Direct Chemical Oxidation: Applications to Demilitarization and Decontamination

John F. Cooper
Bryan Balazs
Patricia Lewis

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John F. Cooper, Bryan Balazs and Patricia Lewis
Chemistry and Materials Science Directorate, L-352
Lawrence Livermore National Laboratory, 7000 East Avenue, PO Box 808 Livermore CA 94550
Tel. (510) 423-6649; Fax 422-0049; E-mail Cooper3@LLNL.gov

Abstract

The applicability of using aqueous solutions of sodium peroxydisulfate in the destruction of mustard gas surrogates has been demonstrated. This technique, known as Direct Chemical Oxidation (DCO), resulted in oxidative destruction of these surrogates, and a refinement was added to prevent the formation of slow-to-oxidize intermediates. Specifically, it was shown that "one-armed mustard" gas could be hydrolyzed to thiodiethanol and free chloride ion, and this species could then be partially oxidized to either the sulfoxide or sulfone depending on oxidant stoichiometry. Hydrolysis was accomplished in a mild basic solution at ambient temperature over a number of hours; oxidation was carried out at 90 °C using peroxydisulfate solutions. Partial oxidation of thiodiethanol in the presence of chloride under basic conditions resulted in a substantially pure mixture of the corresponding sulfone and sulfoxide, with no formation of chlorine gas. Analogous experiments in acid solutions produced a more complex mix of products and some oxidant was consumed in the evolution of chlorine. Complete destruction of the surrogates (to ppm level of detection) was achieved in either acid or base solution with less than a 7-fold excess of oxidant.

Introduction

There is a wide-spread military and civilian interest in developing non-thermal processes for the destruction of chemical warfare agents--either in the form of bulk materials, as components of munitions, or as contaminants in soil or equipment. Direct Chemical Oxidation is an aqueous-based low-temperature process which employs the peroxydisulfate ion ($S_2O_8^{2-}$) to destroy by oxidation any organic material to CO_2 , water and inorganic salts. This oxidant has a standard potential of nearly 2.1 V-- exceeded only by fluorine and its derivatives. Previously, we have shown that acidified peroxydisulfate rapidly destroys surrogates for chemical warfare agents such as methyl phosphonic acid (a surrogate for G-agents), DIMP and triethyl-amine (surrogates for VX destruction by peroxidisulfate oxidation) and thiodiethanol $[(OHH_2CCH_2)_2-S]$ and dimethylsulfoxide $[(CH_3)_2-SO]$, non-toxic surrogates for hydrolyzed Mustard gas, $[ClH_2C-CH_2)_2-S]$.¹

In the case of mustard gas is the direct chemical oxidation process complicated by two unique factors: (1) free chloride competes with organic material for oxidation and (2) mustard tends to partially hydrolyze in water forming a cyclic sulfonium cation,

which may react with organic sulfides (residual or hydrolyzed mustard) to form more stable dimers, trimers or even larger aggregates². The cation and aggregates are more slowly oxidized and may condense into stable micelles.

We hope to develop a method for rapid and selective oxidation of the sulfur to form either mustard sulfoxide $(\text{ClH}_2\text{C}-\text{CH}_2)_2\text{-SO}$ or mustard sulfone $(\text{ClH}_2\text{C}-\text{CH}_2)_2\text{-SO}_2$. In either case, the oxidized mustard is prevented from formation of cyclic sulfonium cation by steric hindrance of the oxygen groups.

Our laboratory policy does not allow the handling of mustard gas on site. In order to study this partial oxidation reaction, we tested the surrogate for mustard, thiodiethanol plus additions of two free chloride ions per molecule of thiodiethanol. In addition, we tested destruction of the same surrogates in base (pH=14) solution, in which the chlorine free-radical intermediate formed during the oxidation of Cl^- to Cl_2 is hindered by a shift in the hydroxyl/chlorine radical balance³: $\text{Cl}^\bullet + \text{OH}^- = \text{Cl}^- + \text{OH}^\bullet$.

The overall oxidation of thiodiethanol is as follows:

Thus 28 equivalents are required to oxidize thiodiethanol to carbon dioxide and sulfate, and two more to oxidize the 2Cl^- to Cl_2 . Thus a hundred-fold molar excess of oxidant over TDE is a 7-fold excess over the stoichiometric equivalent in the balanced reaction.

