Reaction of VX and GD with gaseous ozone†

George W. Wagner,*[a] Philip W. Bartram,[a] Mark D. Brickhouse,[b]‡ Theresa R. Connell,[c] William R. Creasy,[c] Vikki D. Henderson,[a] Joseph W. Hovanec,[a] Kevin M. Morrissey,[c] John R. Stuff[c] and Barry R. Williams[c]

[a] *Research and Technology Directorate, U.S. Army Edgewood Chemical and Biological Center, Aberdeen Proving Ground, MD 21010-5423, USA*
[b] *Geo-Centers, Inc., Gunpowder Branch Box 68, Aberdeen Proving Ground, MD 21010-0068, USA*
[c] *EAI Corporation, 1308 Continental Dr., Abingdon, MD 21009, USA*

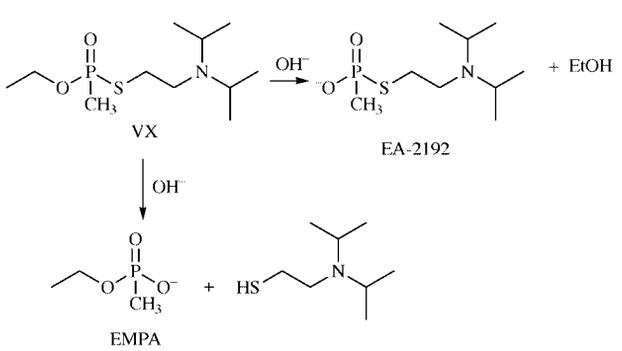
Received (in Cambridge, UK) 12th October 1999, Accepted 3rd April 2000
Published on the Web 15th May 2000

Attempts at decontaminating nerve agents VX {*O*-ethyl *S*-[2-(diisopropylamino)ethyl] methylphosphonothioate} and GD (pinacolyl methylphosphonofluoridate) with gaseous ozone are described. VX reacts like a tertiary amine with oxidation occurring at carbons adjacent to the nitrogen. In this manner a variety of novel VX derivatives still possessing intact P–S bonds are generated, and as such, must be considered to retain formidable toxicity. The major product is *O*-ethyl *S*-[2-(isopropylamino)ethyl] methylphosphonothioate. No reaction of GD with ozone occurs under the conditions employed.

Introduction

Reactive gases such as ozone may offer a means of decontaminating building and vehicle interiors contaminated with chemical warfare agents.[1] Previous work by Snelson *et al.* reported that ozone in fluorocarbons decomposes the chemical warfare agents lewisite (2-chlorovinyldichloroarsine), mustard [bis(2-chloroethyl) sulfide] and GD (pinacolyl methylphosphonofluoridate).[2] Snelson *et al.* also reported reactions between gaseous ozone and bis(2-hydroxyethyl) sulfide (mustard simulant) and dihexyl methylphosphonate (G agent simulant).[3]

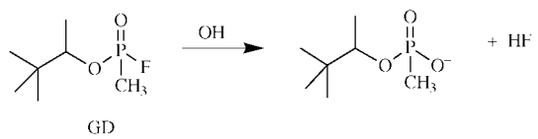
The current study examines the reaction of gaseous ozone with the chemical warfare agents VX {*O*-ethyl *S*-[2-(diisopropylamino)ethyl] methylphosphonothioate} and GD. VX is effectively decontaminated by cleaving the P–S bond, for example, by basic hydrolysis as shown in Scheme 1.[1,4] However, basic hydrolysis (pH > 10) also results in both P–S and P–O bond cleavage yielding 78% EMPA and 22% *S*-[2-(diisopropylamino)ethyl] methylphosphonothioic acid (EA-2192).[4] EA-2192 is nearly as toxic as VX itself.[4] GD is decontaminated by



Scheme 1

† ^{31}P NMR spiking experiments for compounds **1** and **2**, and LC-MS, GC-IRD-MS, GC-MS-EI and CI data for identified compounds **1**–**5** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/a9/a908187i/

‡ *Present address*: Hercules, Inc., Wilmington, DE 19894-0001, USA.



Scheme 2

cleavage of the P–F bond, similarly accomplished by basic hydrolysis as shown in Scheme 2.[1]

Yang *et al.*[4] have reported the oxidation of VX using *m*-chloroperoxybenzoic acid (MCPBA) and Oxone ($2KHSO_5$–K_2SO_4–$KHSO_4$). The MCPBA oxidant was found to exclusively yield a stable *N*-oxide of VX[4] (Scheme 3). The *N*-oxide then either slowly decomposed to *O*-ethyl *S*-vinyl methylphosphonothioate or underwent further oxidation at sulfur followed by hydrolysis to yield ethyl methylphosphonic acid (EMPA) (Scheme 3). As with EA-2192 the vinyl compound retains a P–S bond and is considered toxic.[4] Oxone was found to react immediately with VX *via* the desired exclusive cleavage of the P–S bond to yield EMPA and the corresponding sulfonic acid *N*-oxide, which was quite stable toward oxidation.[4] Thus VX is effectively decontaminated by Oxone, but MCPBA may yield a toxic product.

