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Photoassisted Reaction of Chemical Warfare Agent VX Droplets under UV Light Irradiation

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A photoassisted reaction of *O*-ethyl *S*-[2-(diisopropylamino) ethyl] methylphosphonothioate (VX) droplets in air was carried out. The experimental results indicated that VX droplets could be easily and chemically transformed into other compounds under irradiation of a germicidal lamp over sufficient time. Quantum chemical calculation results demonstrated that UV light less than 278 nm wavelength could possibly initiate photoreaction of VX and that both P−S and P═O bonds in the VX molecule were lengthened. The identification of reaction products by gas and liquid chromatography mass spectroscopy and NMR revealed that the VX molecule in air under UV light irradiation could undergo isomerization of S-esters to O-esters, cleavage of P−S, S−C, and C−N bonds, and ozonation of tertiary amines.

1. Introduction

The chemical warfare agent *O*-ethyl *S*-[2-(diisopropylamino) ethyl] methylphosphonothioate (VX) is a highly lethal compound, which is nonvolatile and persistent. It would encounter a long-term contact hazard once contaminated by VX droplets. Therefore, decontamination of VX was of great importance to chemical defense and countering terrorism. It has been recognized early that hydrolysis of VX proceeded a very slow course through cleavage of P−S, P−O, and C−S bonds. Moreover, some hydrolysis products such as *S*-(2-diisopropylaminoethyl) methylphosphonothioic acid (EA2192) were still of high toxicity and persistence.[1] Therefore, decontamination methods based on hydrolysis were not effective against VX. Instead, VX was frequently detoxified by the oxidation method, typically using hypochlorites and peroxides.[2−5] The reaction commonly proceeded via oxidation-promoted hydrolysis at the P−S bond as well as simultaneous oxidation at the tertiary amino moiety.[2,5] Recently, Wagner and co-workers evaluated the use of gaseous ozone as decontaminant for GD and VX.[6] It demonstrated that the oxidation reaction occurred at the C atom adjacent to the N atom in the VX molecule. In addition, VX could also be detoxified through catalytic hydrolysis,[7−11] photocatalysis,[12] and biodegradation.[13]

The fate of VX droplets in soil and concrete was investigated; the experimental results emerged that VX could be chemically degraded through a slow hydrolysis course.[14−17] It was widely received that, since VX presented to be unstable in the sunlight, little was known about the reaction pathway. It was postulated that VX and its congeners having S-ester structures were known to undergo reversible photoisomerization to produce corresponding O-esters,[18] but details of this isomerization reaction and other photochemistry were scarcely reported.

In the present study, a photoassisted reaction of VX droplets in air was carried out. Gas and liquid chromatography mass spectroscopy (GC/MS and LC/MS) and NMR approaches were applied to identify the reaction products. Quantum chemical calculation was also performed to theoretically elucidate the reaction mechanism.

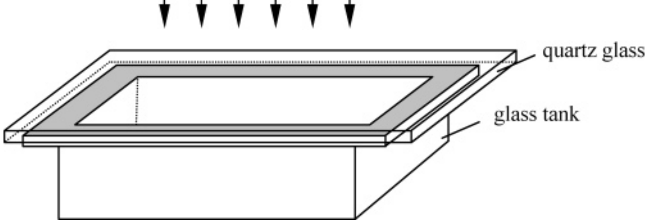

Figure 1. Experimental set up used for photoreactions.

2. Experimental Section

Material. VX has a purity > 95%. Tributyl phosphate (TBP) used as internal standard for GC flame ionization detection (FID) analysis was purified by redistillation. All solvents were of analytical grade. Caution: In view of its high toxicity, VX should only be handled by trained personnel using applicable safety procedures.

Photoassisted Reaction of VX Droplets. The photoreaction was carried out under room temperature at 15−20 °C and relative humidity at 40−60% in a glass tank as reactor, which was schematically shown in Figure 1. A quartz glass plate as a light window was used to cover over the tank. VX liquid (10 drops) were uniformly distributed on a glass plate of 10×5 cm^2 in the tank with a microsyringe. Each droplet had a volume around 1 μL and formed a round spot of ∼1−2 mm on the glass plate; separation distance should be kept around 1 cm to avoid overlapping of the droplets with each other. A germicidal lamp of 20 W with a peak density around 253.7 nm was used to provide UV light irradiation with 0.4mW/cm^2 density at bottom of the tank.

Analysis of VX and Reaction Products. UV−vis absorption spectra of VX was obtained with a UV−vis spectrophotometer (HP-8453), with the scan range located at 190−900 nm. Ethanol was used as a reference and a solvent.

