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The Use of Methyltricaprylylammonium Chloride as a Phase Transfer Catalyst for the Destruction of Methyl Bromide in Air Streams

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Abstract:

Methyl bromide has been used for decades as a pesticide, primarily as an insecticide. It has also been recently advocated as an excellent agent for the destruction of anthrax spores via fumigation. Related to this use is the need to efficiently destroy methyl bromide safely, once fumigation is complete. This paper describes the selection of a nucleophile for instantaneous decomposition of methyl bromide to destroy methyl bromide in a fumigation vent air stream from an office trailer. Our preliminary data showed that sulfide anion dissolved in water is an exceptionally effective nucleophile for the purpose of CH_3Br decomposition. We show data proving the effectiveness of the sodium sulfide aqueous solution accompanied by methyltricaprylylammonium chloride as a phase transfer catalyst for scrubbing methyl bromide present in air.

Introduction

Methyl bromide has been used successfully as an excellent pesticide to destroy various soil-based pests before planting and to protect imports and exports from unwanted invasive species. It is very efficient, creates no resistance, leaves no residue, and kills all life stages of insect pests. Additionally, it has been shown that CH_3Br can be employed in decontamination of anthrax bacteria (*Bacillus anthracis*) and its spore.[1] Recently, it has been advanced that methyl bromide is superior to chlorine dioxide in destroying the anthrax spores.[2] Unfortunately, methyl bromide is highly toxic to humans and, moreover, is known to destroy the ozone layer. Thus, it was added to the Montreal Protocol list of ozone depleters and has been banned for many applications in developed countries. However, methyl bromide has not been banned completely, and its continued use for soil applications under the Montreal Critical Use Exemption (CUE) program is a source of controversy. Methyl bromide is also used for Quarantine and Preshipment (QPS) applications (imports and exports). Continued worldwide use of methyl bromide is on the order of 60 million lbs/y, and its use is increasing for fumigation of solid wood packaging. Thus, the instantaneous chemical destruction of methyl bromide fills a very important need for applications in agriculture, combating terrorism, and green chemistry since it can be destroyed after use without harming the environment.

This paper presents our results in collecting and decomposing methyl bromide from a fumigation sample stream that was used to demonstrate the ability of methyl bromide to kill anthrax bacteria surrogate spores. For destruction of anthrax spores, the most pressing issue is the rapid removal of the bacteria, followed by as rapid a destruction of the methyl bromide as possible. In other circumstances when methyl bromide is used in fumigation of various produce and wood, we have employed a nonhazardous system that takes advantage of thiosulfate anion as a nucleophile.[3] However, it should be pointed out that thiosulfate reaction rates are relatively low. Additionally, it has been proposed to adsorb methyl bromide on activated carbon and decompose it later with an aqueous thiosulfate solution.[4]

Table 1. **Screen of nucleophiles with allyl chloride.**

nucleophile	relative rate
thiosulfate	slow
thioacetate	fast
2-mercaptobenzothiazole	fast
3-mercaptopropionate	slow
cyanide	slow
sulfide	very fast
hydrogen sulfide (HS^-)	very fast

In light of our previous work in the area of phase transfer catalysis applied to the formation of saleable products or destruction of hazardous products present in aqueous waste streams,[5,6] scrubbing methyl bromide from the gas phase with an aqueous solution containing an appropriate nucleophile and a phase transfer catalyst was a logical choice. The crucial question was which nucleophile dissolved in the aqueous phase would be the most effective, i.e. the most rapid. Cyanide was considered and is known to be effective when combined with Aliquat 336 (as a PTC catalyst), in scrubbing various alkyl halides; nevertheless, the obvious drawbacks to the commercial use of cyanide suggested further inquiry.[7] However, more recent experiments have demonstrated that sulfur-containing nucleophiles were particularly fast in replacing bromide with sulfide and thus destroying methyl bromide.

During methyl bromide fumigations of anthrax spores (or surrogates) and imports and exports, a major economic process issue is the large volumes of air that are required to turn over the initial fumigation air volume. While we decided to maximize the area of contact between the gaseous phase and the liquid phases, we expected that the rate-determining step would be the reaction in the water phase and not the mass transfer of