Because of the potential formation of toxic agent byproducts of VX, NMR, LC-MS, GC-MS, GC-IRD-MS (infrared detector) and GC-AED (atomic emission detector) were enlisted to identify the plethora of products generated from the reaction of VX with ozone. The identified products allow a mechanism to be proposed for the reaction of ozone with this agent. However, attempted reactions of GD with ozone resulted in no loss of GD, and no products were generated.

Results and discussion

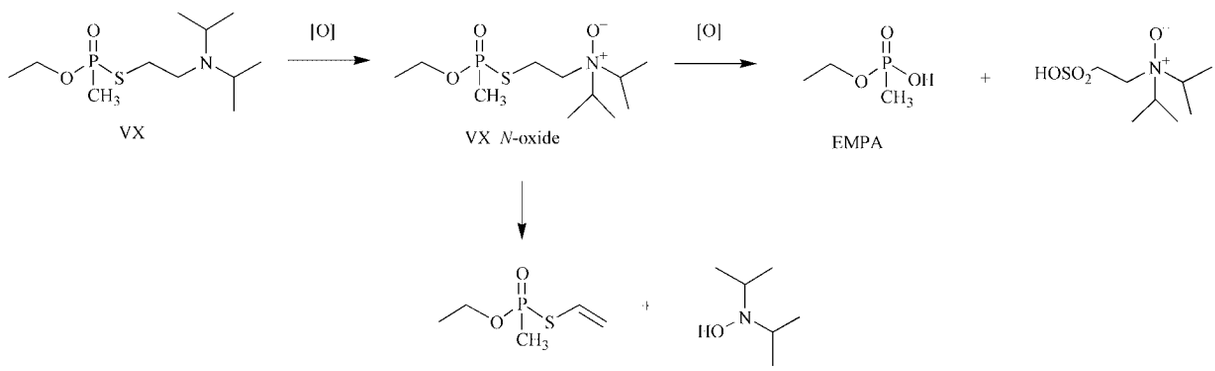
^{31}P NMR analysis of the GD–ozone reaction

After 60 min exposure of 50 μL neat GD to gaseous ozone, the acetonitrile extract contained only GD. No products were detected and the original amount of GD was quantitatively recovered in the extract. This lack of reactivity of neat GD with gaseous ozone is in stark contrast to the reactivity reported by

Table 1 ^{31}P NMR analyses of VX–ozone acetonitrile extracts

Compound	Reaction time[a] 0.5 h	1 h	2 h	2 h[b]
VX	3.4 (58.41)	1.2 (58.59)	0.8[c] (58.59)	9.0 (57.83)
1	22.0 (57.23)	22.6 (57.55)	22.1 (57.64)	20.5 (57.19)
Unknown P–S	—	—	trace (56.85)	—
Unknown P–S	4.8 (55.12)	4.1 (55.20)	4.2 (55.24)	3.6 (56.04)
Unknown P–S	—	—	trace (55.23)	—
Unknown P–S	—	trace (55.29)	trace (55.35)	—
Unknown P–S	—	trace (55.26)	trace (55.30)	—
Unknown P–S	0.8 (54.86)	0.6 (54.92)	0.5 (54.97)	0.6 (55.78)
Unknown P–S	5.8 (54.77)	5.8 (54.83)	5.3 (54.88)	7.8 (55.68)
"VX–NO"[d]	—	—	"(54.79)"	—
2	3.4 (54.61)	3.5 (54.67)	3.2 (54.73)	3.3 (55.51)
Unknown P–S	—	trace (54.34)	—	—
Unknown P–S	3.4 (54.18)	3.2 (54.23)	3.2 (54.27)	3.0 (55.06)
Unknown P–S	0.3 (53.73)	0.3 (53.73)	—	0.6 (55.01)
EA-2192[e,f]	0.8 (42.69)	—	—	—
DEMP[e,g]	1.1 (31.39)	—[h]	0.8 (31.47)	0.3 (31.93)
7, EMPA	30.2 (29.58)	32.3 (31.39)	33.7 (32.13)	42.2 (29.55)
MPA[e,i]	trace (28.12)	0.6 (29.57)	0.8 (30.40)	3.0 (28.39)
VX-pyro[j]	20.1 (23.86, 23.61)	22.7 (23.88, 23.64)	21.9 (23.89, 23.65)	4.2 (24.29, 24.03)
Unknown phosphate or phosphonate	1.3 (23.70)	—	—	—
Unsym. VX-pyro[k]	2.6 (22.22, 22.01, 16.77, 16.56)	2.6 (22.48, 22.27, 17.63, 17.42)	3.2 (22.69, 22.48, 18.46, 18.25)	1.8 (22.61, 22.40, 17.30, 17.09)

[a] ^{31}P NMR peak area %. The ^{31}P NMR shifts for various compounds were different in each sample, and are given in parentheses. [b] Humidified ozone. [c] Corresponds to 1.9 mM VX. [d] Although not observed in any of the reactions, the ^{31}P NMR shift of VX–NO in the 2 h extract, as determined by spiking with the authentic compound, is given for comparison. [e] Tentative assignment, not confirmed by spiking. [f] $(HO)P(O)(CH_3)[SCH_2CH_2N(i\text{-}Pr)_2]$. [g] $(EtO)_2P(O)(CH_3)$. [h] May be hidden under EMPA peak. [i] $(HO)_2P(O)(CH_3)$. [j] $[(EtO)P(O)(CH_3)]_2O$. [k] $(EtO)P(O)(CH_3)O(HO)P(O)(CH_3)$.



