

MOLYBDATE/PEROXIDE OXIDATION OF MUSTARD IN MICROEMULSIONS

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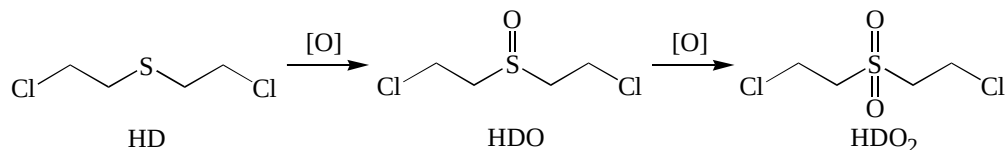
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Environmentally friendly and non-corrosive methods to decontaminate the blister agent mustard (HD), bis(2-chloroethyl) sulfide, are currently being developed. HD may be rendered non-vesicant by oxidation to the corresponding sulfoxide. Results will be presented for the use of the mildly-basic molybdate/peroxide oxidant system to achieve this transformation. Reactions are performed in microemulsions to enable the dissolution of oily, water-insoluble mustard.

INTRODUCTION

Environmentally friendly decontamination systems are needed to replace current, toxic and corrosive decontaminants such as hypochlorite and DS2.¹ Peroxides are a desirable reactant for decontamination owing to their non-toxic, non-corrosive nature. Indeed, hydrogen peroxide is widely used in so-called “Green” industrial processes,² replacing historical hypochlorite-based processes which are environmentally harmful.³ Mustard (HD) may be oxidized to the non-vesicant sulfoxide (HDO),⁴ but care must be taken to avoid further oxidation to the vesicant sulfone (HDO₂).⁴ This reaction is shown in Scheme 1 where [O] represents an active oxidant.

SCHEME 1



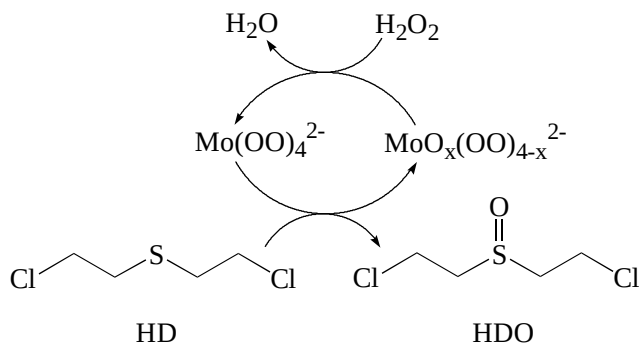
The recently developed peroxide-based “DECON GREEN”^{5a} decontaminant accomplishes the selective oxidation of HD to HDO by using a hydrogen carbonate activator.^{5b,c,6} However, the reaction of DECON GREEN with HD remains slow compared to the V and G agent reactions which are nearly

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instantaneous and involve nucleophilic attack by the peroxy anion.^{5a,b} Other potential peroxide activators are being explored to hasten the oxidation of HD.

Recently, Aubry and Bouttemy⁷ demonstrated the rapid oxidation of a variety of organic compounds by using the peroxide/molybdate system in a water-in-oil (w/o) microemulsion. In this system, molybdate is believed to act as a peroxide activator by generating singlet oxygen (¹O₂) which diffuses out of the microemulsion and reacts with substrates in the bulk organic solvent, although the role of peroxo species was not excluded.⁸ ¹O₂ is reportedly generated from the triperoxomolybdate MoO(OO)₃²⁻, and this species predominates at ratios of [H₂O₂]/[MoO₄²⁻] of four or less.⁸ At higher ratios, the predominant formation of the more stable tetraperoxomolybdate Mo(OO)₄²⁻ decreases ¹O₂ production⁸ and the associated peroxide decomposition. Besides the problem of peroxide decomposition, avoiding ¹O₂ formation is further desirable as this species oxidizes sulfides non-selectively to both sulfoxides and sulfones.⁷ Generation of HD-sulfone is to be avoided as it possesses substantial vesicant activity, similar to HD itself.⁴ Thus Mo(OO)₄²⁻ is a potentially stable and very effective reactant for the selective oxidation of HD to the non-vesicant sulfoxide. This reaction is shown in Scheme 2. In this paper the oxidation of HD in molybdate/peroxide microemulsions will be described with conditions such that the tetraperoxomolybdate species is dominant.

