VAPORIZED HYDROGEN PEROXIDE (VHP®) DECONTAMINATION OF VX, GD, AND HD*

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Vaporized Hydrogen Peroxide (VHP®) has been utilized for more than a decade to sterilize clean rooms and pharmaceutical processing equipment and, quite recently, to decontaminate anthrax-ridden buildings. VHP® is also suitable for the decontamination of VX and HD, which readily converts these agents to ethyl methylphosphonic acid and bis(2-chloroethyl) sulfoxide, respectively. However, GD is quite stable in the presence of VHP®. The simple addition of low-levels of ammonia gas renders VHP® reactive towards GD, converting it pinacolyl methylphosphonic acid. Thus, with suitable activation via ammonia gas, VHP® affords the broad-spectrum decontamination of VX, GD, and HD. Potential decontamination applications for this gaseous reactant system include: buildings, vehicle and aircraft interiors, and sensitive equipment.

INTRODUCTION

Reactive gases suitable for the decontamination of building and vehicle interiors have been sought for many years. Initially this capability was desired for military purposes; but lately it has perhaps become an even more pressing issue for homeland defense. The anthrax attacks perpetrated in the Fall of 2001 showed just how vulnerable the U.S. is to terrorist attacks involving Weapons of Mass Destruction (WMD) and, further, how difficult it is to thoroughly decontaminate buildings affected by WMD. Of course, terrorist attacks of this nature are not limited to bio agents. Just a scant six years prior to the anthrax attacks occurred the premiere unleashing of WMD on a general populace by a terrorist group: the infamous Sarin nerve gas attack on a Tokyo subway in 1995. As for military use of WMD against the U.S., U.S. troops have not suffered *enemy inflicted* chemical gas attacks since WWI.[1] Regardless of the relative urgency of military or homeland defense needs, it is clear that suitable decontamination systems for buildings and vehicle interiors are required, and reactive gases will be the quintessential component of these systems.

The decontamination of chemical agents with reactive gases has been fraught with problems. In part, the difficulty arises from the rich chemical diversity of these agents. For example, recent studies have shown that ozone, although a well-known, broad-spectrum sterilant for pathogens, does not enjoy similar wide-ranging effectiveness against chemical agents. Indeed, ozone has no effect on nerve agent GD;[2] generates a plethora of presumed toxic by-products of nerve agent VX,[2,3] yet works quite well against blister agent HD,[3] selectively oxidizing it to the non-vesicant sulfoxide.[4]

There is another, broad-spectrum gaseous sterilant that has seen increasing industrial applications: Vaporized Hydrogen Peroxide (VHP®). For over 10 years VHP® has been a standard biodecontamination technology in the pharmaceutical industry with proven efficacy against a wide variety of microorganisms,[5] and recently, VHP® was successfully employed to decontaminate a Government anthrax-contaminated

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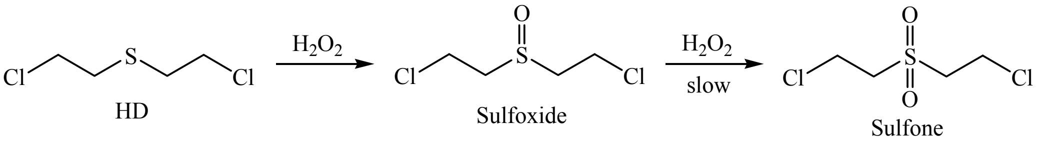
building.[6] Effective hydrogen peroxide-based liquid decontaminants such as Decon Green™ [7] have been under development for nearly ten years as well. Decon Green™ is a broad-spectrum decontaminant for anthrax, VX, GD and HD; thus proving that with proper activators, hydrogen peroxide is an effective chem/bio decontaminant. The current study examines the use of VHP®, in conjunction with a suitable gaseous activator, for the broad-spectrum decontamination of VX, GD and HD.