Scheme 3

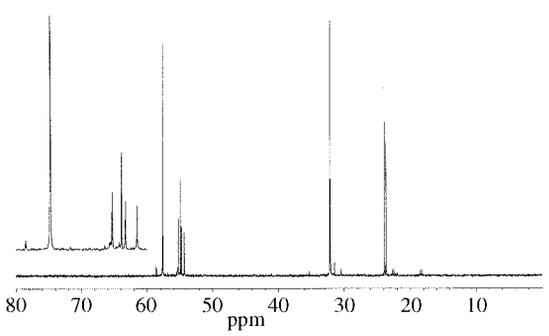


Fig. 1 ^{31}P NMR spectrum obtained for the acetonitrile extract of the 2.0 h reaction of neat VX with dry gaseous ozone. Inset shows the P–S compound region.

Snelson *et al.*[2] for GD in ozone-containing fluorocarbons. This apparent discrepancy may be the result of a retarded overall reaction rate in the case of the heterogeneous liquid GD–gaseous ozone system. The GD–ozone–fluorocarbon system is homogeneous, a condition conducive to facilitating the reaction.

Analyses of acetonitrile extracts of VX–ozone reaction

^{31}P NMR spectra obtained for acetonitrile extracts of 50 μL neat VX exposed to dry ozone for 0.5, 1.0 and 2.0 h, and a sample exposed for 2.0 h to humidified ozone revealed, in addition to residual VX, at least a dozen compounds containing intact P–S bonds (five of which are major). ^{31}P NMR data for the samples is given in Table 1 and the spectrum obtained for the 2.0 h sample is shown in Fig. 1.

In view of the oxidative behavior of MCPBA for VX reported by Yang *et al.*,[4] formation of the VX *N*-oxide (VX–NO) is perhaps anticipated in the reaction with ozone. However, addition (spiking) of authentic VX–NO to the 2.0 h sample showed that this species was not present in any detectable amount; a new peak merely arose at 54.79 ppm for the VX–NO spike (Table 1). Indeed, the major P–S compound suspected of being VX–NO persisted for at least several weeks in the extract. This behavior is inconsistent with the 2 h half-life exhibited by VX–NO in *t*-BuOH.[4] The major P–S product is actually the mono-isopropyl derivative of VX, *O*-ethyl *S*-[2-(isopropylamino)ethyl] methylphosphonothioate (**1**) (identified by the other methods, see below). The presence of *O*-ethyl *S*-[2-(*N*,*N*-

Table 2 LC-MS, GC-IRD-MS, GC-AED, GC-MS-EI and GC-MS-CI data for VX and identified P–S products

Method	VX	**1**	**2**	**3**	**4**	**5**
LC-MS-CI[a]						
UV band (210 nm)	No	No	Yes	Yes	Yes	Yes
$[M + H]^+$ *m/z*	268	226	282	268	254	240
GC-IRD-MS-EI						
IR Carbonyl band	—	No	Yes	Yes	Yes	—
Molecular ion *m/z*	—	225[b]	281	267	253	ND[c]
Fragment ions		167 $[C_5H_{12}O_2PS]^+$ 85 $[C_5H_{11}N]^+$ 79 $[CH_4O_2P]^+$	181 $[C_5H_{12}NO_2PS]^+$ 141 $[C_3H_{10}O_2PS]^+$ 79 $[CH_4O_2P]^+$	167 $[C_5H_{12}O_2PS]^+$ 127 $[C_8H_{17}N]^+$ 79 $[CH_4O_2P]^+$	167 $[C_5H_{12}O_2PS]^+$ 113 $[C_7H_{15}N]^+$ 79 $[CH_4O_2P]^+$	
GC-MS-CI[a]						
$[M + H]^+$ *m/z*	—	ND	282	268	254	ND
GC-MS-EI						
Fragment ions *m/z*	—	ND	153 $[C_4H_{10}O_2PS]^+$ 128 $[C_8H_{18}N]^+$ 181 $[C_5H_{12}NO_2PS]^+$ 141 $[C_3H_{10}O_2PS]^+$	224 $[C_8H_{19}NO_2PS]^+$ 114 $[C_7H_{16}N]^+$ 127 $[C_8H_{17}N]^+$	224 $[C_8H_{19}NO_2PS]^+$ 100 $[C_6H_{14}N]^+$ 113 $[C_7H_{15}N]^+$	ND
GC-AED						
Molecular formula	—	ND	$C_{11}H_{24}NO_3PS$	$C_{10}H_{22}NO_3PS$	$C_9H_{20}NO_3PS$	ND

[a] CI yielded protonated molecular ion $[M + H]^+$ only; fragmentation pattern not obtained. [b] GC-IRD-MS-EI assignment of compound **1** confirmed with authentic standard. [c] Not detected.

diisopropylamino)-2-oxoethyl] methylphosphonothioate (**2**) was confirmed by spiking with the authentic compound. These products, and others identified by the other methods, reveal that although ozone does not yield a stable *N*-oxide, the oxidant is similar to MCPBA in that initial attack does occur at the nitrogen rather than at sulfur as in the case of Oxone.[4]

