

Decomposition of Nerve Gas and Mustard Gas Analogs Using Nicotine and Ultrasound

JOHN L. MEISENHEIMER, LAWRENCE R. MILLER, AND WILLIAM D. SCHULZ

Department of Chemistry, Eastern Kentucky University,
Richmond, Kentucky 40475

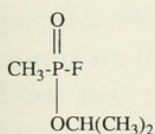
ABSTRACT

There are appreciable amounts of mustard gas (HD) and the nerve gases GB and VX stored in Madison County, Kentucky. This research employed nicotine and ultrasound in a study of the chemical decomposition of chemical-physical analogs of these toxic agents. The insecticide malathion was selected as an analog of VX due to the presence of phosphorus-sulfur bonds in both compounds and similar physical properties. 2-Chloroethyl ethyl sulfide was used as the analog of mustard gas (HD), bis(2-chloroethyl) sulfide. Nicotine alone was found to effect a complete decomposition of these compounds, but the reaction with 2-chloroethyl ethyl sulfide was slow. The application of ultrasound to the nicotine-analog mixtures induced a substantial increase in the rate of analog reaction, thus indicating this method has the potential for practical, "closed-loop" demilitarization of the corresponding warfare agents.

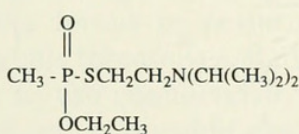
INTRODUCTION

There are 8 locations about the continental United States, and one at Johnston Island, where some 25,000 tons of chemical warfare agents are stored (1). These agents need to be demilitarized for two reasons, (1) to be in compliance with international treaties on destruction of these agents, and (2) because the containers for these agents are gradually corroding and present a long-term hazard to persons living or working in the vicinity of the storage areas.

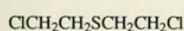
The second reason is of particular concern to the citizens of central Kentucky, and especially those in proximity to the Lexington-Blue Grass Army Depot, where the nerve gases GB (I) and VX (II) are stored as well as the vesicant agent mustard gas or HD (III).



I (GB)



II (VX)



III (HD)

Some of these agents are contained in rockets that also hold both explosive bursters and propellant chemicals that make them doubly dangerous as they age. Safe destruction and/or disposal of these agents is complicated by the fact that the storage and pro-

posed disposal sites are close (2-3 miles) to civilian housing, businesses, and schools. This proximity leaves absolutely no margin for human error or mechanical accident or malfunction in demilitarization, all possibilities in agent destruction by the army-favored incineration process.

The proposed incineration of the chemical agents in Kentucky, and at several other storage sites around the country, has been opposed by citizen's groups for a variety of reasons:

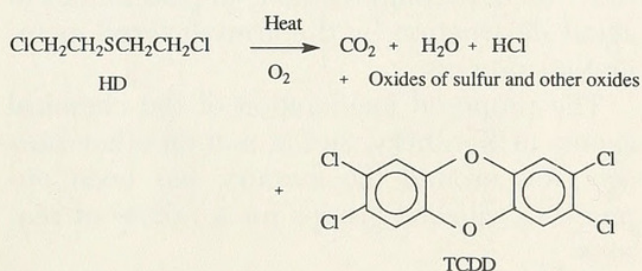
(1) There is concern because the incineration process requires an "open-loop" system. There is a finite possibility that due to error or accident a major emission of agent could escape from the incinerator stack. Residents of this area believe there would be so many unprotected people close to the incinerator that the possibility of adequate warning and safe evacuation is, arguably, impossible. Such a disaster would thus result in the loss of many lives and the magnitude of the tragedy would be incalculable.

(2) Minor amounts of agent might persist in stack effluent even though the health consequences of this continued exposure to trace amounts of chemical warfare agent have never been adequately studied.

(3) There is a logical concern that after the disposal of the chemical warfare agents no effort would be made to dismantle the incinerator. Rather, such an expensive facility would be converted into a general toxic waste incin-

erator and be perpetually used to burn commercial as well as government toxic wastes. It would serve as a magnet for the transportation of toxic wastes from all of the Eastern United States into central Kentucky.

