SUFFIELD MEMORANDUM NO. 59/70

A STUDY OF THE STABILITY OF MUSTARD STORED SINCE WORLD WAR II (C)

by

A.H. Gray and R.V. Jardine

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ABSTRACT

Samples of mustard from Vat No. 10 at DRES were distilled and the fractions analyzed by various means. On a water and carbon tetrachloride-free basis it was found that the material from the vat was about 70% pure.

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INTRODUCTION

During World War II, tests were carried out with quantities of mustard gas, I. At the conclusion of hostilities significant quantities remained. The material was stored in lead lined concrete vats and has remained undisturbed since that time. From time to time the question of the actual percentage of mustard in the mass contained in the vats at DRES is raised.

$$Cl - CH_2 - CH_2 - S - CH_2 - CH_2 - Cl$$

I

Recently, a thermal destructor for incineration of DDT was built at DRES and in the design allowance was made for the possible burning of mustard in the facility. For this purpose it will be important to know the chemical constituents of the material in the mustard vats as well as the elemental composition. In addition, if mustard were to be destroyed at DRES, then a thorough knowledge of its spectra and methods of detection and analysis would be mandatory. The brief study, now being reported, employed distillation of a sample from Vat 10 to cause a gross separation of the components followed by thin layer chromatography (TLC), nuclear magnetic resonance (n.m.r.), mass spectroscopy and gas chromatography to ascertain purity and confirm the structure. Preliminary work[1] using gas chromatography had indicated that there is between 70 and 75% of a major component, assumed to be I, in Vat No. 10.

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[1] G.N. Schmitz, Unpublished Report

RESULTS AND DISCUSSION

a) Sample Preparation

The sample of mustard for this study was obtained from Vat No. 10 on 20 March, 1970 by DRES Munitions Group personnel. The standard practice is to use a stoppered cup on a long rod. Before a sample could be taken, it was first necessary to break through a solid layer or crust, probably frozen water and mustard, on top of the mass in the vat. When the cup was at a depth judged sufficient, the stopper was removed and the cup allowed to fill. The material in the cup was brought to the laboratory in a glass bottle.

b) Sample Examination

Visual examination of the contents of the crude material revealed a black mass divided into at least three layers. The top layer accounted for approximately 10% of the material while the bottom layer amounted to no more than 2%.

c) Vacuum Distillation

Three vacuum distillations of the mustard from Vat No. 10 were carried out. In addition to the fractions collected in the normal way, the contents of the trap (cooled in liquid N_2) were examined and weighed. Since the vats are partially buried in a fenced compound, rain water can enter through air vents in the top of the vat. This material was expected in the trap along with carbon tetrachloride, the solvent used in manufacture.

Table I presents the combined data (addition of pot and fraction weights) from two distillations. This shows that, on a solvent free basis, the percent mustard is 62.0. For the third distillation, the mustard sample was washed with water, dried over anhydrous sodium sulfate and distilled. Table II shows the combined mustard fractions to be 74.5% of the pot charge. Because of the pretreatment, no volatile material was found in the trap. It is interesting to note that the amount of residue, after the water wash (Table II), is much less than from a straight distillation. From the combined data in Tables I and II, the mustard (on a solvent and water free basis) is 68% of the sample.

Table III presents combustion data for the distilled material in fraction 3 in Table II, as well as elemental composition of a typical pot residue.

d) Analytical Results

The preliminary analysis of all fractions was by thin layer chromatography, TLC. Fractions from the simple distillation all showed a major spot of R_f = 0.67, a smaller spot at R_f = 0.57 and a third minor spot at R_f = 0.27. All of these were clear and well defined. However, the fractions from the anhydrous distillation showed only the two upper spots. Thus, since the spray reagent is specific for the mustard group, the water wash removed some mustard like impurity. A visual inspection of the TLC plates indicated about 95-98% of the material to be of higher R_f. This was verified by gas chromatography. It is interesting to speculate on the nature of the two lower spots.

It is possible that the one with R_f = 0.57 may be II.

$$Cl - CH_2 - CH_2 - S - CH_2 - CH_2 - S - CH_2 - CH_2 - Cl$$

II

As for the water soluble material of R_f = 0.27, it may be compounds III or IV as shown below.

$$Cl - CH_2 - CH_2 - S - CH_2 - CH_2 - O - H$$

III

$$H - O - CH_2 - CH_2 - S - CH_2 - CH_2 - O - H$$

IV

TABLE I

DISTILLATION OF HS FROM VAT NO. 10

POT CHARGE 136.6g					
FRACTION	B.P. °C	PRESSURE mm of Hg	WEIGHT (g)	% BASED ON	
				POT CHARGE	CHARGE LESS TRAP
1	forerun	0.5	6.5		
2	43-58	0.5	25.4		
3	58-95	0.5	26.7		
4	74-95	0.5	9.0		
Fr 1-4 (Combined)			67.6	49.5	62.0
Residue			41.5	30.4	38.0
Trap Contents			27.5	20.1	-
Total			136.6	-	-

TABLE II

DISTILLATION OF WATER WASHED HS
FROM VAT NO. 10

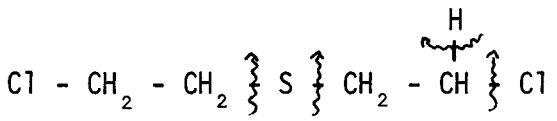
POT CHARGE 52g				
FRACTION	B.P. °C	PRESSURE mm of Hg	WEIGHT (g)	% OF POT CHARGE
1	30-45	0.2	3.5	
2	43	0.2	12.0	
3	43	0.2	15.5	
4	45-60	0.2	7.7	
Fr 1-4 (Combined)			38.7	74.5
Residue			13.5	26.0
Total			52.0	-