The other phosphorus-containing compounds found in the samples are anticipated reaction products, and/or common impurities, *i.e.* EA-2192, diethyl methylphosphonate (DEMP), ethyl methylphosphonic acid (EMPA, **7**), methylphosphonic acid (MPA), VX-pyro $\{[(EtO)P(O)(CH_3)]_2O\}$ and the unsymmetrical VX-pyro $[(EtO)P(O)(CH_3)O(HO)P(O)(CH_3)]$. VX-pyro is believed to form *via* nucleophilic attack on VX by EMPA.[4b] These compounds are easily identified from their ^{31}P NMR shifts.[5] A few minor, unidentified compounds were also detected. The stability of EMPA and other compounds in the presence of ozone is consistent with the non-reactivity exhibited by GD. Spiking the 2 h sample (1 ml volume) with 3 μL VX and comparing the relative increase in area of its ^{31}P NMR peak indicated that this sample contained 0.5 μL residual VX. The VX concentration is thus calculated to be about 1.9 mM.

Results for the 2 h reaction of VX with humidified ozone given in the last column of Table 1 reveal no major differences in the formation of the major P–S compounds. But humidification did hinder VX reactivity, perhaps *via* protonation at N. As anticipated, fewer pyro compounds were found, presumably because they were hydrolyzed after formation. Corresponding increases in the amounts of EMPA and MPA also occurred.

LC-MS, GC-IRD-MS, GC-AED-MS and GC-MS methods identified four additional P–S compounds and confirmed the presence of compound **2** identified by the ^{31}P NMR spiking experiment. These results are summarized in Table 2.

The MS-EI spectrum of VX is dominated by β-cleavage of the tertiary amine group to form the base ion at *m/z* 114 ($[C_7H_{16}N]^+$). This feature is also present in many of the identified P–S compounds. All of these compounds exhibit prominent ions resulting from cleavage of the S–C bond accompanied by proton transfer to sulfur. A detailed discussion of the identification of the P–S compounds follows.

LC-MS-CI analysis of the acetonitrile extract of the 2 h dry ozone sample found several compounds of interest with $M + H^+$ ions at 125, 102, 226, 240, 254, 268, 268, 130 and 282 *m/z*. As CI was used, fragmentation patterns were not obtained. The gradient elution run yielded two quickly eluting peaks possessing $M + H^+$ 125 and 102 *m/z*, which correspond to EMPA (**7**) and diisopropylamine, respectively. The gradient elution run also yielded a series of slowly-eluting, closely-spaced peaks. The largest of these peaks possesses an $M + H^+$ of 226, and is assigned to **1**. Its relative intensity identifies it as the major P–S compound formed in the VX–ozone reaction. This enables the assignment of **1** to the major P–S compound detected in ^{31}P NMR spectra (Fig. 1, Table 1). The remainder of the smaller peaks observed in the gradient elution run, and their assignments, include: **2** ($M + H^+$ 282); VX ($M + H^+$ 268), *O*-ethyl *S*-[2-(*N*-acetyl-*N*-isopropylamino)ethyl] methylphosphonothioate, **3** ($M + H^+$ 268); *O*-ethyl *S*-[2-(*N*-formyl-*N*-isopropylamino)ethyl] methylphosphonothioate, **4** ($M + H^+$ 254); and *N*,*N*-diisopropylformamide, **6** ($M + H^+$ 130). The peaks for **3** and VX (both possessing $M + H^+$ 268), which overlapped in the gradient elution run, were resolved in the isocratic run and identified (see below). Compounds **2**, **3**, and **4** were also identified by the GC-IRD-MS-EI and GC-MS-CI/EI methods (see below). The remaining peak found in the gradient elution run yielded $M + H^+$ 240 *m/z*, and is tentatively assigned to *O*-ethyl *S*-[2-(*N*-isopropylamino)-2-oxoethyl] methylphosphonothioate (**5**). The isocratic run gave resolved peaks and $M + H^+$ for **1** ($M + H^+$ 226), **6** ($M + H^+$ 130), **4** ($M + H^+$ 254), VX ($M + H^+$ 268), and **3** ($M + H^+$ 268). UV absorption traces for the isocratic run assisted in the assignments of the carbonyl-containing compounds, and enabled VX to be discerned from **3** (both $M + H^+$ 268). LC-MS did not detect any sulfonic acids or phosphonic acids other than EMPA.

GC-IRD-MS confirmed the presence of EMPA (**7**), the major phosphorus-containing product detected by NMR. And although not detected in appreciable amounts by NMR, *O*-ethyl methylphosphonothioic acid was also present. One mechanistically-important non-phosphorus compound, *N*,*N*-diisopropylformamide (**6**, $m/z = 129$; see Scheme 4) was detected. Also detected were **1** ($m/z = 225$), **2** ($m/z = 281$), **3** ($m/z = 267$), and **4** ($m/z = 253$). Compound **1** was the most abundant P–S compound detected, consistent with its identification as the major P–S compound formed in the VX–ozone