Weight of the residue was measured using a balance with precision of 10^{-4} g. The amount of VX was determined by

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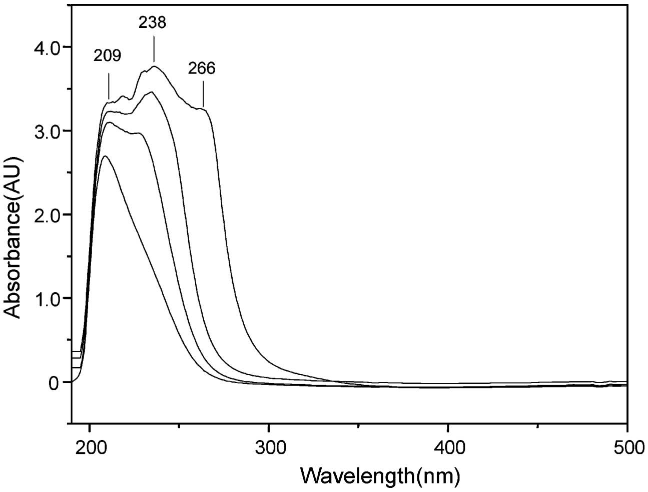


Figure 2. UV−vis absorption spectra of VX in ethanol. Concentrations of the solution were 4×10^{-2}, 4×10^{-3}, 4×10^{-4}, and 4×10^{-5} M from top to bottom, respectively.

GC-FID (Agilent 6890N) equipped with a HP-5 capillary column (30mm × 0.25mm × 0.25μm), dichloromethane was served as solvent to extract the residue, and a certain dose of TBP was added in the solution as internal standard.

For identification of the reaction products, both dichloromethane and methanol were used to extract the residue of VX droplets upon 5 h of on irradiation. The extractant of dichloromethane was analyzed using an Agilent 6890/5973 GC/MSD equipped with a HP-5 column, employing the temperature ramp 40−280 °C at 15 °C/min. Qualitative analysis of methanol solution was done by Agilent 1100 LC/MS equipped with a nonpolar column (Zorbax SB−C18 column 30 mm × 2.1 mm × 3 μm); the used mobile phase was 0.1% acetic acid at a rate of 0.2 mL/min, column temperature 40 °C, and scan range over 50−2000 *m*/*z*.

The residue of VX droplets upon 2 h of on irradiation was washed into $CDCl_3$. $^{31}P\{1H\}$, $^{13}C\{1H\}$, and ^{1}H NMR spectra were obtained using a Varian Mercury Vx300 NMR spectrometer. The observation frequencies were 121 MHz for ^{31}P, 75 MHz for ^{13}C, and 300 MHz for ^{1}H. Chemical shifts were referenced to external 85% H_3PO_4 (0 ppm), CS_2 (0 ppm), and TMS (0 ppm), respectively.

TABLE 1: Retention Percentage of VX Droplets Determined by Weighing and GC Analysis at the Conditions of No Irradiation and UV Light Irradiation

irradiation time (min)	percentage of retention (%)			
	no irradiation		UV light irradiation	
	weighing	GC analysis	weighing	GC analysis
30	91	92	86	73
60	99	90	73	34
120	95	99	76	6
180	95	90	75	4

Quantum Chemical Calculation. An HF/STO-3G method was used to optimize the structure of VX molecule at ground state. Calculation for molecule at excited state was done by a CIS/STO-3G method to obtain the structure parameter and electron transition between energy levels. The above calculations were performed by the Gaussian03 program.

3. Results and Discussion

UV−Vis absorption Spectra of VX. It was clearly shown that VX of 4×10^{-2} M in ethanol emerged a relative strong absorption ability in the UV region with three peaks at 209, 238, and 266 nm, as presented in Figure 2. When one lowered down the solution concentration of VX, absorbance of the three peaks was observed to decrease down accordingly. Absorption peaks at 266 and 238 nm would gradually disappear along with decrease of the solution concentration. This suggested that the absorption ability of the three peaks at 209, 238, and 266 nm weakened in turn and probably corresponded to different electron transitions, which will be confirmed by quantum chemical calculation.

Photoassisted Reaction of VX Droplets. The retention percentage of VX droplets under no light and UV light irradiation was determined, respectively, by weight method and GC-FID and presented in Table 1. The experimental results proved that VX droplets in the reactor in darkness were nearly nonvolatile and chemically stable in air, whereas VX droplets upon UV light irradiation were observed to turn yellow