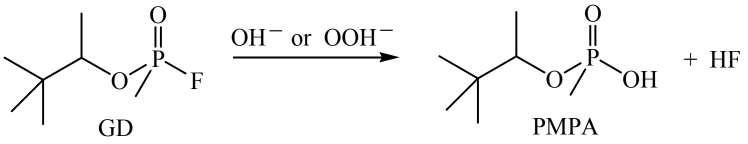
RESULTS AND DISCUSSION

Early in the development of Decon Green™ it was found that H_2O_2, mixed with a suitable organic co-solvent to permit the dissolution of water-insoluble HD, enabled the selective oxidation of HD to the non-vesicant sulfoxide (Scheme 1) with half-lives on the order of 42 minutes.[8] (Fortunately, it was found that secondary oxidation to the vesicant sulfone is orders of magnitude slower and does not appreciably occur during the desired reaction time.) However, such mixtures of H_2O_2/solvent are not as reactive for G agents and VX: GB (Scheme 2) exhibits a slow hydrolysis with a half-life of about a month, whereas VX (Scheme 3) undergoes an initial, fast hydrolysis, consuming about 50% within an hour, before the reaction abruptly halts with no further conversion for at least 16 h.[8] However, prior work had shown that both GB and VX react quite rapidly with basic peroxide,[9,10] in which the powerful peroxyanion OOH^- is generated. Indeed, the initial reaction of VX is attributed to protonation of its amine group (pK_a about 8.6[11]) with concomitant generation of OOH^-. The VX *per*hydrolysis is not sustained, however, as accumulating acidic products neutralize OOH^-. Of course, with proper buffering to maintain OOH^- levels, H_2O_2/solvent mixtures will react rapidly and completely with both VX and G agents.[8] Two important benefits of perhydrolysis (OOH^-) vs. normal, basic hydrolysis (OH^-) are that fast reactions for G agents and VX are achievable at substantially lower pH, and that perhydrolysis of VX is selective, avoiding formation of up to 20% toxic EA-2192 (Scheme 3).[12]

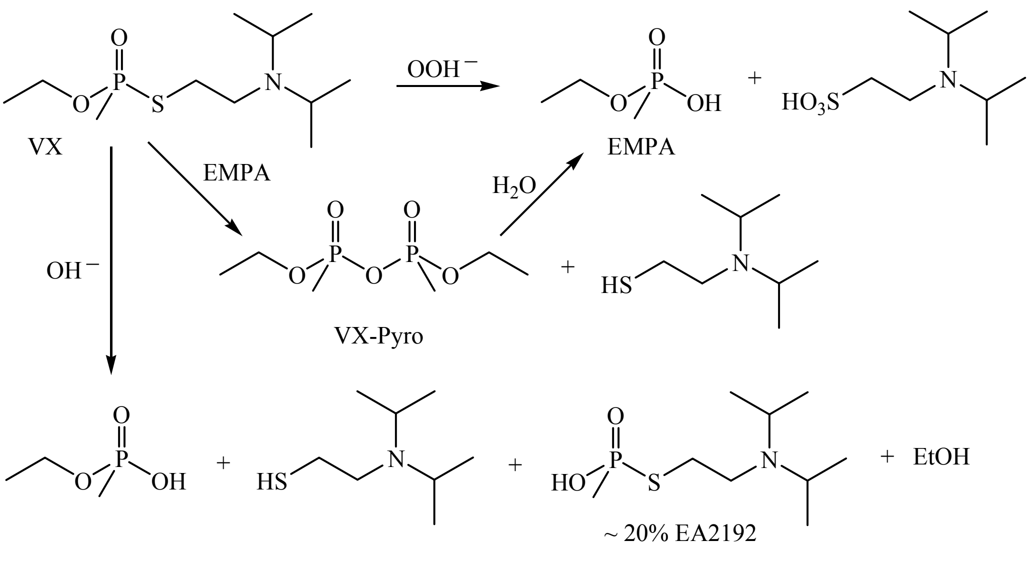
Scheme 1



Scheme 2



Scheme 3



The reaction behavior of VX, GD and HD with H_2O_2 solutions is quite similar to their behavior with VHP®.[13] As shown in Figure 1, HD is rather quickly and steadily selectively oxidized to the non-vesicant sulfoxide (Scheme 1). No vesicant sulfone is detected during this reaction time. A mass balance is not maintained for the reaction owing to competing HD evaporation, but the reaction goes to completion within 2 hours. Addition of NH_3 gas (see below) results in a slight slowing of the oxidation reaction.