Table 3 ^{31}P and ^{13}C NMR data for neat VX–ozone

	Reaction time[a]/min				
	15	25	35	45	60
^{13}C, acetone	203.85, 30.42	203.97, 30.44	204.10, 30.46	204.20, 30.47	204.62, 30.53
^{13}C, ketones, aldehydes	—	—	—	—	210.34, 208.07
^{13}C, amides, carboxylates	—	—	168.89	168.93	169.12
	—	—	—	—	166.09
	—	—	—	—	162.83
	—	—	—	162.03	162.19
	—	—	160.79	160.86	160.99
^{31}P, P–S compounds	52.48	52.64	52.74	52.65	53.08
	—	52.44	52.60	52.60	52.90
	52.27[b]	52.34[b]	52.53[b]	52.53[b]	52.87[b]
	—	—	52.43	52.42	52.74
	51.98 (91.1)[c]	**52.07** (85.6)[c]	**52.18** (82.3)[c]	**52.19** (68.5)[c]	**52.59** (57.0)[c]
	51.67	51.76	51.86	51.88	52.46
	—	—	—	—	52.43

[a] NMR peak shifts of relevant species. [b] Major product **1**. [c] VX, mol% remaining in parentheses. $t_{1/2}$ = 78 min.

reaction. The TMS-derivative of **1** was also detected by GC-MS-EI (MW = 297). The GC-IRD-MS-EI assignment of **1** was confirmed with an authentic sample. Significant fragment ions supporting these assignments include *m*/*z* 167 for **1** (loss of NHC_3H_7), *m*/*z* 181 for **2** (loss of NC_6H_{14}), *m*/*z* 167 for **3** (loss of $NC_5H_{10}O$), and *m*/*z* 167 for **4** (loss of NC_4H_8O). Also consistent with these assignments, compounds **2**, **3**, **4**, and **6** yielded intense carbonyl bands in their IR spectra, whereas **1** did not.

GC-AED found several phosphorus-containing compounds, and provided candidate molecular formulas (see Experimental section) for each of the three major species containing all six elements of interest (C, H, N, O, P and S). GC-MS-EI and CI analysis of the mixture detected the same three major species and, consistent with the GC-AED molecular formulas, identified the compounds as **2**, **3** and **4** from their fragmentation patterns. GC-MS-CI yielded a $[M + H]^+$ ion at *m*/*z* 282 for compound **2**, in agreement with the formula indicated by GC-AED ($C_{11}H_{24}NO_3PS$, $M = 281$). Significant fragment ions detected by GC-MS-EI for **2** include: *m*/*z* 153 and 128 from cleavage of the C–C bond α to the carbonyl group; *m*/*z* 181 from cleavage of the C–N bond α to the carbonyl group; and *m*/*z* 141 from cleavage of the S–C bond and proton transfer to sulfur. For **3** the $[M + H]^+$ ion at 268 agrees with the GC-AED formula ($C_{10}H_{22}NO_3PS$, $M = 267$), and fragmentation includes: *m*/*z* 224 for loss of $CH_3C{=}O$; *m*/*z* 114 for β-cleavage of the amine group; and *m*/*z* 127 from cleavage of the S–C bond and proton transfer to sulfur. For **4** the $[M + H]^+$ ion at 254 agrees with the GC-AED molecular formula ($C_9H_{20}NO_3PS$, $M = 253$), and fragmentation includes: *m*/*z* 224 from loss of the aldehyde group; and *m*/*z* 100 from β-cleavage of the amine; *m*/*z* 113 from cleavage of the S–C bond and proton transfer to sulfur.

^{31}P and ^{13}C NMR analysis of neat VX–ozone reaction

To better characterize the evolution of the P–S products, six neat samples of 1 mL VX bubbled with ozone for 5, 15, 25, 35, 45 and 60 min, were examined by both ^{31}P and ^{13}C NMR. The results are shown in Table 3. The apparent half-life of VX was 78 min. The quick appearance of acetone, and the absence of any aldehyde/ketone/amide functionalities, are consistent with the facile formation of **1**, the major P–S product. The assignments of the other compounds remain unclear, and it can only be concluded that they contain amide and/or ketone/aldehyde functional groups. These findings are in agreement with the types of compounds identified by GC-MS and LC-MS.

Nature of the unidentified P–S compounds

Possible candidates for the remaining half-dozen or so unidentified P–S compounds detected by ^{31}P NMR may be postulated based on identified products **1**–**4** and the known mechanism of tertiary amine ozonation[6,7] (shown for tertiary amine VX in Scheme 4). These structures are shown in Fig. 2, and encompass all iterations of the three basic reaction motifs exhibited by the detected products: loss of isopropyl groups and formation of amides and formamides (see Scheme 4). Many of the candidates possess identical molecular weights.

VX–ozone reaction mechanism

The P–S bond-containing compounds result from the known amine oxidation mechanism.[6,7] A proposed mechanism is shown in Scheme 4.

Compound **4** is postulated to arise from a secondary reaction of **3** with ozone *via* its enol form. Alternatively, perhaps in a less probable reaction, **4** may also form *via* reaction of the major P–S product **1** with adventitious formic acid.[8] Although not shown in Scheme 4, tentatively identified compound **5** could form from the major P–S product **1** in a reaction analogous to the production of **2** from VX. The non-phosphorus compound observed, *N*,*N*-diisopropylformamide (**6**), is evidence for the proposed mechanism involving the eventual cleavage of the P–S bond as shown. Following formation of the major phosphorus-containing product, EMPA (**7**), the sulfur-containing fragment may be predominantly oxidized to sulfur dioxide and lost. Formation of sulfur dioxide is supported by the non-detection of sulfonates by LC-MS and the observation of thick, white smoke during the ozonation of VX.