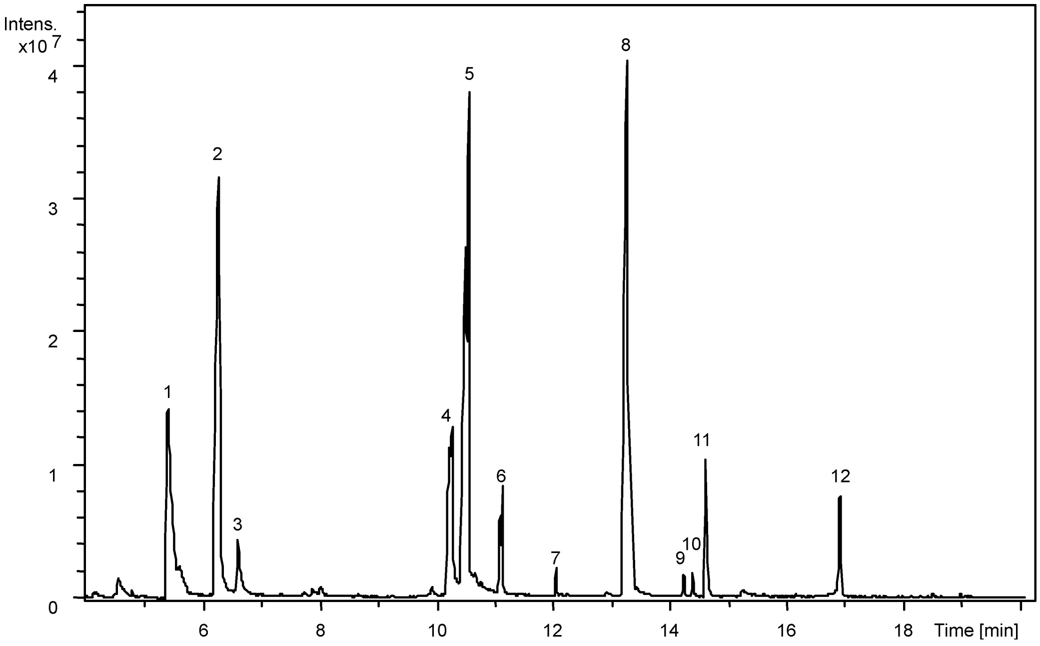


Figure 3. GC/MS total ion chromatogram of the residue of VX droplets upon 2 h of on irradiation.

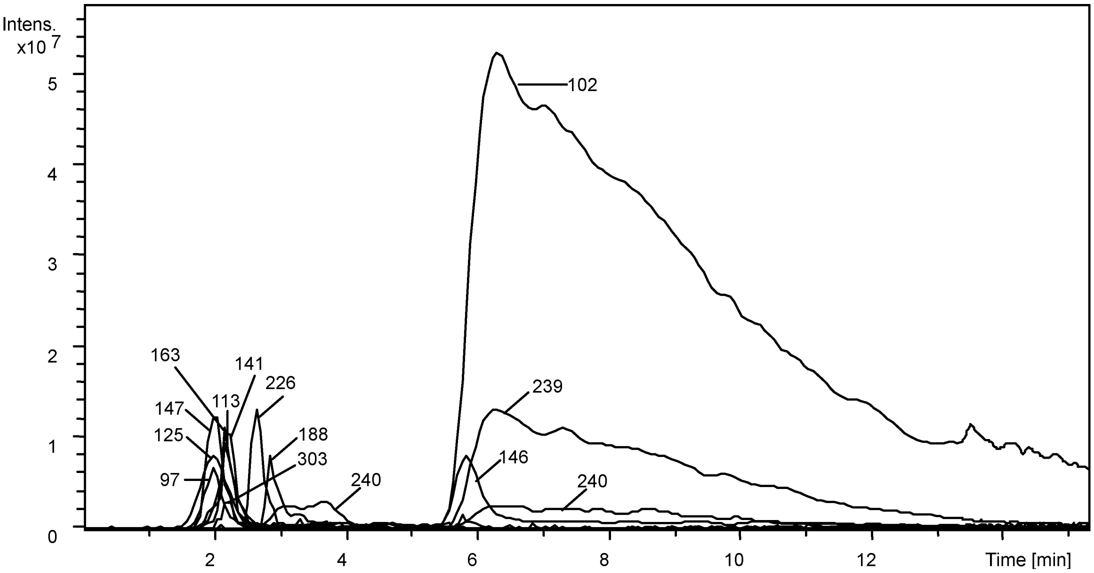
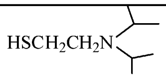
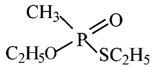
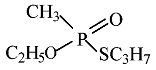
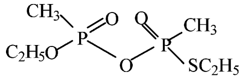
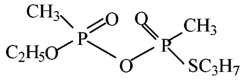
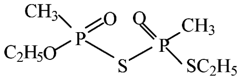
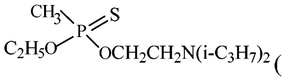
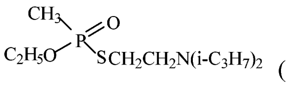
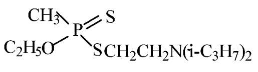
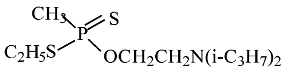
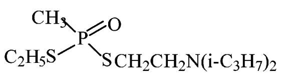


Figure 4. Liquid chromatogram with extracted ion chromatograms of VX droplets upon 2 h of on irradiation, showing the M + H$^+$ peaks that are labeled.

