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Photoassisted removal of sarin vapor in air under UV light irradiation

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Abstract

The photoassisted reaction of sarin vapor in air was carried out in a self-designed photoreactor, and several factors influenced upon the reaction were experimentally examined. The experimental results showed that sarin vapor in air could be destructively eliminated under the irradiation of a germicidal lamp. It was demonstrated that photoreaction of sarin was the main pathway that lead to the elimination of sarin vapor. The relative elimination rate of sarin vapor was significantly promoted by strengthening the irradiation density or lowering the initial concentration, and yet was less significantly influenced by the air humidity. The photoreaction products analyzed by liquid chromatography/mass spectrometry (LC/MS), and nuclear magnetic resonance (NMR) strongly supported that sarin molecules were finally converted into a kind of nontoxic polymer under UV light irradiation.

Keywords: Sarin (GB; isopropyl methylphosphonofluoridate); Photoreaction; UV light irradiation; Decontamination

1. Introduction

Decontamination of air polluted by the chemical and biological warfare agents (CBWAs) is of great importance to the chemical and biological defense, as well as the technology needs for countering terrorism. Over the last decades, military chemists have always been trying to develop new methods to safely and conveniently eliminate these pollutants, including the most toxic nerve agents [1]. Early studies have investigated the catalytic decomposition of dimethyl methylphosphonate (DMMP, a widely used simulant for nerve agents) using metal and metal oxides, and high DMMP conversions were obtained with CO_2 and H_2O as the major products [2–5]. Klabunde and co-workers have extensively developed a series of nanoparticulate metal oxides for decontaminating CBWAs at ambient temperature, which were demonstrated to be much more reactive than the common oxides [6–9]. Recently, reports emerged that photocatalysis has a favorable technical potential to mineralize a range of toxic substances [10,11]. Studies on photocatalytic degradation of organophosphonates were frequently documented both in air and aqueous solution, typically using TiO_2 [12–17]. Results on photocatalytic degradation of DMMP indicated that both the P–C and P–O bonds can be destroyed, products like CO, CO_2 and methanol were detected in the gas phase, P-containing species including PO_4^{3-} were proved to form over the catalysts [13,14]. However, photodegradation of these pollutants was scarcely mentioned in these studies. In fact, the phosphate group, despite having a weak UV–vis absorption, is viewed as a relatively photoreactive function group [18]. As one of the phosphate substances, sarin is also expected to be decomposed by photo irradiation.

In this work, the photoassisted reaction of sarin vapor under UV light irradiation was carried out. Several influencing factors such the initial concentration of sarin, the irradiation intensity and air humidity influenced upon the reaction were experimentally examined. Gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS) and nuclear magnetic resonance (NMR) approaches were employed to identify the reaction products.

2. Experimental

2.1. Materials

Sarin has a purity >99%. All solvents were of analytical grade or distilled prior to use. *Caution*: In view of its high toxicity, sarin should be handled only by the trained personnel using applicable safety procedures.

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2.2. Photoassisted reaction of sarin vapor

A self-designed photoreactor was used in the experiment. It was composed of a quartz light window and a columnar steel-stainless chamber, both of which were adhered together by thermo-melting adhesive to form a space of approximately 3.3 L, detailed description of the photoreactor has been reported previously [19]. Sarin vapor was generated by a method of static vacuum, i.e., to degas the reactor, to inject sarin liquid into the chamber with microsyringe, and then to introduce air upon complete vaporization. The UV light was introduced into the reactor through the crystalline quartz light window. An 8 W germicidal lamp (type ZSZ8) with 253.7 nm peak density was used as the illuminator. The irradiation intensity was determined with an ultraviolet photometer (Photoelectric Instrument Factory of Beijing Normal University) close to the inner surface of the light window. The photoassisted reactions were carried out under the conditions of room temperature at 20–25 °C.