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Table 2. **Rate of destruction of methyl bromide.**

run time h	sample no.[a]	flow rate cc/min	trailer loading oz/ft^3	trailer loading[b] ppm	sample reading ppm	actual ppm	% removed	comments
0.0	na	170	320	82560	na	na	na	start MeBr feed
0.3	1	185	320	82560	30	7.5	99.991	
0.8	2	170	320	82560	15	3.8	99.995	
1.3	3	175	314	81012	13	3.3	99.996	
1.8	4	250	310	79980	10	2.5	99.997	
3.1	6	250	284	73272	8	2.0	99.997	
3.4	7	250	284	73272	7	1.8	99.998	
3.7	8	250	284	73272	8	2.0	99.997	
4.0	9	250	284	73272	8	2.0	99.997	
4.8	10	250	284	73272	50	12.5	99.983	
					ave	4.1	99.995	

[a] All samples used four pumps from Kitagawa Tube Syringe Pumps, sample data is divided by 4 per instructions. [b] Trailer loading is methyl bromide concentration taken from the average of two readings.

methyl bromide to the aqueous phase. Thus, the selection of a fast-reacting nucleophile was a critical design parameter, and this led to a series of experiments to select the most effective one. As models for methyl bromide, alkyl halides were chosen because they are not gases at ambient temperature and pressure and react in nucleophilic reactions at rates that are comparable to those of methyl halides.[8] Therefore, allyl bromide was selected as a substitute for methyl bromide in the preliminary experiments.

The experimental design consisted of an aqueous solution of the selected nucleophile to which the phase transfer catalyst, Adogen 464, was added. 3-Methylanisole was added as an internal standard, and finally allyl bromide dissolved in butyl phenyl ether was introduced. Samples of the organic phase were taken after 0, 2.0, 6.0, 13.5, and 25 min after the addition of allyl bromide and were then analyzed by gas chromatography (GC). Since some products are water soluble and more than one product could be formed, the formation of the product(s) was difficult to observe via GC of the organic phase. Therefore, the disappearance of the allyl bromide peak in the organic phase was measured as the indication of the reaction rate. The results were as follows: thiosulfate solution required more than 25 min for complete reaction, and thiocyanate required approximately 25 min. Surprisingly, the sulfide system showed 100% completion after 2 min, and the reaction time was probably even shorter. It is clear that the reaction of allyl bromide with the sulfide anion is significantly faster than the reaction with thiocyanate or thiosulfate and was so fast that we could not measure it accurately.

For a second screen of nucleophiles, a series of experiments was run comparing cyanide and various sulfur nucleophiles. Some reaction rates were again too fast to be measured quantitatively by GC. Instead, a parallel series of experiments with allyl chloride instead of allyl bromide was run since allyl chloride is a slower reacting electrophile. Since very small volumes of reactants were used, the results are qualitative only. All the reactions were performed at 22 °C, >10 pH (NaOH or $KHCO_3$), and with the same phase transfer catalyst (Aliquat 336 or Adogen 464, i.e., methyltricaprylylammonium chloride). The results are summarized in Table 2.

On the basis of these qualitative results, sulfide was selected as the nucleophile for the destruction of methyl bromide.

Figure 1 shows a schematic diagram of the experimental apparatus. Figure 2 shows our system scrubbing methyl bromide from a sample stream from the office trailer at the University of Florida.

The yellow upper phase consists mostly of the tetraalkylammonium salt {PTC}, and the aqueous phase containing the sulfide is at the bottom. We believe that most of the methyl bromide is dissolved in the quaternary ammonium chloride phase which acts as a phase transfer catalyst but can be also considered as an ionic liquid.[9] The sulfide ion is transferred by the PTC catalyst to the upper phase where most of the reaction takes place. Additionally, since methyl bromide solubility in water is significant (1.75 g/100 g of solution at 20 °C and 748 mm.)[10] it is likely that some alkylation also takes place in the aqueous phase. A blank experiment demonstrated that, without the phase transfer catalyst, the reaction is about 10 times slower.

To explain why sulfide reacts significantly faster than other sulfur nucleophiles we can offer the following rationale: one of the products—dimethyl sulfide—is present mainly in the ionic liquid phase. It can react further with a molecule of methyl bromide to form trimethylsulfonium bromide which can be transferred to the aqueous phase for the reaction with sulfide or methylsulfide ions as shown below:

$$\begin{aligned} &Na_2S + 2CH_3Br \rightarrow CH_3{-}S{-}CH_3 \\ &CH_3{-}S{-}CH_3 + CH_3Br \rightarrow (CH_3)_3S^+Br^- \end{aligned} \tag{1}$$

$$(CH_3)_3S^+Br^- + S^{2-} \rightarrow (CH_3)_2S + CH_3S^- + Br^- \tag{2}$$

Thus, we hypothesize that trimethyl sulfide formed in situ acts as an inverse phase transfer catalyst.[11] In order to confirm or disprove this hypothesis, further research will be necessary.