SCHEME 2



EXPERIMENTAL

K₂MoO₄, n-BuOH, CH₂Cl₂, sodium dodecyl sulfate (SDS, an anionic surfactant), Triton X-100 (a non-ionic surfactant), i-PrOH, hexane, and 50 % H₂O₂ were all obtained from Aldrich. Microemulsions were mixed by first adding the solid ingredients (e.g., SDS and/or K₂MoO₄), followed by cosurfactant (e.g., n-BuOH or i-PrOH), surfactant, organic solvent, and finally 50 % H₂O₂ to a 3 mL vial. The vial was capped and vortex mixed briefly. The microemulsions spontaneously formed and generation of Mo(OO)₄²⁻ was immediately apparent from the amber color of the potassium salt of this species. Reactions were initiated by adding 9 μ L neat liquid HD to 0.75 mL of the decon solution contained in a 5 mm NMR tube. The concentration of HD was 0.1 M. The tube was capped and shaken to assure complete dissolution of HD. Reactions were monitored by ¹H NMR by using a Varian Unityplus 300 NMR spectrometer to obtain kinetic data.

RESULTS AND DISCUSSION

Half-lives observed for the reaction of HD in various microemulsions (ME's) are shown in Table 1. The concentration of K₂MoO₄ in each ME was 0.01 M, which was low enough in most cases to allow

measurements of the half-lives. Higher concentrations would have rendered the reactions essentially instantaneous. It should be noted that 0.1 to 0.2 M hydrogen carbonate activator (or ten to twenty times the concentration of molybdate ion) would be required to achieve similar half-lives.⁵ Thus as a peroxide activator for HD oxidation, molybdate ion is at least an order of magnitude more powerful than hydrogen carbonate ion.

TABLE 1. Half-Lives Observed for HD in Microemulsions.

ME	K ₂ MoO ₄	Surfactant	Cosurfactant	Oil Phase	50 % H ₂ O ₂	t _{1/2}
		SDS ^a	n-BuOH ^a	CH ₂ Cl ₂ ^a		
1	2.4 mg	99 mg	0.198 g	0.403 g	0.354 g	1.0 min
2	2.4 mg	96 mg	0.193 g	0.501 g	0.248 g	1.4 min
3	2.4 mg	86 mg	0.173 g	0.602 g	0.165 g	1.8 min
4	2.4 mg	76 mg	0.146 g	0.698 g	0.098 g	1.2 min
		Triton X-100	i-PrOH	Hexane		
5	2.5 mg	0.214 g	0.395 g	0.0786 g	0.300 g	< 30 sec
		Triton X-100	Solvent			
6	2.6 mg	0.224 g	0.695 g		0.307 g	< 30 sec ^b
7	2.4 mg	0.224 g	0.654 g		0.295 g	1.1 min
8	2.4 mg	0.224 g	0.713 g		0.236 g	53 sec
9	2.4 mg	0.224 g	0.773 g		0.177 g	1.3 min
10	2.4 mg	0.224 g	0.832 g		0.118 g	1.8 min

^aAdapted from Aubry and Bouttemy.⁷ ^bt_{1/2} = 47 min for HDO → HDO₂.

Water-in-oil (w/o) ME's #1-4 were adapted from the work of Aubry and Bouttemy,⁷ and these contain the constituents typical of such ME's: SDS (surfactant), n-BuOH (cosurfactant), CH₂Cl₂ (oil phase), and 50 % H₂O₂ (aqueous phase). Although HD dissolution and oxidation proceeded well in these ME's, they contain toxic CH₂Cl₂ and are thus environmentally unacceptable. Additional ME's were formulated using more environmentally friendly ingredients, which also yielded good HD dissolution/reaction. For example ME #5, composed of Triton X-100 (surfactant), i-PrOH (cosurfactant), hexane (oil phase) and 50 % H₂O₂ (aqueous phase), rapidly dissolved and oxidized HD with a half-life too fast to measure by NMR (t_{1/2} < 30 sec). As a further step to meet "Green" criteria and to minimize the number of necessary components, an additional series of "ME's" were examined using only Triton X-100, 50 % H₂O₂, and a non-toxic industrial solvent currently being utilized in DECON GREEN formulations. The industrial solvent may be functioning merely as a cosolvent rather than a true cosurfactant. The resulting solutions are not true ME's as these streamlined mixtures lack a conventional cosurfactant and oil phase and can be regarded as modified micelles. However, HD is readily dissolved; and thus briefly becomes the "oil phase" prior to reacting in these ME's. It is important to note that compared to the toxic series of ME's #1-4, no loss in HD reactivity is observed using the "Green" ingredients of ME's #6-10. For ME #6, the secondary oxidation of HDO to HDO₂ was monitored by ¹H and ¹³C NMR, with a half-life of 47 min. Thus, fortunately, the undesired secondary oxidation of HDO is about two orders of magnitude slower than primary oxidation of HD.

CONCLUSIONS

As a peroxide activator molybdate ion affords at least an order of magnitude increase in the rate of HD oxidation compared to hydrogen carbonate ion, rendering the reaction nearly instantaneous. Secondary oxidation to the sulfone does occur, but this reaction is slower by about two orders of magnitude. The molybdate/peroxide reactive system functions in a variety of microemulsions, including those composed of non-toxic ingredients. These latter formulations in which tetraperoxomolybdate is the major peroxy species would be suitable for decontamination of HD and other toxic sulfides in the environment.

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