(4) The incineration of mustard gas (HD) has the potential of forming small amounts of the very toxic and persistent 2,3,7,8-tetrachlorodibenzodioxane (TCDD or "dioxin") and other polychlorinated dibenzodioxanes. In animal tests, TCDD is found to be embryotoxic, teratogenic and perhaps carcinogenic (2, 3). In fact, the organizations Physicians for Social Responsibility and the Environmental Defense Fund have jointly released recommendations for a new national policy to reduce dioxin pollution. These recommendations include a requirement that all incinerators operate under conditions that produce virtually no dioxins (4). The general reaction for TCDD production during incineration is shown below:



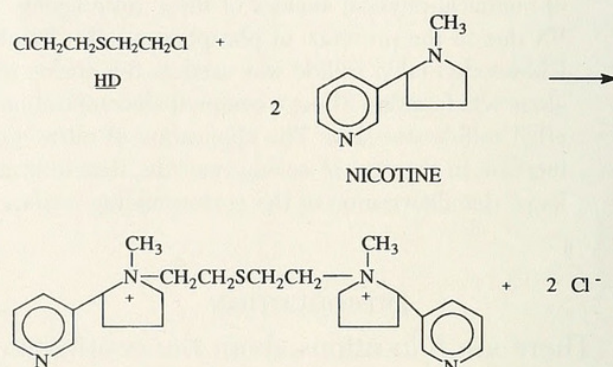
DISCUSSION

The army has stated its intention to use a demilitarization method that will decompose all of the different types of warfare agents by the same process. Their position is that incineration is the only current process that meets that criterion. In part, the argument has some validity. In the past, some GB agent has been satisfactorily demilitarized by using aqueous hydroxide or hypochlorite solutions. However, unlike GB, VX and mustard gas (HD) are not readily or completely soluble in water (5, 6). Therefore, it is difficult to attain complete decomposition of these agents at low temperature-low pressure in aqueous solutions by hydrolysis (7).

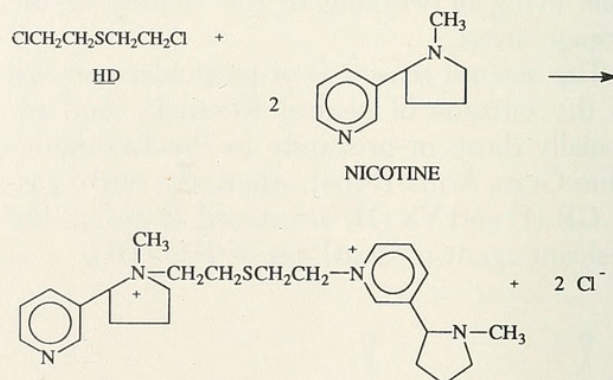
We propose that since all of these agents have a leaving group subject to removal by nucleophilic attack, all should be able to be decomposed by simple mixing with an effective nucleophile in which they are soluble. We fur-

ther suggest that the natural alkaloid nicotine possesses these solubility-nucleophilic properties, thus presenting a novel approach to demilitarization. In addition, we have studied the use of sonochemistry as a method to enhance the decomposition of these agents. Below are listed the expected reaction of each of the agents with nicotine:

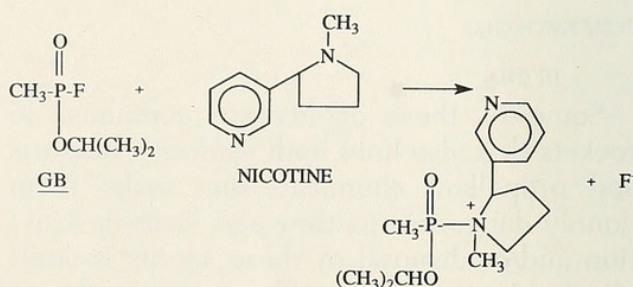
MUSTARD GAS (HD) + NICOTINE



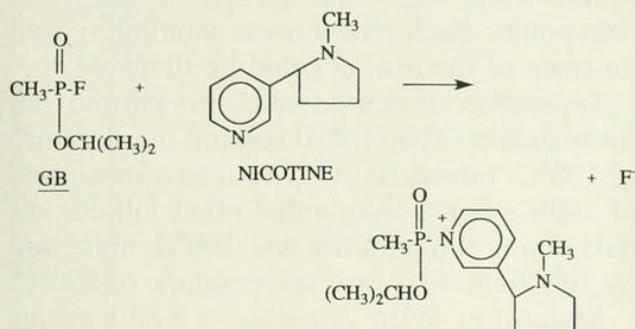
In addition, there are some less likely by-products where the pyridine moiety rather than the N-methylpyrrolidine moiety of nicotine displaces one or two chlorines. The reaction that follows shows a one-chlorine displacement by that process:



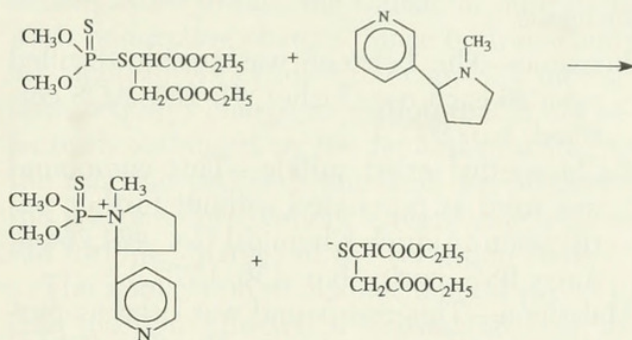
GB + NICOTINE



Plus small amounts of:

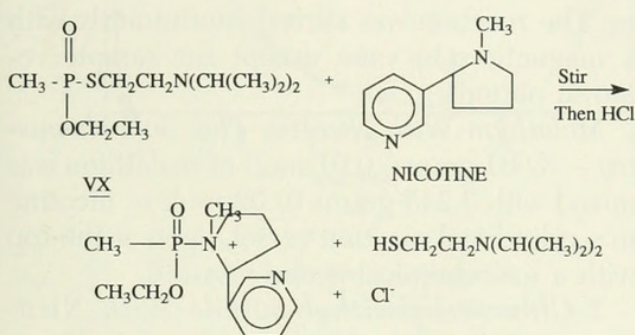


MALATHION + NICOTINE

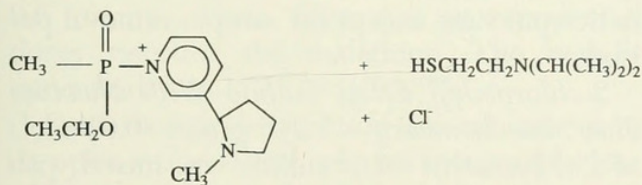


Plus small amounts of this product:

VX + NICOTINE



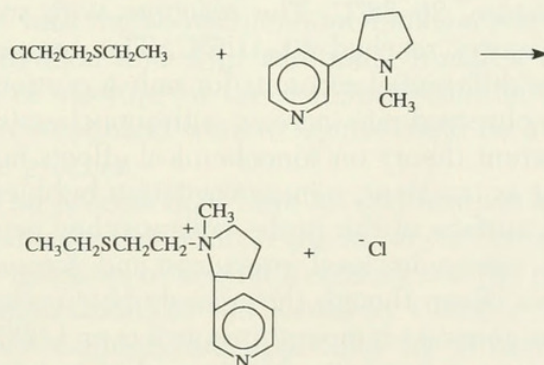
and small amounts of:



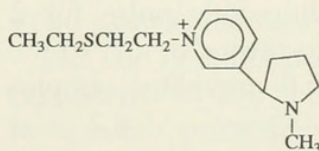
Due to the extreme toxicity and unavailability of the warfare agents, it has not been possible, to date, for us to perform experiments on the agents themselves. Rather, it has been necessary to use commercially available compounds that are reasonable chemical analogs for this research. The insecticide malathion was selected to serve as the analog of VX since it has a similar phosphorus-sulfur bond, similarly sized substituents on the phosphorus atom, and similar solubility properties. Its chemical reactivity is sufficiently close to that of VX to cause it, and especially its oxidized metabolite malaoxon, to possess some anticholinesterase activity (8). The equations for the expected decomposition of malathion by nicotine are given below:

2-Chloroethyl ethyl sulfide was the logical choice to employ as the experimental analog of mustard gas (HD or bis(2-chloroethyl)sulfide). The sensitive 2-chloroethyl sulfide functional group is the same in both compounds, just one in the analog and 2 in mustard gas, and they have obvious similarities of size and solubility. The expected nucleophilic displacement reactions of nicotine and 2-chloroethyl ethyl sulfide are shown below:

2-CHLOROETHYL ETHYL SULFIDE + NICOTINE



Plus small amounts of the isomer below:



MATERIALS, INSTRUMENTATION,
AND METHODS*Reagents:*

Benzene—The benzene was freshly distilled prior to each use (Fisher, #B-245, ACS certified, b.p. 80°C).