2.3. Analysis of sarin and its photodegradation products

The UV–vis absorption spectra of sarin in air and ethanol solution was measured with a HP-8453 UV–vis spectrophotometer. A quartz absorption cell with a length of 10 mm was used for the measurement in both air and ethanol solution. The spectrum was obtained with neat air and ethanol as the blank reference, respectively.

The concentration of sarin vapor was determined by a colorimetric method, i.e., to purge the reactor with fresh dry air, to absorb the sweep gas by cooled ethanol. Sarin in ethanol was quantitatively measured by a colorimetric method based on the Schöenemann reaction [20].

To collect the photodegradation products of sarin vapor, a dynamic photoreaction was designed and performed. The dynamic photoreaction was carried out in a quartz tube with an inside radius of 2 cm and length of 15 cm as photoreactor. One can make a sarin-contaminated airflow through a quartz tube under the irradiation of a germicidal lamp; the tail gas was absorbed by cooled dichloromethane and methanol. The dichloromethane absorbent was analyzed with an Agilent 6890/5973 GC/MS, equipped with a HP-5 capillary column employing the temperature ramp 40–280 °C at 15 °C/min. And qualitative analysis of the methanol absorbent was performed with an Agilent 1100 LC/MS, equipped with a nonpolar column (Zorbax SB-C18 column 30 mm × 2.1 mm × 3 μm). The mobile phase used was 0.1% acetic acid at a rate of 0.2 mL/min, column temperature was 40 °C and scan range over 50–2000 *m*/*z*.

The substance adhered on the inner surface of light window was washed into the $CDCl_3$, and analyzed by a Varian Mercury Vx300 NMR spectrometer. The observation frequencies were 121 MHz for $^{31}P\{^1H\}$, 75 MHz for $^{13}C\{^1H\}$ and 300 MHz for ^1H. Chemical shifts were referenced to external 85% H_3PO_4 (0 ppm), CS_2 (0 ppm), and TMS (0 ppm), respectively.

3. Results and discussion

3.1. UV–vis absorption spectra of sarin

As presented in Fig. 1, sarin in ethanol solution only presents a very weak absorption peak around 204 nm, and sarin vapor in air yields no obvious absorption peak in UV–vis region. The peak around 204 nm may be associated with the residual absorption of the ethanol solvent. Thus, it can be seen that sarin has a very weak absorption in UV–vis region so that it is undetectable with the spectrometer.

3.2. Photoassisted removal of sarin vapor

As presented in Fig. 2, sarin vapor behaved to be somewhat unstable in air, the concentration of sarin would slightly decrease after it was generated. It would decrease down to a half dose after stewing in darkness over 12 h. This was mainly attributed to the hydrolysis of sarin molecules within the reactor. When sarin vapor in air was directly exposed to the UV light from a germicidal lamp, the concentration of sarin was observed to decrease quickly. Nearly 99% of the sarin vapor was eliminated

