2S oxidation by $[MO_2(mnt)_2]^{2-}$ involving an oxo/η^2-peroxo intermediate as the active oxidant. Optimized structures and reaction free energies are shown for M = W; nearly identical structures and energetics were calculated for M = Mo. Calculations were conducted at the M062X-D3//def2TZVPP/6-31+G** level of DFT with implicit methanol solvation (SMD model).

An alternative mechanism that has been proposed for Mo-promoted OAT in some cases involves further oxidation of the dioxo intermediate to an oxo/η^2-peroxo species that serves as the active oxidant generated *in situ*.[22,39,40] In agreement with this peroxo mechanism, OAT from $[M(O)(\eta^2\text{-}O_2)(mnt)_2]^{2-}$ to Me_2S to produce $[MO_2(mnt)_2]^{2-}$ and DMSO was calculated to be thermodynamically favorable with reaction free energies of ΔG = -30 kcal mol^{-1} for both M = Mo (**1**) and W (**2**). Reoxidations of the dioxo intermediates with H_2O_2 to regenerate the oxo/η^2-peroxo intermediates were also calculated to be thermodynamically favorable (ΔG = -8 kcal mol^{-1} for both cases), thus providing substantial support for this proposed catalytic mechanism (Figure 3). The calculated O-O bond distances for the η^2-peroxo ligands (M = Mo: 1.407 Å; M = W: 1.428 Å) are consistent with the $[O_2]^{2-}$ formulation.

In conclusion, Mo and W catalysts with bioinspired bis(dithiolene) ligation were found to be unusually efficient and selective catalysts for oxidation of the sulfur mustard analogue, CEES, to its corresponding sulfoxide using a green oxidant, aqueous H_2O_2. A mechanistic investigation indicated that catalysis likely proceeds through an oxo/η^2-peroxo intermediate as the active oxidant rather than the dioxo form proposed for biological oxygen atom transfer processes. Because sulfur mustard undergoes oxidation ~5 times more slowly than CEES,[2] it is critical to identify detoxification catalysts in research settings that exhibit extremely high activity along with good selectivity. The results presented in this study indicate that bioinspired Mo and W catalysts represent promising candidates with which to develop sulfur mustard detoxification technologies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental methods & supporting data (PDF)

Computational output (XLSX)

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

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