Conclusions

In the reaction with ozone, VX behaves like a tertiary amine where initial oxidation occurs at carbons adjacent to the nitrogen. In this manner novel, stable VX derivatives still possessing intact P–S bonds are formed, which must be considered to retain formidable toxicity. GD showed no reactivity with ozone under the heterogeneous conditions studied. Ozone is not a viable decontaminant for VX or GD.

Experimental

Materials

VX, GD, *O*-ethyl *S*-[2-(isopropylamino)ethyl] methylphosphonothioate (**1**),[9] and *O*-ethyl *S*-[2-(*N*,*N*-diisopropylamino)-2-oxoethyl] methylphosphonothioate (**2**)[9] were obtained or prepared at U.S. Army Edgewood Chemical and Biological Center. VX *N*-oxide was prepared by reacting VX with *m*-chloroperoxybenzoic acid in CH_3CN. **CAUTION**: these compounds are extremely toxic and should only be handled by trained personnel using applicable safety procedures.

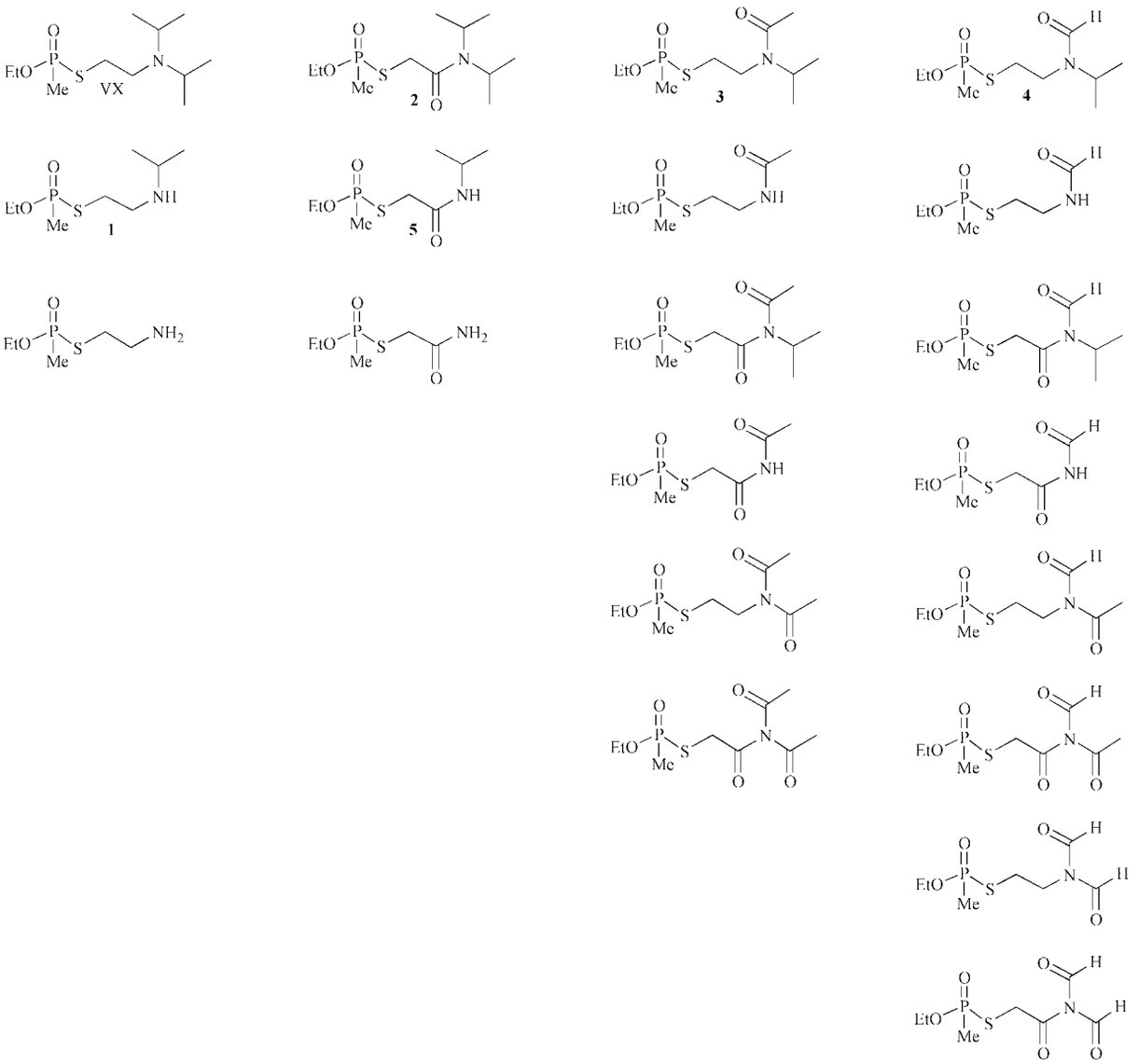


Fig. 2 Families of possible VX-derivatives based on identified products **1**–**5**.

Ozone was generated from pure oxygen (>99.9%) using a Clear Water Tech, Inc. (San Luis, Obispo, CA), corona discharge M-1500 ozone generator. The ozone concentration was 5.5 to 8.5%.