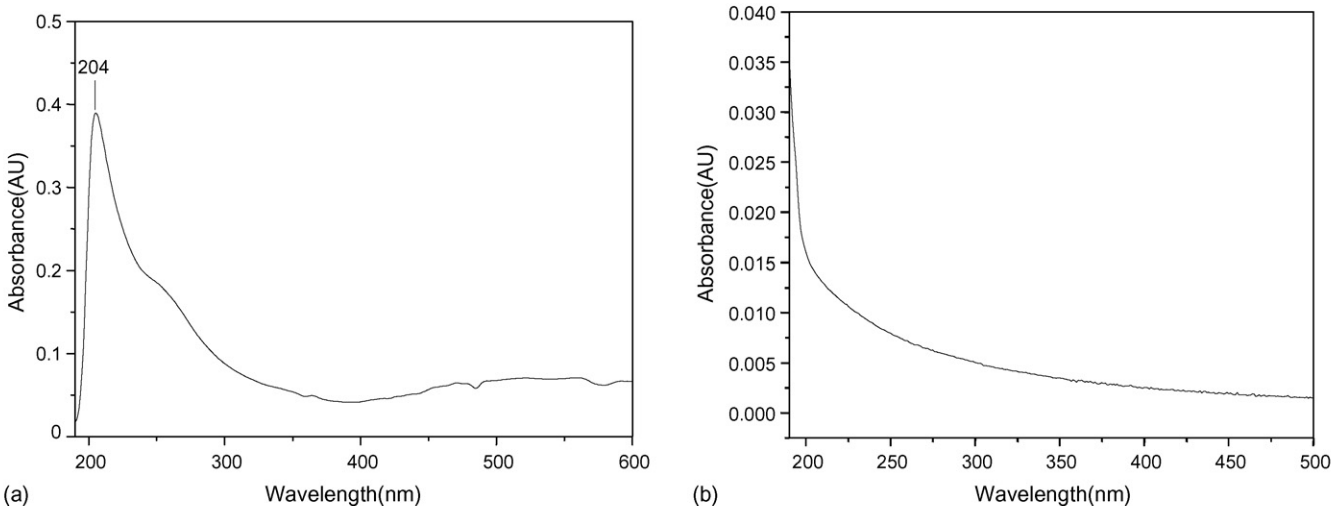


Fig. 1. UV–vis absorption spectra of sarin: (a) 0.2 M of sarin in ethanol and (b) saturated sarin vapor in air at 20 °C.

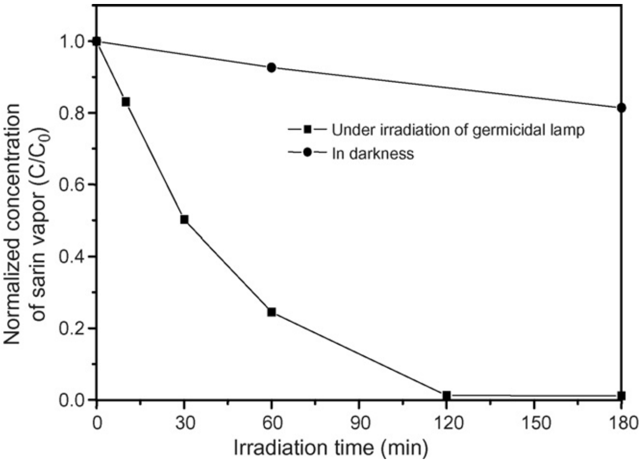


Fig. 2. Photoassisted reaction of sarin vapor under UV light irradiation. The initial concentration of sarin vapor is 1.67 mg/L, the irradiation intensity is 0.6 mW/cm^2, and the relative humidity is 32%.

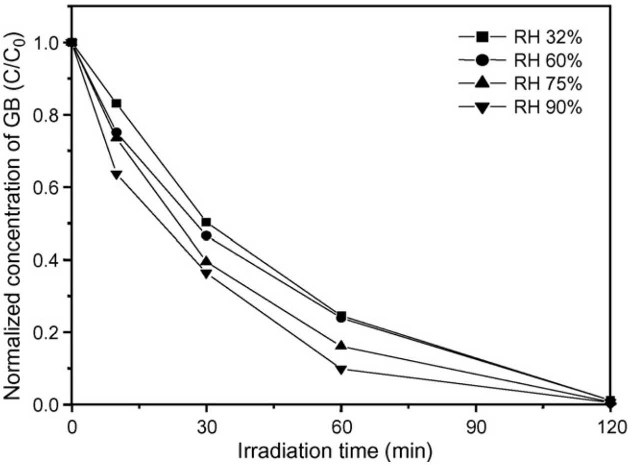


Fig. 4. Photoassisted reaction of sarin vapor under different relative humidity. The irradiation intensity of germicidal lamp is 0.6 mW/cm^2, and the initial concentration of sarin vapor is 1.67 mg/L.

after being irradiated for 2 h. This indicated that sarin vapor could be destructively eliminated under UV light irradiation.