2-Chloroethyl ethyl sulfide—This compound was used as purchased without further purification (Aldrich Chemical Co., #24,264-0, Assay 98% purity, b.p. 156–157°C).*

Malathion—This compound was used as purchased without further purification (Chem Service, #PS-86, Assay 98% purity, b.p. 156–157°C).*

Nicotine—This compound was used as purchased without further purification (EM Science, #NX0370-1, Assay 98% purity, b.p. 123–125°C).*

Instrumentation:

Gas Chromatograph/Mass Spectrometer—Hewlett Packard 5890 GC and 5970 MS with an automatic sampler 7673A.

Column—J & W Inc., DB-5, 50 m × 0.20 mm ID, 0.33 micron polysiloxane film.

Sonochemical Reactor—Ace Glass Incorporated #9830 Sonochemical Reaction Assembly with #9818 microtip.

Experimental Procedure:

All reactions were carried out without heating, except for any heat increase caused by the sonochemical probe. The reactions without sonochemistry were carried out at room temperature, 20–22°C. The reactions with sonochemistry reached 40–41.5°C. This temperature differential accounts for only a portion of the observed rate increase with sonochemistry. Current theory on sonochemical effects holds that as transient, minute cavitation bubbles at the surface of the probe collapse they generate enormous local pressures and temperatures. Even though the microbubble collapse may generate temperatures well over 1,000°K, the macroscopic temperature change is only some 15–20° (9).

In all sonochemical procedures the probe was programmed to alternately pulse for 2 seconds and rest for two seconds.

In all experiments, 5.0 microliter samples

were removed for analysis, diluted in 6.0 ml of benzene, and the concentration of analog determined by GC/MS. The small sample size caused some slight, but acceptable scatter of data points. Each reaction was monitored until no trace of the analog could be detected.

Separation of components was carried out for malathion at an initial column temperature of 150°C, increased 10°C/min. to a maximum of 280°C. For 2-chloroethyl ethyl sulfide, initial column temperature was 100°C, increased by 10°C/min. to a final temperature of 230°C.

Malathion With Nicotine.—0.330 grams (0.001 mol) of malathion was mixed with 0.324 grams (0.002 mol) of nicotine in a 3.0 ml reaction vial fitted with a water-cooled condenser. The reaction was stirred continuously with a magnetic-spin vane except for sample removal periods.

Malathion With Nicotine Plus Sonochemistry.—3.301 grams (0.01 mol) of malathion was mixed with 3.245 grams (0.02 mol) of nicotine in a cylindrical reaction vessel, open at the top with a sonochemical probe inserted.

2-Chloroethyl Ethyl Sulfide With Nicotine.—0.249 grams (0.002 mol) of 2-chloroethyl ethyl sulfide was mixed with 0.649 grams (0.004 mol) of nicotine in a 3.0 ml reaction vial fitted with a water-cooled condenser. The reaction was stirred continuously with a magnetic-spin vane except for sample removal periods.

2-chloroethyl Ethyl Sulfide With Nicotine Plus Sonochemistry.—1.246 grams (0.01 mol) of 2-chloroethyl ethyl sulfide was mixed with 3.24 grams (0.02 mol) of nicotine in a cylindrical reaction vessel, open at the top with a sonochemical probe inserted.

EXPERIMENTAL RESULTS

Malathion:

The experimental results for the reaction of malathion and nicotine, with and without the sonochemical probe, are summarized in Figure 1. Without sonochemistry the 0.33 gram sample (0.001 mol) of malathion was completely decomposed in 600 minutes, with a reaction half-life of 99 minutes. The decay rate was exponential, with $y = 113.9 \times 10^{-0.004x}$ in the best-fit curve.

Using the sonochemical reactor, 3.30 grams (0.01 mol) of malathion was decomposed in 42

* Gave a single peak upon GC analysis.