Reaction apparatus

Ozone-laden oxygen was supplied to a stainless steel reactor *via* 0.025 in§ Teflon tubing. All connections were stainless steel fittings. A Sierra Instruments (Monterey, CA) model 821-2 flowmeter was inserted between the oxygen source and the ozone generator. The flow was set between 200 and 500 mL min^{-1} to obtain maximum ozone concentration (5.5 to 8.5%). The concentration of ozone was assessed by a PCI Ozone & Control Systems, Inc. (West Caldwell, NJ) model HC-400 ozone monitor. The monitor was placed downstream from the reactor. A catalytic ozone decomposition unit (PCI P/N 3000-40) was attached to the monitor exhaust. For humidification, a water-bubbler containing distilled water was inserted between the ozone generator and the reactor.

General reaction procedure

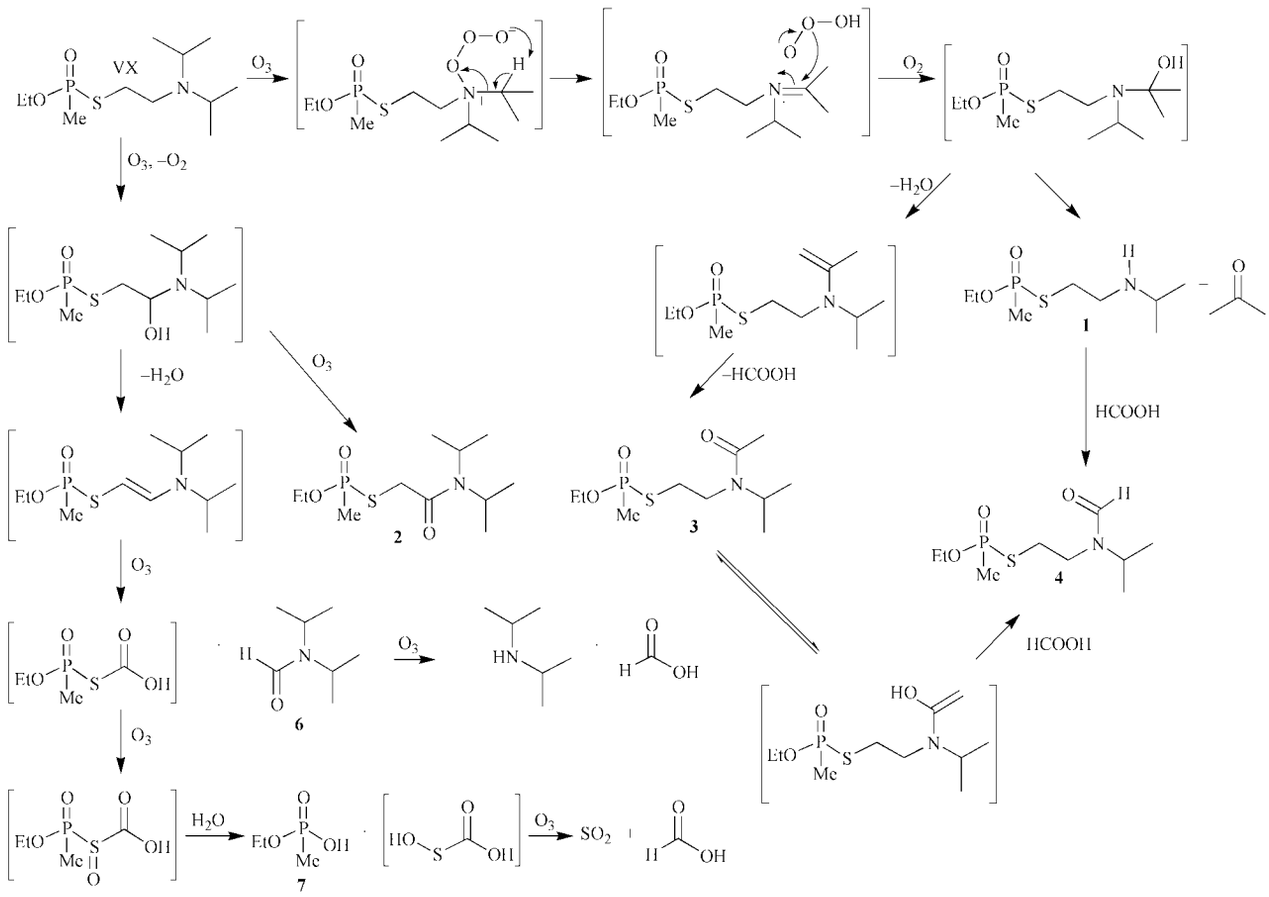
Neat VX or GD (10 μL per pan) was deposited in five Perkin-Elmer aluminium sample pans (kit no. 0219-0041), and placed in the reactor. Ozone exposure periods ranged from 15 to 120 min. Control experiments using only oxygen flow showed no significant evaporation of VX occurred over the course of 120 min. Quantitative recovery of GD from the ozone reaction (see results) also indicated insignificant evaporation of GD. Exposed VX and GD were extracted from the pans using 1 mL acetonitrile for analysis. VX (1 mL) was also bubbled with the ozone and the resulting VX solution was analyzed (neat) by NMR.