TABLE 2: Determined Structural Formula of the Detected Products Analysis by GC/MS and Main Mass Fragments of the Detected Species

No.	Structural formula	Main mass fragments of the detected species
1		44, 61, 72, 86, 114, 146, 161
2	 $CH_3P(=O)(C_2H_5O)(SC_2H_5)$	47, 65, 79, 80, 95, 96, 108, 124, 140, 168
3	 $CH_3P(=O)(C_2H_5O)(SC_3H_7)$	45, 79, 80, 95, 96, 108, 121, 140, 182
4	 $CH_3P(=O)(C_2H_5O)\text{-}O\text{-}P(=O)(CH_3)(SC_2H_5)$	47, 63, 79, 95, 97, 157, 159, 188, 190, 218, 246
5	 $CH_3P(=O)(C_2H_5O)\text{-}O\text{-}P(=O)(CH_3)(SC_3H_7)$	63, 79, 95, 97, 157, 159, 172, 174, 188, 190, 218, 260
6	 $CH_3P(=O)(C_2H_5O)\text{-}S\text{-}P(=O)(CH_3)(SC_2H_5)$	63, 79, 95, 112, 157, 172, 174, 185, 206, 234, 262
7	 $CH_3P(=S)(C_2H_5O)(OCH_2CH_2N(i\text{-}C_3H_7)_2)$ (isomer of VX)	43, 70, 114, 127, 167, 190, 224, 252
8	 $CH_3P(=O)(C_2H_5O)(SCH_2CH_2N(i\text{-}C_3H_7)_2)$ (VX)	43, 70, 114, 127, 167, 224, 252
9	 $CH_3P(=S)(C_2H_5O)(SCH_2CH_2N(i\text{-}C_3H_7)_2)$	43, 72, 95, 114, 127, 155
10	 $CH_3P(=S)(C_2H_5S)(OCH_2CH_2N(i\text{-}C_3H_7)_2)$	43, 72, 114, 127
11	 $CH_3P(=O)(C_2H_5S)(SCH_2CH_2N(i\text{-}C_3H_7)_2)$	43, 72, 114, 127
12	$(H_7C_3\text{-}i)_2CH_2CH_2S\text{-}SCH_2CH_2N(i\text{-}C_3H_7)_2$	43, 72, 114, 127, 144, 193

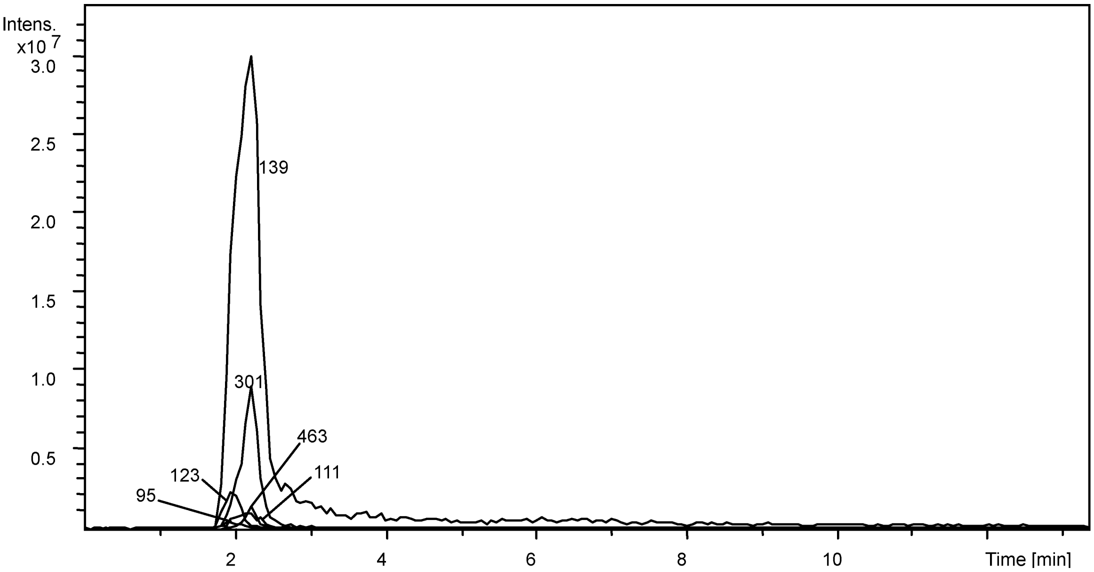
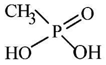
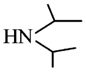
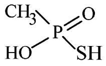
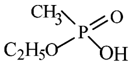
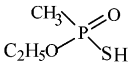
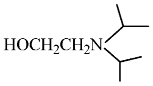
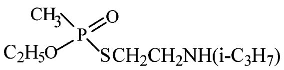
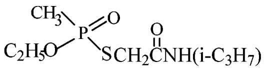


Figure 5. Liquid chromatogram with extracted ion chromatograms of VX droplets upon 2 h of on irradiation, showing the $M - H^+$ peaks that are labeled.