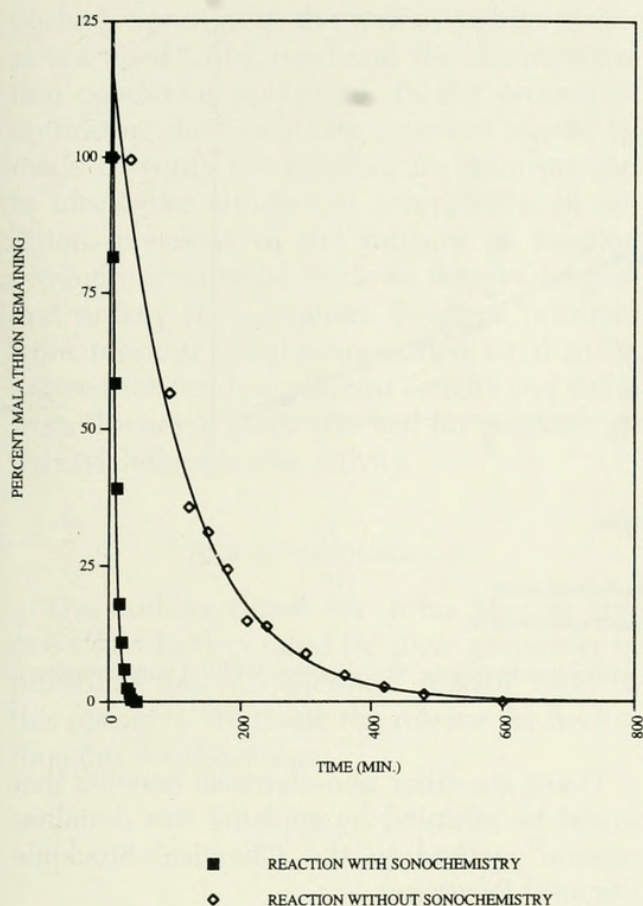


FIG. 1. Malathion + nicotine. ■—reaction with sonochemistry; ◇—reaction without sonochemistry.

minutes, the reaction half-life dropping to only 9.6 minutes. Again, there was an exponential decay rate for the malathion. The best-fit curve had $y = 176.7 \times 10^{-0.068x}$.

Even though the reaction was carried out in an open vessel, there was no measurable loss of reactants by evaporation during the reaction.

2-Chloroethyl ethyl sulfide:

The experimental results for the reaction of 2-chloroethyl ethyl sulfide are displayed on the graph in Figure 2. The decomposition of 0.249 grams (0.002 mol) of this compound by nicotine alone was quite slow, taking 290 hours for completion. The reaction half-life was approximately 150 hours. It is obvious from Figure 2 that the decomposition rate of this compound is not exponential like that of malathion. In fact, the best-fit curve is a second-order polynomial type that has the sign of the change in slope with time opposite to that of the malathion curve. The 2-chloroethyl ethyl sulfide reaction with nicotine begins slowly,

suggesting an induction period. This is probably due to a solvent effect because as the reactants move toward the transition state there must be forming charges. Since both reactants are neutral, either an S_N1 or an S_N2 mechanism requires charge formation that is not effectively stabilized by the neutral mixture. As the reaction proceeds and ions are produced the reaction environment is more amenable to the forming charges in the transition state.

The application of a sonochemical probe to this reaction effected a substantial rate increase. The 1.246 gram (0.10 mol) sample of 2-chloroethyl ethyl sulfide was completely decomposed in 41 hours compared to 290 hours without sonochemistry. The reaction half-life was reduced to 15.5 hours in comparison to the 150 hours required without sonochemistry. There was no loss of reactants from the open reaction vessel by evaporation.

CONCLUSIONS

This work demonstrates that analogs of VX nerve gas and mustard gas (HD) can be completely decomposed chemically using nicotine as both reactant and reaction solvent. Also, the experimental results demonstrate that using a sonochemical probe affords a great increase in reaction rate. Additional rate increases would be readily effected by lengthening the time of the sonochemical pulse and increasing the reaction temperature. Further studies to optimize solvent polarity should provide even greater rates, especially in the case of mustard gas (HD) decomposition. One can conclude that with the above mentioned enhancements in method and with additional research the use of nicotine for the demilitarization of the aforementioned warfare agents could be a viable process.

The process does have several features and advantages that address the major concerns of the residents of central Kentucky and the recommendations of the Kentucky Citizens Advisory Commission, appointed by Governor Brereton Jones, with respect to demilitarization of the chemical agent stockpile.

(1) It would permit a "closed-loop" system so no gases could escape into the atmosphere.