Instrumentation

NMR spectra were obtained on a Varian Unityplus 300 NMR spectrometer. Spectra were referenced to either external 85% H_3PO_4 (^{31}P, 0 ppm) or internal VX (^{13}C, 16.27 ppm, J_{POCC} = 6.8 Hz). The GD extract was spiked with triethyl phosphate for quantification. The VX extracts were spiked with VX, VX–NO and compound **2** for assignment and quantification purposes.

Liquid chromatography–mass spectrometry (LC-MS) analyses were run on a Hewlett-Packard 1090 HPLC equipped with a Hewlett-Packard 5989A MS using an atmospheric pressure chemical ionization source. In this standard CI method used in LC-MS, ionization is effected by the solvent to yield the $[M + H]^+$ ion, and negligible fragmentation occurs. The LC column was a Zorbax Eclipse XDB-C18, with dimensions 2.1 mm × 15 cm. A flow rate of 0.25 mL min^{-1} was used along with the following chromatography conditions: 1) gradient elution

§ 1 in = 2.54 × 10^{-2} m.



Scheme 4

using 100% aqueous 0.05 M ammonium acetate (hold for 5 min) to 95% acetonitrile at 15 min (hold for 10 min) and 2) isocratic elution using 70% 0.05 M aqueous ammonium acetate solution and 30% HPLC grade methanol.

Samples for gas chromatography-IR detector–mass spectrometry (GC-IRD-MS) and gas chromatography–mass spectrometry (GC-MS) analysis were derivatized with the trimethylsilylating agent *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) (Aldrich). GC-IRD-MS analyses were done with an HP 5890 Series II GC with a Model 5965B IRD and Model 5972 MSD in series using electron impact (EI) ionization. The column was an HP-5, 25 m × 0.32 mm with a 0.17 μm film thickness. The injection port temperature was 250 °C and the temperature program was 40 °C (1 min), 20 °C min^{-1} to 80 °C (0 min), 10 °C min^{-1} to 200 °C (2 min), 25 °C min^{-1} to 280 °C (3 min). The IRD settings were as follows: optical resolution 8 cm^{-1}, coadd factor 4, scanning speed 1.5 scans s^{-1}, transfer lines 300 °C, and flow cell 280 °C.

GC-MS electron impact (EI) and chemical ionization (CI) analyses were performed on the derivatized sample using an HP 5890 Series II GC with a Model 5972 MSD. The column was an HP-5MS. The injection port temperature was 250 °C and the temperature program was 60 °C (2 min) and 10 °C min^{-1} to 280 °C. The detector temperature was 280 °C. CI was accomplished with methane or ammonia. Although other molecular ions are possible, only the $[M + H]^+$ ions were used for identification purposes.

Gas chromatography–atomic emission detector (GC-AED) analyses were performed on the underivatized sample using an HP 5890 Series II GC with a Model 5921 AED. The column was an HP-5MS. The injection port temperature was 250 °C and the temperature program was 60 °C (2 min) and 10 °C min^{-1} to 280 °C. The transfer line and cavity temperatures were both 280 °C. The following element lines were monitored: C (193 nm), S (181 nm), N (174 nm), P (178 nm), H (486 nm) and O (777 nm). The compound independent nature of the microwave induced helium plasma allows calibration of the instrument for elemental response using compounds containing elements common to that of the analytes. The compound independent calibration software on the HP Chemstation provides an empirical formula based on this external calibration. VX was used for the external calibration.

Acknowledgements

The authors thank Dr Frederick J. Berg for the synthesis of compounds **1** and **2**. This work was performed while Dr George W. Wagner was employed by Geo-Centers, Inc.

References

1 Y.-C. Yang, J. A. Baker and J. R. Ward, *Chem. Rev.*, 1992, **92**, 1729.
2 A. Snelson, D. Clark and R. Brabets, *Fluorocarbon/Ozone and UV Decontamination Concept*, Oct. 1986, CRDEC-CR-87017, Aberdeen Proving Ground, Maryland, Unclassified Report.
3 A. Snelson and K. Taylor, *Decontamination by the Use of UV/Ozone*, Final Report C06577, Contract No. DAAG29-81-D-0100, 1981, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, Maryland, unpublished data.
4 (*a*) Y.-C. Yang, L. L. Szafraniec, W. T. Beaudry and D. K. Rohrbaugh, *J. Am. Chem. Soc.*, 1990, **112**, 6621; (*b*) Y.-C. Yang, L. L. Szafraniec, W. T. Beaudry, D. K. Rohrbaugh, L. R. Procell and J. B. Samuel, *J. Org. Chem.*, 1996, **61**, 8407.
5 Y.-C. Yang, F. J. Berg, L. L. Szafraniec, W. T. Beaudry, C. A. Bunton and A. Kumar, *J. Chem. Soc., Perkin Trans. 2*, 1997, 607.
6 P. S. Bailey, *Ozonation in Organic Chemistry*, Vol. II, Academic Press, New York, NY, 1982, p. 162.
7 H. B. Henbest and M. J. W. Stratford, *Chem. Ind.*, 1961, 1170.
8 J. March, *Advanced Organic Chemistry*, 2nd edn., McGraw-Hill, New York, NY, 1977, p. 384.
9 F. J. Berg and L. R. McMahon, manuscript in preparation.