TABLE 3: Possible Photoreaction Products of VX Based on LC/MS Profile for $M-H^+$ and $M+H^+$

No.	Structural formula	Mass
1		$M-H^+=95$ $M+H^+=97$
2		$M+H^+=102$
3		$M-H^+=111$ $M+H^+=113$
4		$M-H^+=123$ $M+H^+=125$
5		$M-H^+=139$ $M+H^+=141$
6		$M+H^+=146$
7		$M+H^+=226$
8		$M+H^+=240$
9	Unknown compound	$M+H^+=147$
10	Unknown compound	$M+H^+=163$
11	Unknown compound	$M+H^+=188$
12	Unknown compound	$M+H^+=239$
13	Unknown compound	$M+H^+=303$

obviously and to lose around 20% weight. The percentage of VX detected by GC-FID has greatly decreased down to 6% upon 2 h of on irradiation. This would demonstrate that VX droplets could easily and chemically be destroyed upon UV light irradiation into nonvolatile species. The following experimental work will be devoted to analyzing the residual products from the photoassisted reaction of VX droplets.

Reaction Products. Table 1 indicated that about 25% of the photoassisted reaction products have been volatilized into air. The residual products that were slightly volatile would be analyzed by the methods of GC/MS, LC/MS, and NMR and try to identify each compound in the products to the greatest extent.

The total ion chromatography of GC/MS for the residue of VX droplets upon 2 h of on irradiation was presented in Figure 3. Twelve compounds were distinctly detected as the photoreaction products, and the possible structural formulas were determined according to the retention time and mass spectra of detected species and presented in Table 2.

Polar compounds involved in the products were analyzed by LC/MS. The spectrum of LC/MS mostly provides only the molecular ion ($M + H^+$ or $M - H^+$), so little molecular information is available. One could only identify compounds based on the retention time in LC column and $M \pm H^+$ peaks. Liquid chromatogram with extracted ion chromatograms ($M + H^+$ and $M - H^+$) of VX droplets upon 2 h of on irradiation was present in Figure 4 and Figure 5, respectively.

It was shown that a great variety of $M + H^+$ peaks were detected in this chromatogram; possible structural formulas for these species were deduced and presented in Table 3. The $M - H^+$ peaks at 95, 111, 123, and 139 could also demonstrate the existence of ethyl methylphosphonate and ethyl methylphosphonothioate in the residue of VX droplets upon UV light irradiation. On the other hand, there was still lack of evidence to possibly determine the structural formulas for the $M + H^+$ peaks at 147, 163, 188, 239, and 303 and the $M - H^+$ peaks at 301 and 463.

Several phosphorothionates, 7, 9, and 10 in Table 2 as the photoisomers of compounds 8 and 11 in Table 2, were detected by GC/MS and had a short retention time in GC column in comparison with their parent compounds. This clearly indicated that the VX molecule could undergo a photoisomerization to convert an S-ester to a corresponding O-ester. It was quite consistent with what was previously described in the literature.[18] On the other hand, a small amount of oxidation product of VX (compound 8 in Table 3) was also detected by LC/MS. This revealed that the VX molecule possibly has reacted with photogenerated ozone in air at room temperature.

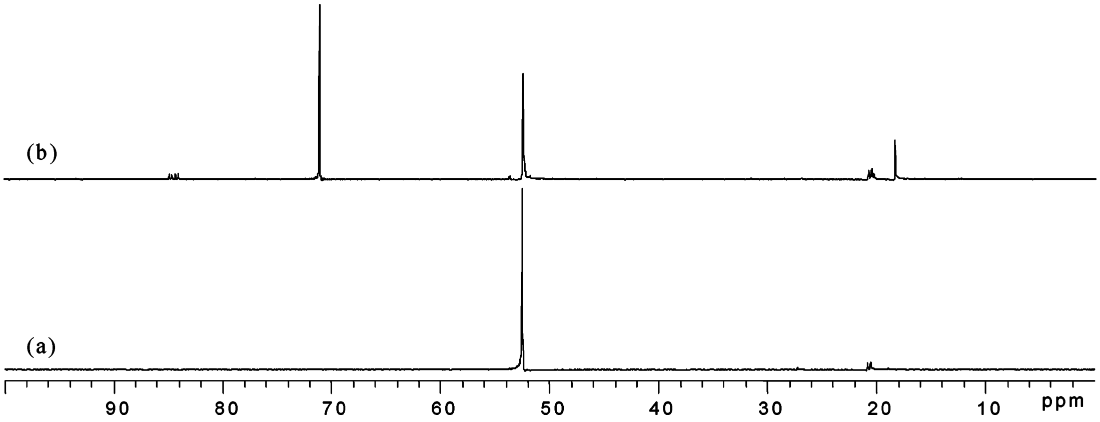


Figure 6. ^{31}P NMR spectra for: (a) neat VX; (b) residue of VX droplets upon 2 h of on irradiation.