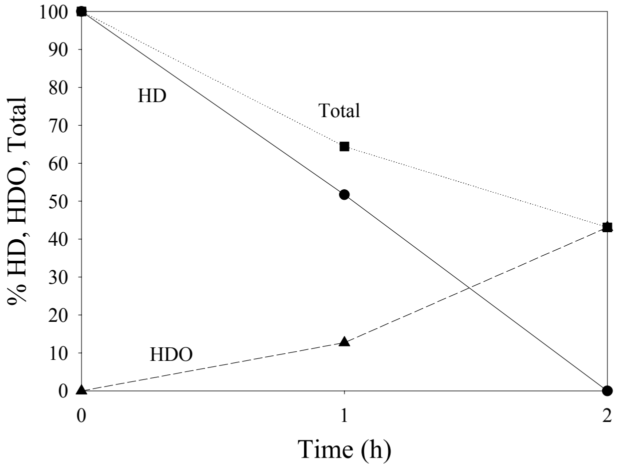


Figure 1. Reaction profile of HD with VHP®.[13]

On the left side of Figure 2 is shown the reaction profile for VX with VHP® where the expected perhydrolysis to selectively form EMPA is observed (Scheme 2). No toxic EA-2192 is formed. Some toxic VX-pyro is observed via a side reaction with EMPA (Scheme 3), but this common impurity/intermediate is unstable in the presence of water and rapidly fades as the VX is exhausted. Negligible evaporation of VX, EMPA or VX-pyro is observed over the 24 h period, thus preserving the mass balance for the reaction. Surprisingly, unlike VX perhydrolysis in the absence of buffer the VX reaction with VHP® goes to completion. The reason for the different behavior in the gas-phase reaction is not clear. However, as shown on the right side of Figure 2 introducing a small amount of basic ammonia (NH_3) gas into the VHP® stream dramatically hastens the reaction of VX which goes to completion in less than 6 hours. Thus, the basicity of NH_3 is effective for enhancing the reaction of VX with VHP®.

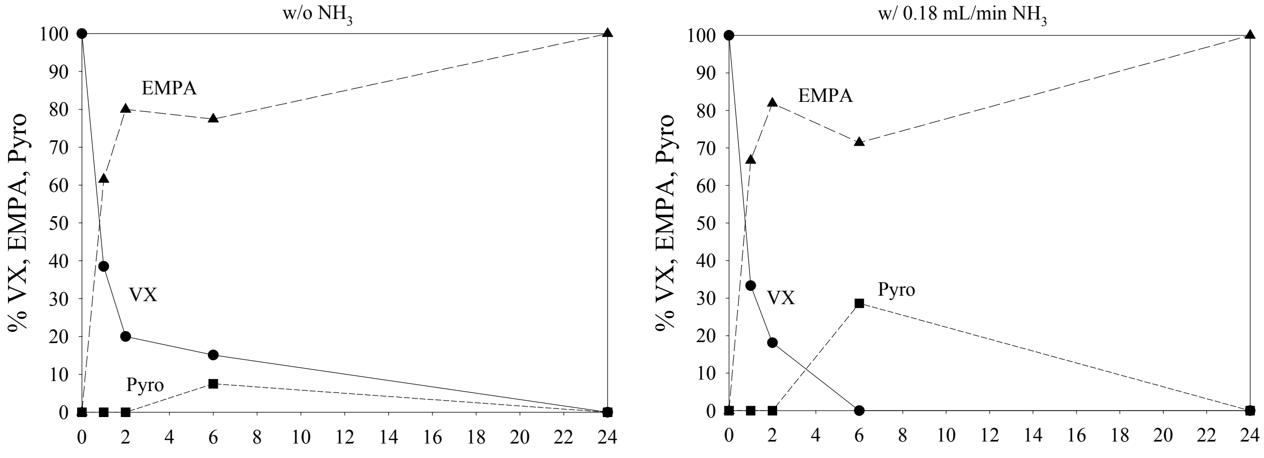


Figure 2. Reaction profiles of VX with VHP® without (left) and with (right) added NH_3 gas.[13]

Preliminary work with GD showed no reaction with VHP® alone; but NH_3 gas was found to react quickly with GD in either a VHP® or moist air stream.[14] However, as shown in Figure 3 the reaction of GD with basic water vapor (right side of Figure 3) is appreciably faster than that with basic VHP® (left side of Figure 3). Although the PMPA product (Scheme 2) was observed in preliminary work,[14] it is not observed under the current conditions as the high flow rates employed[13] caused rapid evaporation of both GD and PMPA. Although VHP® actually retards the rather facile reaction of GD with NH_3 gas, the combination remains an effective decontaminant for GD.