TABLE III

ANALYSIS OF DISTILLED MUSTARD AND POT RESIDUE

ELEMENTS	FRACTION 3 (TABLE II)		POT RESIDUES
	% Found	$C_4H_8Cl_2S$ % Calculated	% Found
C	30.47	30.08	18.96
H	5.07	5.03	3.05
Cl	43.37	44.70	25.42
S	20.87	20.19	54.30
Ash	-	-	0.29

The n.m.r. investigation of fraction 3 of the anhydrous distillation, the purest material, showed a 14 line spectrum, typical of a second order A_2B_2 pattern centered at τ = 6.72 (J_{H-H} 7.5 Hz, δAB = 30.5 Hz). The mass spectrum of this fraction showed three parent masses at M/e = 158, 160 and 162 accounted for by the presence of the two major isotopes of chlorine, Cl^{35} and Cl^{37}, relative abundance 75.4% and 24.6% respectively. This clearly establishes the presence of two chlorine atoms and yields the correct molecular weight for I. Fragmentation was straightforward as indicated in Ia below.



Ia

During the vacuum distillations volatile material condensed in the liquid nitrogen cooled trap used to protect the pump. When this trap was allowed to come to room temperature, two liquid layers were seen. The bottom layer, approximately 2-5%, exhibited no proton resonance spectrum. Since it is known that CCl_4 was used in mustard manufacture, there is little doubt that the lower layer is carbon tetrachloride. (Since the smell of mustard prevails, the characteristic odor of CCl_4 cannot be detected).

The top layer of liquid in the trap had the appearance of water and indeed it gave rise to an n.m.r. signal identical to that well known material.

The residue, on a solvent free basis, accounts for 30% of the material in Vat No. 10. Data on its elemental composition as well as the distilled mustard, is presented in Table III.

CONCLUSIONS

On a CCl_4 and water free basis, the mass in Vat No. 10 at DRES contains 68% mustard of proven structure I. There is about 20% volatile material of which 5% of this is carbon tetrachloride and the balance water.

Since water has been in contact with the mustard, and has been there for many years, it serves as another example of the stability of the compound. Thus, unless the temperature or pH are increased, water is ineffective as a means of destroying or detoxifying the DRES supply. In fact, the water wash experiment (Table III) shows that this is a good way to purify the material before distillation.

Techniques have been developed in the analytical techniques of TLC, mass spectroscopy and gas chromatography as applied to mustard and although the structures of the impurities in the distilled material have not been elucidated, this could now be achieved.

EXPERIMENTAL

The gas chromatographic analysis was carried out on a Varian 1800 instrument using a 6' x 1/8" glass column packed with 5% DC-200 on chromasorb W, AW DMCS 80/100. A Melpar FPD detector was used to detect sulfur. Temperatures, pressures and flow rates were as follows: Column, 145°; injection part 205°; detector 225°. Hydrogen 150 ml/min; oxygen 28 ml/min; air 100 ml/min; nitrogen 30 psi @ 145°. The injection volume was 0.2 µl of a 50% ether solution. N.m.r. spectra were obtained on a modified Varian Associates model A-60 using 25% w/v solutions in deuterochloroform, with tetramethylsilane as internal standard. Mass spectra were recorded on a Perkin Elmer model 270B spectrometer.

The TLC study was carried out as described by Sass (1) *et al* using Eastman silica gel Chromagram sheet and developing with methylene chloride. The spots were visualized by spraying the air-dried plates with 5% DB3 in acetone, spraying with an aqueous solution of 5% sodium perchlorate (in 92.1 mg/100 ml potassium acid phthalate adjusted to pH 5.0 with 1N NaOH), heating at 105° for 10 minutes, cooling and spraying with piperidine. DB3 is [4-(*P*-Nitrobenzyl) pyridine]. Alkylating agents such as mustards are seen as deep blue spots.

Distillation of Mustard From Vat No. 10

The stock bottle containing the sample of the contents of Vat No. 10 was shaken vigorously and a pot charge quickly poured into a 200 ml three-neck flask. All low boiling material was removed using high vacuum (down to 0.5 mm of Hg). This is contrary to standard practice where a water pump would be used first to remove dissolved gasses, etc. However, in this case a liquid nitrogen-cooled trap was used throughout making the use of water vacuum undesirable. The distillation head assembly used was the standard apparatus for all toxic agent distillations in the organic chemistry laboratories at DRES. The weights of the fractions separated were obtained by simply weighing the previously tared containers. This data appears in Table I. Two distillations were carried out and the combined data is shown in Table I.

Distillation of Water Washed Mustard

The well shaken sample (67 grams) was decanted into a separatory funnel, 50 ml of methylene chloride and 50 ml of water added and the contents shaken for 30 seconds. After standing for 30 minutes the lower layer was separated and dried over Na_2SO_4.

The data for the distillation of the organic layer is presented in Table II. Fractions 3 and 4 were combined and sent for microanalysis. Mustard, H, calculated for $C_4H_8Cl_2S$: C, 30.08; H, 5.03; Cl, 44.70; S, 20.19. Found: C, 30.47; H, 5.07; Cl, 43.37; S, 20.87.

Pot Residue

In another experiment a sample of the material from Vat 10 was pipetted from the center of the sample bottle, and distilled at 0.2 m-Hg and 160° pot temperature. When all liquid ceased to distill, the pot residue was sent for elemental analysis. Found: C, 18.96; H, 3.05; Cl, 25.42; S, 54.30; Ash 0.29. This combustion data is presented in Table III.

REFERENCES

1. Stutz, Martin H. and Sass, Samuel. "Qualitative Thin-Layer Chromatography of Some Mustards", EATR 4283, (1969). UNCLASSIFIED

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