Table 1 shows the measured concentration of methyl bromide in air after passing through our system from the

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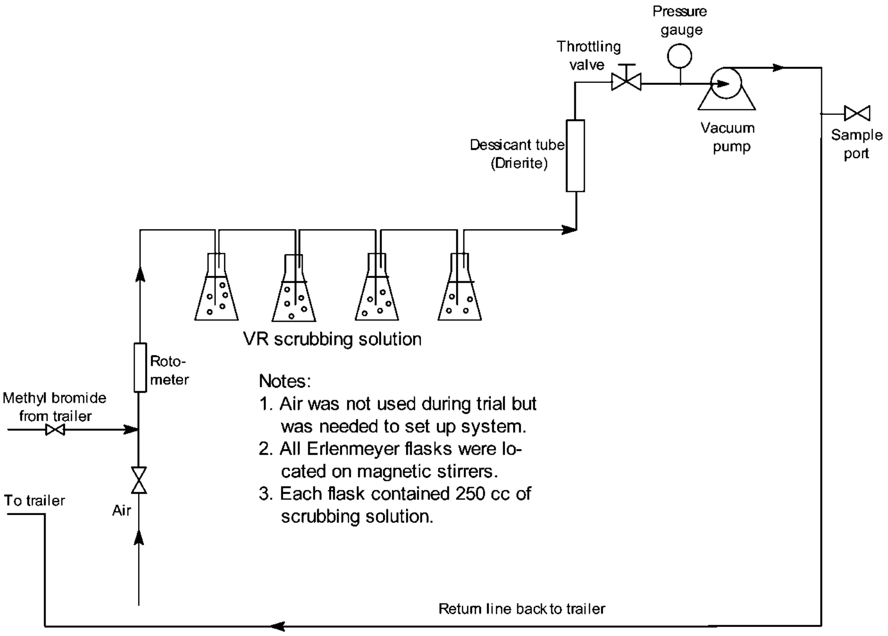

Notes:
1. Air was not used during trial but was needed to set up system.
2. All Erlenmeyer flasks were located on magnetic stirrers.
3. Each flask contained 250 cc of scrubbing solution.

Figure 1. **Experimental schematic drawing of methyl bromide sampling train.**

Figure 2. **Gas sampling apparatus used to destroy methyl bromide from a slipstream of methyl bromide.**

fumigation slip stream used to destroy anthrax surrogates at the University of Florida:

The data show that the applied method offers very high removal efficiency of methyl bromide from air streams. Since the initial concentrations of methyl bromide in the air were about 80,000 ppm (8.0%) and the exhaust concentrations were less than 10 ppm, the corresponding number for methyl bromide removal efficiency is above 99.99%. Due to the hazardous character of the spent scrubber liquor, the sulfide anion PTC system is not applicable to methyl bromide uses under commodity fumigation conditions found when fumigating produce or wood. However, when the use of methyl bromide or other gaseous alkyl halides is necessary to destroy hazardous microorganisms within contained spaces, this PTC-based method is very powerful for quickly and safely destroying the toxic gas and for protecting the ozone layer.

Experimental Section

The experimental design for allyl bromide experiments was as follows: a sample of 40 mmol of a selected nucleophile was dissolved in water (about 160 g). Next, the phase transfer catalyst, Adogen 464 (4 mmol), was added to the mixture followed by 3-methylanisole (0.30 g, internal standard). Finally, allyl bromide (20 mmol) dissolved in butyl phenyl ether (6.0 g) was introduced to the reaction mixture kept at a constant temperature (22 °C) and stirred at 600 rpm. Samples of the organic phase were taken 0, 2.0, 6.0, 13.5, and 25 min after the addition of allyl bromide and were then analyzed by GC. Since some products are water soluble and more than one product could be formed, the formation of the product(s) was difficult to observe analyzing the organic phase with GC. Therefore, the disappearance of the allyl bromide peak was measured as the indication of the reaction rate.

The scrubbing solution used during the field experiments consisted of sodium sulfide (188 g), sodium hydroxide (50 g), Aliquat 336 (115 g), and water (647 g) and was about evenly distributed in four Erlenmeyer flasks. The flasks were sealed and contained glass dispersion tubes immersed deeply into the liquid. Since the biphasic mixtures in the Erlenmeyer flasks were stirred magnetically, the dispersion tubes could not be immersed too deeply.

The methyl bromide concentration in air was measured using Kitagawa Tube Syringe Pumps.

$$CH_3Br + S^{2-} \xrightarrow[\text{catalyst}]{\text{phase transfer}} CH_3S^{-} + Br^{-} + CH_3SCH_3$$

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