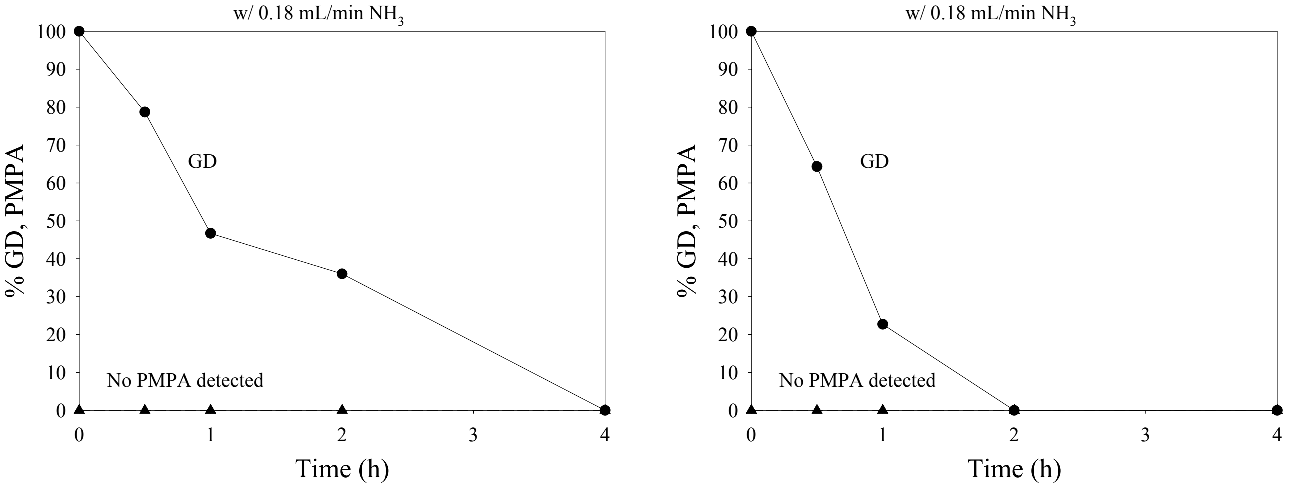


Figure 3. Reaction profiles of GD with NH_3 gas with VHP® (left) and water vapor (right).[13]

CONCLUSIONS

VX, GD and HD can be decontaminated using VHP® with the simple addition of NH_3 gas. HD is selectively oxidized to the non-vesicant sulfoxide. VX is selectively hydrolyzed to non-toxic EMPA and formation of toxic EA-2192 is avoided. GD is hydrolyzed to non-toxic PMPA. Under the current conditions, 600 ppm VHP® and 8 ppm NH_3 gas effect decontamination of VX, GD and HD within 6 hours.

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13. VHP® reactions were carried out by depositing 5 µL VX, GD or HD onto 1 cm diameter glass wool filter discs; suspending the discs contained in aluminum wire baskets inside a ca. 4 cu. ft. stainless steel chamber; exposing the contaminated discs to ca. 600 ppm H_2O_2, with or without 8 ppm NH_3, for desired periods at 23 to 24 °C; removing the discs from the chamber and extracting with 10 mL CH_3CN; and using ^{1}H and ^{31}P NMR (Varian 300 Unityplus or Varian 400 Inova NMR spectrometers) to analyze the extracts for products and unreacted agent. VHP® was generated using a Steris VHP® M100 Biodecontamination System (Steris Corp.) employing the minimum 1 cu. ft./min flow rate and either a 0.4 or 0.5 g/min injection rate for the 35% H_2O_2 feed. These parameters provided a ca. 600 ppm H_2O_2 concentration as measured inside the chamber. NH_3 gas (Aldrich) was introduced at a rate of 0.18 mL/min into the 1 cu. ft./min VHP® stream just prior to the chamber using an Aalborg mass flow controller (Model GFC171S) resulting a calculated 8 ppm value for the NH_3 concentration.
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