3.3. Several influencing factors to the photoassisted removal of sarin vapor

In order to make a further knowledge on the photoassisted removal of sarin vapor, the effects of several influencing factors such as the vapor concentration, air humidity and irradiation intensity were examined upon the photoreaction. The initial concentration of sarin vapor can be adjusted by varying the volume of the injected sarin liquid. The irradiation intensity was adjusted by changing the distance between the lamp and the light window. And the air humidity can be augmented by injecting water into the photoreactor.

Effects of the initial concentration, air humidity and irradiation intensity to the photoassisted reaction of sarin vapor were, respectively, presented in Figs. 3–5. In order to have a kinetic comparison, the apparent first order reaction rate constants for different reaction conditions were calculated and presented in Table 1. It can be seen that the sarin elimination reaction rate increases along with decreasing the initial concentration of sarin vapor. The photolytic reaction rate was somewhat influenced by the air humidity, and a high relative humidity would favor the photolytic reaction of sarin vapor. Moreover, the elimination rate of sarin vapor could be greatly accelerated by strengthening the irradiation intensity.

For the influence of air humidity, one may expect that the hydrolysis of sarin in darkness will simultaneously be accelerated along increasing the air humidity. In order to make clear whether the increase of humidity increases photodegradation step or just hydrolysis, a dark degradation experiment of sarin in air humidity of 75% was performed. It was observed that hydrolysis of sarin would be slightly accelerated when the air humidity was increased from 36% to 75%, as shown in Fig. 6. In fact, the concentration of H_2O has achieved around 30 times higher than that of sarin at the humidity of 36%, which would be sufficient for the hydrolytic reaction. Then, the increase of humidity seemed to be nonsignificant for the hydrolysis of sarin vapor. It also can be seen from Fig. 5 that the elimination rate of sarin

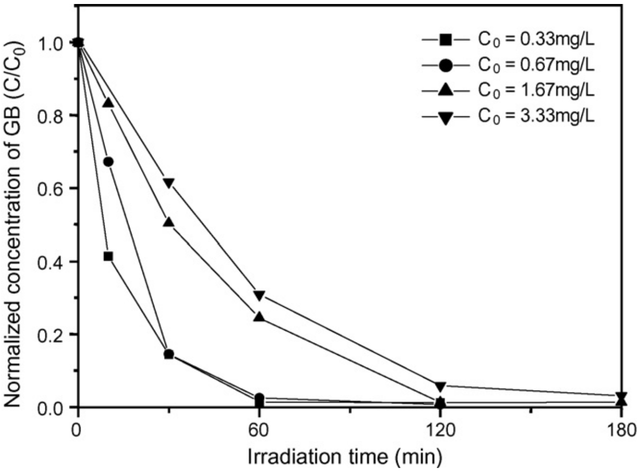


Fig. 3. Photoassisted reaction of sarin vapor of varied initial concentrations. The irradiation intensity is 0.6 mW/cm^2.

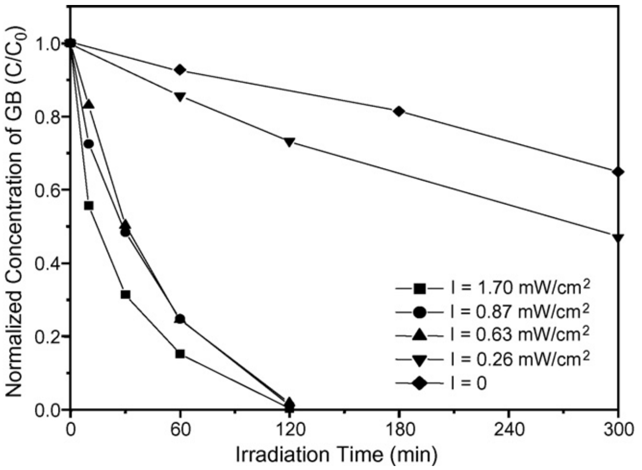


Fig. 5. Photoassisted reaction of sarin vapor under different UV light irradiation intensity. The initial concentration of sarin vapor is 1.67 mg/L.