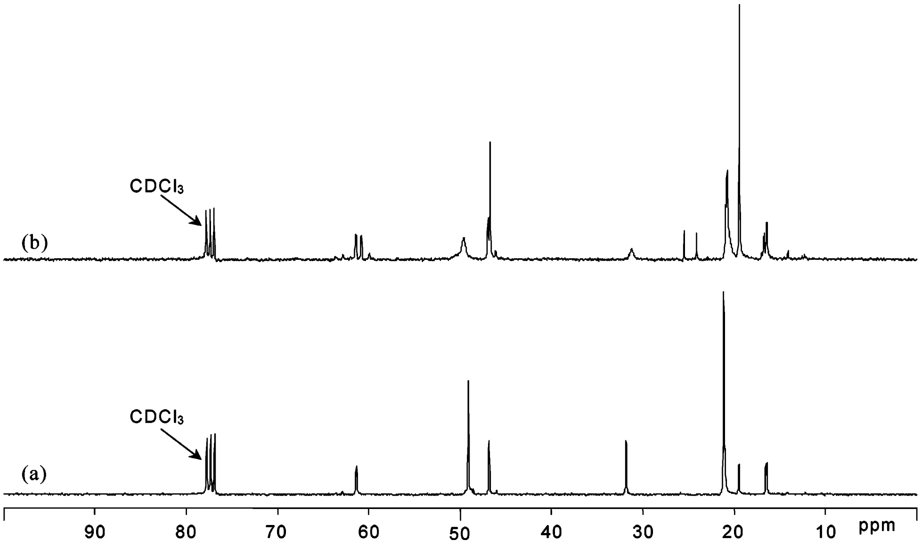


Figure 7. ^{13}C NMR spectra for: (a) neat VX; (b) residue of VX droplets upon 2 h of on irradiation.

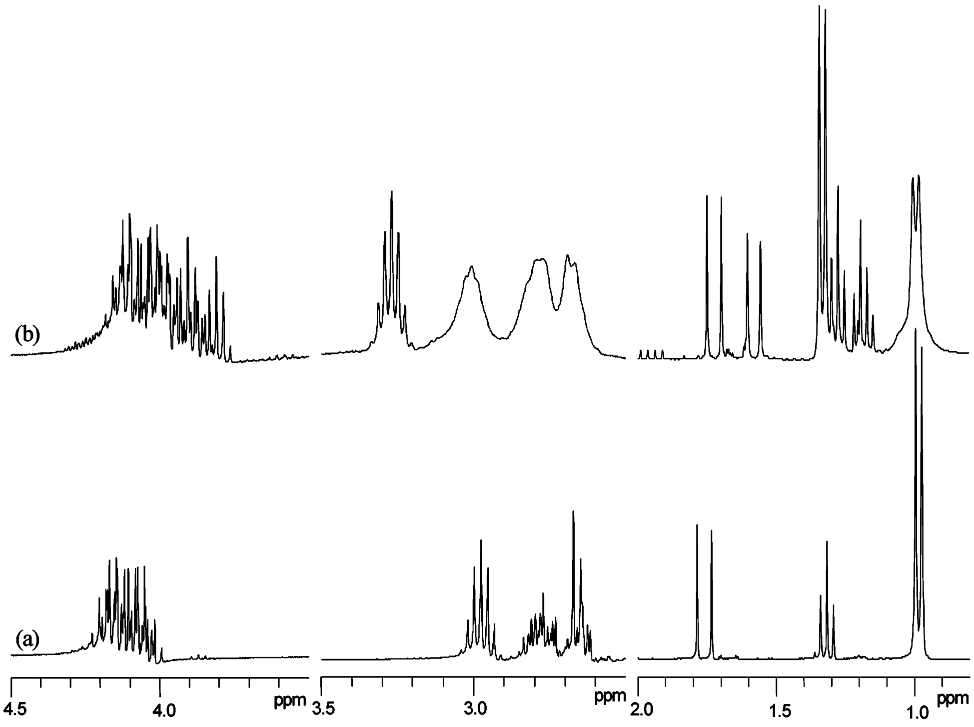
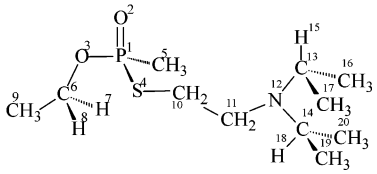


Figure 8. ^{1}H NMR spectra for: (a) neat VX; (b) residue of VX droplets upon 2 h of on irradiation.

TABLE 4: Exited Orbits and Corresponding Excitation Energy of the VX Molecule from the Ground State to a Triplet Excited State

orbits excited (from → to)	coefficients of the wave function	excitation energy (eV)	wavelength (nm)	intensity factor
74 → 76	0.606	4.47	278	0.0212
71 → 73	0.917	4.75	261	0.0145
74 → 77	0.934	5.69	218	0.0357

CHART 1



Both GC/MS and LC/MS analysis results showed that photoassisted reaction of VX droplets yielded a complex mixture of products. It was likely that the VX molecule probably underwent a photoreaction via a cleavage of P−S, C−S, and C−N bonds and was destroyed chemically in skeletal structure. This will be furthermore supported by the following results of NMR analysis.