(2) The demilitarization reactions could be carried out at low temperature-low pressure by a batch process. No transfer of reaction products into transport or storage containers

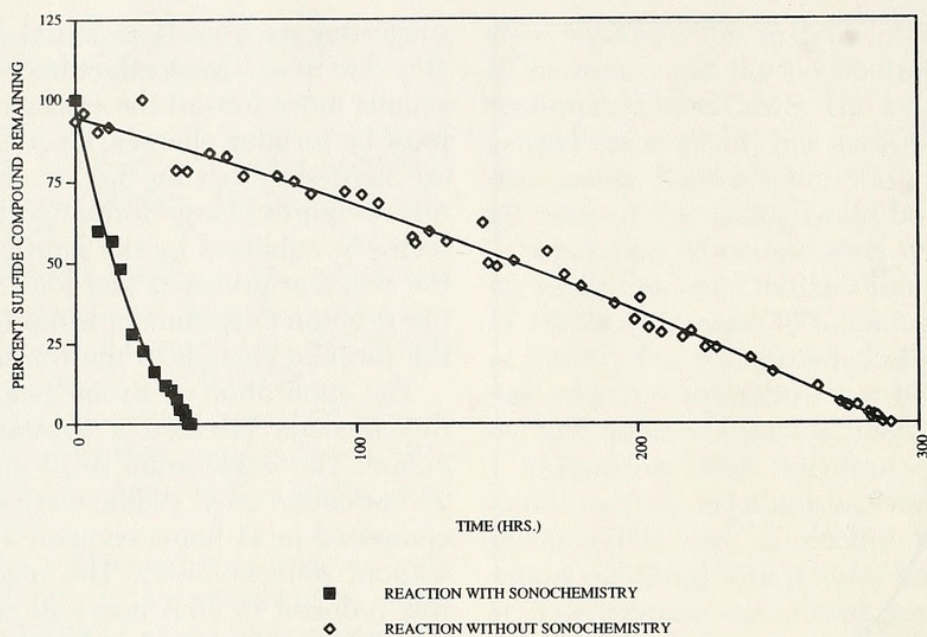


FIG. 2. 2-Chloroethyl ethyl sulfide + nicotine. ■—reaction with sonochemistry; ◇—reaction without sonochemistry.

would need to occur until the products could be assessed for the presence of residual warfare agent, thus providing this process with a level of safety not possible with incineration. We further propose that dedicated railroad tank-cars could be constructed that would serve both as “reaction vessels” and as a means to transport the reaction products to a toxic waste dump. This would minimize the number of times transfer of the chemicals would be required.

(3) The proposed chemical demilitarization reagent nicotine will mix well with GB, VX and HD and thus improve the effectiveness of destroying these agents completely. All of these agents could be demilitarized in the same batch reactors (tank-cars), thus adding an additional economical benefit to this process.

(4) A closed-loop batch reactor of the type that would be used for this process would not be useful for the destruction of most industrial toxic wastes and therefore would not serve to be converted into a general toxic waste disposal unit after the chemical warfare agents are demilitarized.

(5) Chemical demilitarization of the agents would not produce TCDD, “dioxin.”

(6) The reaction products are non-volatile salts or high-boiling liquids, substantially reducing any hazard in handling or transportation.

There are other non-chemical benefits that would be afforded by applying this demilitarization method to the Chemical Stockpile Disposal Program:

(1) The Department of Defense and its executive agent for chemical stockpile disposal, the U.S. Army, would benefit. Their support of this project, or even support for a serious study of the method, would indicate a willingness to explore alternatives to the incineration program and thereby improve their credibility with the civilian populations surrounding the eight continental storage sites. This is no small matter since incidents at storage-disposal sites over the past few years have reduced their credibility and recent revelations about secret government tests with radioactive agents on civilians in the 1940s and 1950s will make it even more difficult for these agencies to convince the civilian population that concern for their health has a top priority.

(2) The use of nicotine as the demilitarizing reagent in the destruction of the chemical warfare agents would provide an economic boon to the tobacco farmers not only of Kentucky, but also of several other tobacco-growing states, some with depressed economies, as well as to the businesses and workers associated with the recovery of nicotine from tobacco.

The work reported in this paper suggests that additional research needs to be accom-

plished. Specifically, the warfare agents themselves need to be used and the demilitarization conditions optimized. In the process of optimizing the conditions, an effort should be made to verify the reaction mechanisms and to insure the absence of reversibility. In addition, bioassays of the mixture of reaction products need to be made to determine general toxicity (LD_{50}) values. Reaction mixtures from mustard gas decomposition need to be assayed for residual vesicant activity and those from the nerve gases checked for residual anticholinesterase activity.

ACKNOWLEDGMENTS

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