Table 1
The apparent first-order reaction rate constants k_1 for photodegradation of sarin vapor under different conditions

Reaction conditions			k_1 (min^{-1})
Initial concentration (mg/L)	Air humidity (%)	Irradiation intensity (mW/cm^2)	
0.33	30–50	0.63	0.0670
0.66			0.0464
1.67			0.0232
3.33			0.0205
1.67	32	0.63	0.0232
	60		0.0259
	75		0.0306
	90		0.0377
1.67	30–50	0	0.0012
		0.26	0.0024
		0.63	0.0232
		0.87	0.0286
		1.70	0.0406

vapor through hydrolysis was much slower than that through photodegradation. Therefore, the increasing of sarin hydrolysis can be negligible during the photodegradation process.

Thus, it can be seen that the degradation rate of sarin vapor was significantly promoted by strengthening the irradiation density or lowering the initial concentration, and yet was less significantly influenced by the air humidity. Generally, the photodegradation rate of sarin vapor was possibly dominated by the primary photoreaction step, which was largely relied on the irradiation intensity. Nevertheless, H_2O molecule might possibly be involved in the secondary steps, and affected the degradation rate slightly.

3.4. Photoassisted reaction products of sarin vapor

The forementioned experimental results have demonstrated that sarin vapor could be eliminated by UV light irradiation, but we still could not detect any intermediates or products in the gas phase by the direct sampling MS, GC/MS and in situ FTIR. In spite of that, one could obviously observe that a kind of sticky substance (hereafter named as "light window fog") was formed onto the inner surface of the light window during the photoassisted reaction of sarin vapor. The experiments have testified that this substance has no inhibiting effect against the acetylcholinesterase (Ache), which means it has no neurotoxicity. Besides, it has an ultra low volatility, even sweeping the reactor could not get rid of it. This substance was suspected to be a kind of polymer as the photoreaction products. Then, the NMR and LC/MS approaches were applied to identify the photoreaction products.

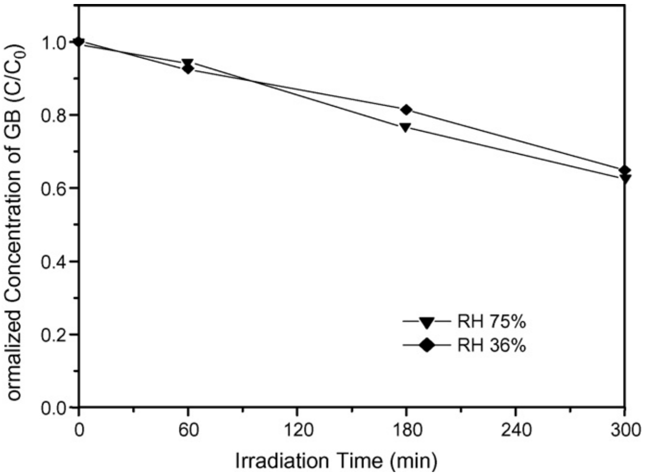


Fig. 6. Degradation of sarin vapor in darkness in different humidity. The initial concentration of sarin vapor is 1.67 mg/L.

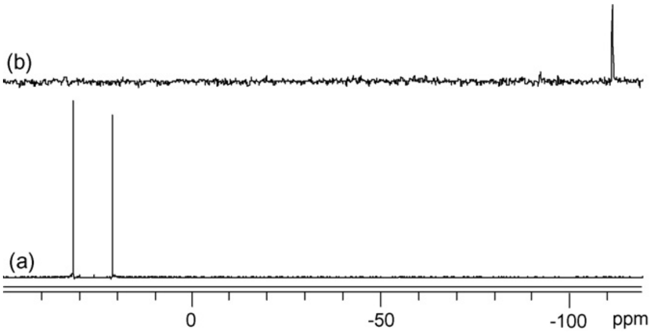


Fig. 7. ^{31}P NMR spectra for: (a) neat sarin; (b) "light window fog" substance.