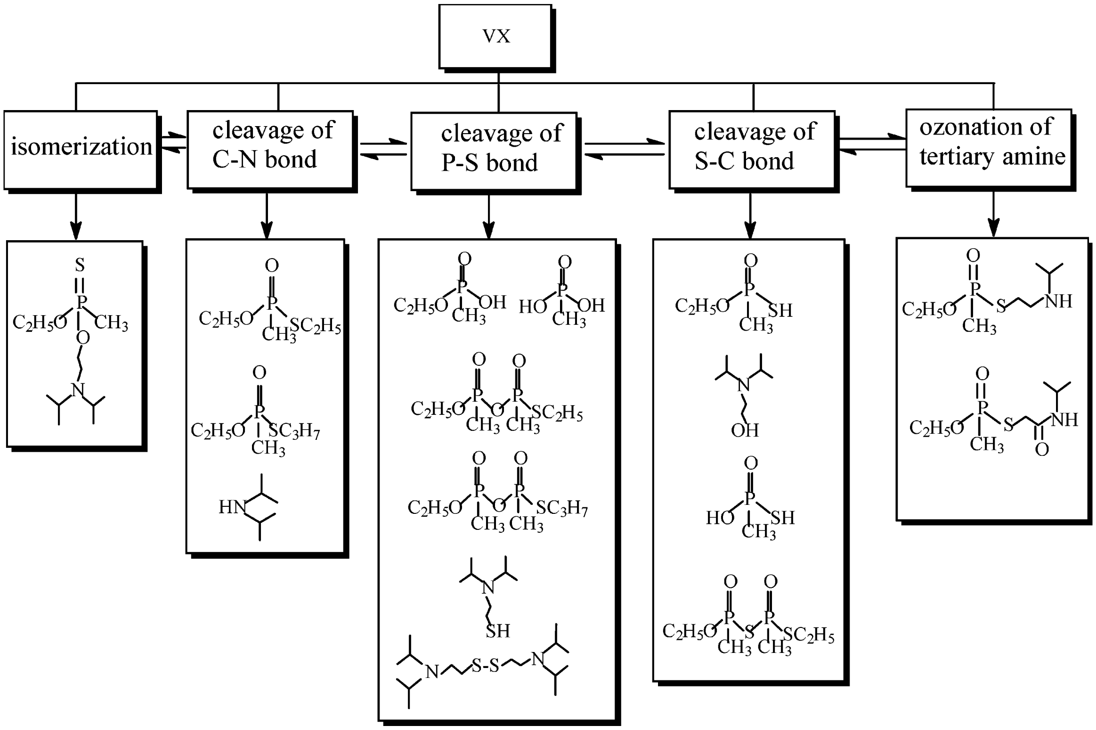
^{31}P NMR spectra for neat VX and its residue upon 2 h of on irradiation were illustrated in Figure 6. VX yielded a sharp peak at 52.5 ppm, and several small peaks around 20 ppm which probably associated with a trace amount of impurities such as methylphosphonic acid, ethyl methylphosphonate, etc. It can be seen from Figure 6b that several P-containing compounds were involved in the residue. A singlet peak at 71.0 ppm was possibly yielded by the main product ethyl methylphosphonothiolate. A trace amount of other phosphonothionates was also detected and gave several small peaks at around 85 ppm. Besides, peaks around 20 ppm were observed to rise, which could further prove that phosphonic acid and phosphonate were generated during photoassisted reaction of VX droplets. It was certain that the singlet peak at 52.4 was yielded by VX, but whose amount seemed to be more than that detected by GC (Table 1). This might indicate that the isomer of VX, phosphonothionate, as detected by GC/MS within several hours upon irradiation of UV light, has returned back to VX upon deposition of sample over days. This would be in agreement with that stated in the literature.[18]

TABLE 5: Comparison of the Ground- and Excited-State Bond Lengths in the VX Molecule