Experimental Procedure and Results

All experiments were done in 500 ml vessels at $90 \pm 5^\circ\text{C}$ with 0.01 moles of thiodiethanol (TDE), 28 equiv/mol; with and without NaCl (0.02 moles); with additions of solid sodium peroxydisulfate, and sulfuric acid or sodium hydroxide (for pH=1 or 14, respectively). The oxidant was added in two stages: the first stage was treated with a deficiency of oxidant (0.14, 0.28, and 0.43 equiv-oxidant/equivalent thiodiethanol); the second stage was treated with a 7-fold excess of oxidant, based on equivalence (i.e., a 100x excess based on moles). In acidic solution, 50% of the chloride was oxidized to chlorine; in base, no chlorine was detected (<1%).

By GC/MS analysis (Table 2), the pre-oxidation step in acid showed numerous cyclic species in addition to sulfone and sulfoxide products, while basic solutions showed only the sulfoxide and sulfone (predominate species) for 0.14- and 0.28 oxidant ratios. GC/MS analysis shows that in general, basic conditions were better for the formation of a sulfone or sulfoxide. Numerous other products were formed in acid. Generally, the sulfone or sulfoxide formed dehydrated to form a cyclic compound with an oxygen and sulfur atom separated by two carbon (-CH₂-) groups between them on each side of the ring.

Finally, the basic solutions showed essentially complete carbon oxidation after addition of 7-fold excess oxidant: roughly 1000 fold reduction in initial carbon content to the limit of TOC detection (1 ppm).

In separate experiments on a smaller scale, we sought to determine whether we could produce our surrogate hydrolyzed mustard solutions (i.e., a mixture of thiodiethanol and 2 moles of chloride) by hydrolysis in the presence of basic solutions. Since mustard gas could not be handled at LLNL, we conducted hydrolysis experiments with chloroethyl-ethyl-sulfide (CEES, or "one-armed mustard"). Two (2) microliters of CEES were treated with 100 microliters of 0.5M NaOH with agitation overnight at ambient temperature. The samples were extracted with

methylene chloride, and analyzed by GC/MS. This analysis showed that about 70% of the original CEES had vanished (evidently by hydrolysis).

Conclusions

In conclusion, it appears that partial oxidation of the TDE surrogate to sulfoxide and sulfone is possible in both acid and basic solutions, and that these intermediates are fully oxidized by subsequent treatment with 7-fold stoichiometric excess of oxidant. The basic solution is favored because the chloride remains unoxidized and the parallel products were not found.

The surrogate appears to be well chosen, as simple hydrolysis of mustard gas to soluble products is known to occur and the hydrolysis of CEES was verified by this work. Further work is needed to test the process on mustard gas at a surety laboratory (not at LLNL), which is capable of handling mustard and related agents.

Table 1. Partial oxidation of thiodiethanol in the presence of free chloride ion. Note: X = moles of TDE = 0.01 mols.

Sample #	media	moles Cl ⁻	moles oxidant in stage 1	moles CO ₂ obs in stage 1	moles CO ₂ obs. in stage 2*	moles "Cl ₂ " obs. total
3	acid	0	2X	0	2.7X	0.00043
7	acid	0.02	4X	0	1.9X	0.0051
4	acid	0	4X	0	2.3X	0.0005
8	acid	0 02	6X	0 08X	2.0X	0.0047
1	base	0	2X	0	3.0	0
5	base	0.02	4X	0	2.3	0 0004
2	base	0	4X	0	3.4	0
6	base	0 02	6X	0	2 4	0.0004

*4X would correspond to quantitative conversion of thiodiethanol to carbon dioxide.

Table 2. GC/MS analysis of products of partial oxidation and TOC analysis of products of full oxidation.

Sample #	media	moles Cl ⁻	moles oxidant in stage 1	GC/MS ¹ sulfoxide	GC/MS ¹ sulfone	TOC final (ppm)
3	acid	0	2X	28.3	17 3	
7	acid	0.02	4X	2.85	35.4	5
4	acid	0	4X	0	19.8	19
8	acid	0 02	6X	0	12.0	
1	base	0	2X	367	535	2
5	base	0 02	4X	4 63	180	1 ²
2	base	0	4X	52.6	395	2
6	base	0.02	6X	0	0	

¹Integral area under GC/MS peaks, divided by 100,000

²TOC of intermediate product after stage one oxidation gave 759 ppm total carbon.

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References

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