^{31}P NMR spectra for neat sarin and the "light window fog" were illustrated in Fig. 7. Sarin exhibits a well-resolved doublet at 27.2 ppm ($^2J_{P–F} = 1046.5$ Hz). In the spectrum of the "light window fog", a single resonance was observed in the high field, and its chemical shift $\delta = -111.9$ ppm. This was quite similar to that of the phosphorus-containing polymers. The fact that chemical shifts appeared in high field might suggest that the coordination circumstances of P atom probably changed significantly.

Fig. 8 presented the ^{1}H NMR spectra of neat sarin and "light window fog" substance. In spectrum of sarin, a 14-fold peak was observed at 4.8 ppm corresponding to the tertiary H in $-C_3H_7$ coupling to ^{1}H and ^{31}P nuclei. Whereas, a doublet of doublets ($^2J_{H–H} = 6.2$ Hz, $^2J_{P–H} = 0.4$ Hz) appears around 1.3 ppm could be attributed to the coupling effect of the primary H in $-C_3H_7$ to the tertiary ^{1}H and ^{31}P nuclei. The primary H in the P–CH_3 group also yield a doublet of doublets ($^2J_{P–H} = 18.6$ Hz, $^3J_{F–H} = 5.7$ Hz) resonance around 1.6 ppm. However, the ^{1}H NMR spectrum of "light window fog" was widely different from that of sarin. A single resonance was observed at 7.26 ppm, which suggested that $-$OH was probably involved in the substance. Besides, there were four broad peaks with a chemical shifts less than 1.6 ppm appeared in the ^{1}H spectrum, which were also quite similar to those of macromolecular compounds. This could evident that a polymerization might occur during the photoassisted reaction of sarin vapor.

The "light window fog" was also washed into the methanol and analyzed by the LC/MS. However, it was still not possible to observe any peak of the "light window fog" by LC/MS under this experiment condition. This was possibly because its molecular weight was too heavy to get through the liquid chromatography column. Hence, another dynamic experiment as described in the experimental section was designed to capture the photoreaction

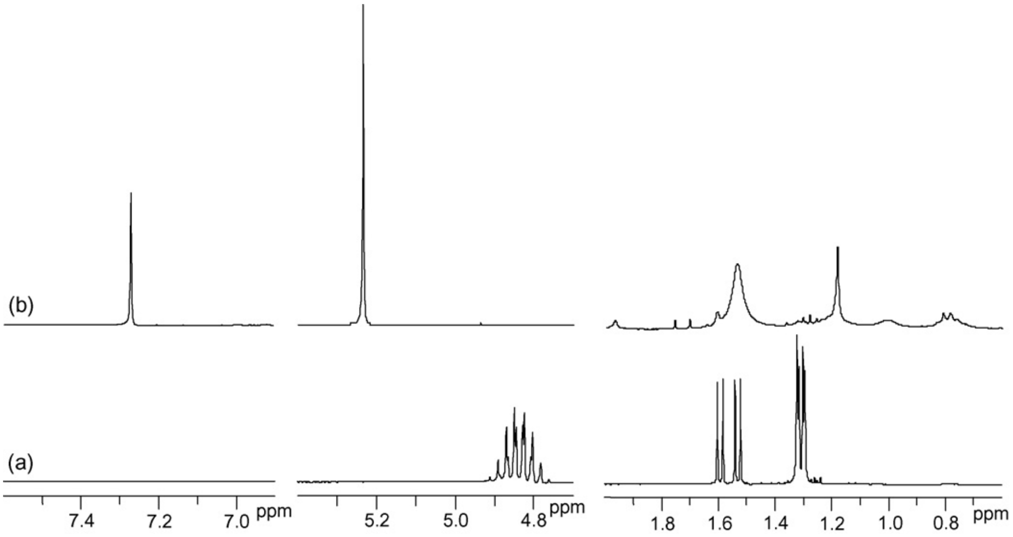


Fig. 8. ^{1}H NMR spectra for: (a) neat sarin; (b) "light window fog" substance.

products. The polymerization degree was expected to be lower because of a shorten contact time (only 15 s) of sarin with the UV light.