bond	bond length (Å)		
	ground state	singlet excited state	triplet excited state
$P_1=O_2$	1.45	1.58	1.70
P_1-O_3	1.76	1.69	1.69
P_1-C_5	1.86	1.84	1.83
P_1-S_4	2.10	2.21	4.32
O_3-C_6	1.43	1.43	1.43
C_6-C_9	1.53	1.54	1.54
C_6-H	1.06	1.08	1.08
C_9-H	1.06	1.08	1.08
C_5-H	1.06	1.08	1.08
S_4-C_{10}	1.78	1.80	1.79
$C_{10}-H$	1.06	1.08	1.08
$C_{10}-C_{11}$	1.53	1.55	1.55
$C_{11}-H$	1.06	1.08	1.08
$C_{11}-N_{12}$	1.46	1.48	1.48
$N_{12}-C_{13}$	1.47	1.48	1.48
$C_{13}-H$	1.06	1.08	1.08
$C_{13}-C_{16}$	1.53	1.55	1.55
$C_{13}-C_{17}$	1.53	1.55	1.55
$C_{16}-H$	1.06	1.08	1.08
$C_{17}-H$	1.06	1.08	1.08
$N_{12}-C_{14}$	1.47	1.48	1.48
$C_{14}-H$	1.06	1.08	1.08
$C_{13}-C_{19}$	1.53	1.55	1.55
$C_{13}-C_{20}$	1.53	1.55	1.55
$C_{19}-H$	1.06	1.08	1.08
$C_{20}-H$	1.06	1.08	1.08

^{13}C NMR spectra of the residue indicated that there had no significant change in chemical environment around C atom in comparison with that of neat VX. This would suggest that no significant reaction occurred upon C atom in VX molecule.

SCHEME 1



^{1}H NMR spectra provided a complex information of the residue, as presented in Figure 8b. It indicated that some compounds in the residue still maintain the $CH_3(CH_3CH_2O)P$ structure frame, as evidenced by two doublet peaks at 1.5 and 1.7 ppm and a multifold peak at 4.1 ppm. In addition, one could also observe a 7-fold peak at 3.3 ppm and a doublet peak at 1.0 ppm due to the isopropyl in the products. This suggested that P−C and C−H bonds in the VX molecule were not significantly cleaved in the photoassisted reaction.

Quantum Chemical Calculation. Quantum chemical calculations were used to study the photoreaction of VX molecule. Table 4 presented the calculated exited orbits and corresponding excitation energy of VX molecule from ground state to a triplet excited state. The calculated result was quite consistent with the measured UV−vis spectrum of VX in ethanol, as presented in Figure 1. This would indicate that the three absorption peaks around 209, 238, and 266 nm really resulted from VX instead of any impurity. It can be seen that the wavelength of the photon should be less than 278 nm, which could possibly excite VX molecule to a triplet excited state and initiate a photoreaction. On the other hand, photon energy should be no less than 6.2 eV, that is to say a wavelength less than 200 nm, for the excitation of VX molecule to a singlet excited state. Obviously, photons of near UV light could not meet this challenge. Therefore, photoreaction of VX under UV light irradiation would start only from the triplet-excited-state molecule.

Once the VX molecule was excited upon absorption of sufficient energy under UV light irradiation, structure parameters would be expected to vary. The calculated bond lengths in VX molecule (labeled in Chart 1) of ground state, singlet excited state, and triplet excited state were listed in Table 5. No significant change was observed in bond length for the molecule of VX at the singlet excited state in comparison with that of ground state. Nevertheless, once the VX molecule was excited to a triplet exited state, the length of the P−S bond would change dramatically from 2.10 Å (ground state) to 4.32 Å (triplet excited state) and the P═O bond was also observed to lengthen from 1.45 Å (ground state) to 1.70 Å (triplet excited state). This would imply that both P═O and P−S bonds were able to be activated, and the molecule of VX at triplet excited state would be expected to undergo a photoreaction.

Mechanism Aspect. It has been experimentally demonstrated that the molecule of VX droplets in air could be easily and chemically degraded into other compounds under UV light irradiation from germicidal lamp over sufficient time. The identification of the products in the photoassisted reaction by GC/MS, LC/MS, and NMR would come to the conclusion that the VX molecule in air under UV light irradiation could undergo cleavage of P−S, S−C, and C−N bonds, isomerization of S-esters to O-esters, and ozonation. Therefore, two principal pathways at least should be considered in the photoassisted reaction of VX droplets upon UV light irradiation. First, VX molecule could absorb a photon with sufficient energy and perform an effective electron transition to a triplet excited state. Both P−S and P═O bonds in VX molecule were lengthened, as supported by quantum chemical calculation result. Consequently, the VX molecule would undergo an isomerization, and a cleavage of P−S, S−C, and C−N, which in turn followed by rearrangement in skeletal structure and hydrolysis. Second, the VX molecule could be oxidized by photogenerated ozone via an ozonation of tertiary amines. This reaction pathway was schemed as shown in Scheme 1.

4. Conclusions

VX droplets in air could be significantly eliminated under germicidal lamp irradiation. Reaction of VX droplets under UV light irradiation could mainly be summarized as two pathways, i.e., photoreaction of VX molecule as well as reaction between VX and photogenerated ozone. The photoreaction of the VX molecule would undergo an isomerization, and a cleavage of P−S, S−C, and C−N, which in turn followed by rearrangement in skeletal structure and hydrolysis. Reaction between VX and photogenerated ozone would undergo via an ozonation of tertiary amines in VX molecule.

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