Fig. 9 illustrated the LC/MS spectra for the products collected within 3 h in the photoreaction of sarin at the dynamic condition. It can be seen from the negative chromatogram profile that some substances with molecular weight more than 1400 were formed during the photoreaction. This could confirm that a polymerization occurred during the photoreaction of sarin vapor, and the molecular weight of the polymer produced in dynamic quartz tube was much smaller because of a very short contact time of sarin vapor with the UV light.

3.5. Removal pathway of sarin vapor

It has been demonstrated above that sarin vapor could be eliminated under UV light irradiation. Then we imagined three possible pathways that might lead to the elimination of sarin vapor: (a) direct photolysis of sarin molecules; (b) reaction between the excited sarin molecules and other species within the reactor, such as H_2O, O_2, or ground-state sarin molecules; (c) decomposed by the photogenerated oxidative species or free radicals. To clarify the main pathway that lead to the elimination of sarin vapor, a series of experiments were designed

Table 2
The photoassisted elimination ratio of sarin vapor after being irradiated for 1 h in different gas media

Gas media	Elimination ratio (%)
Air of 30% humidity	75
Dry air	65
Pure nitrogen	68

The initial concentration was generated as 1.67 mg/L. The irradiation intensity is measured as 0.6 mW/cm^2.

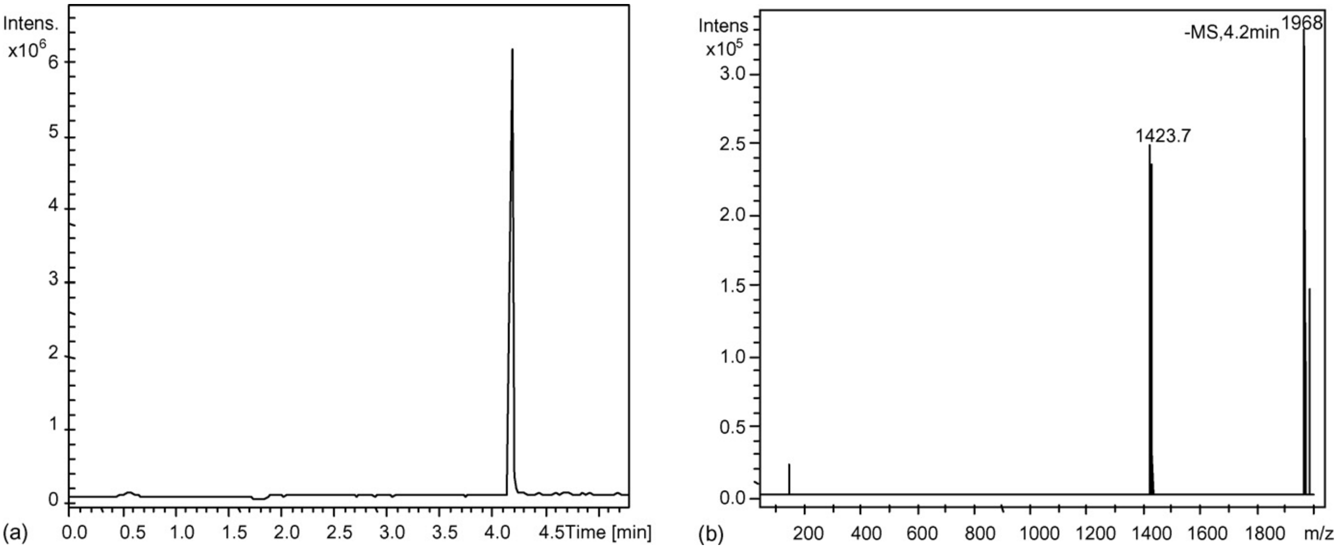
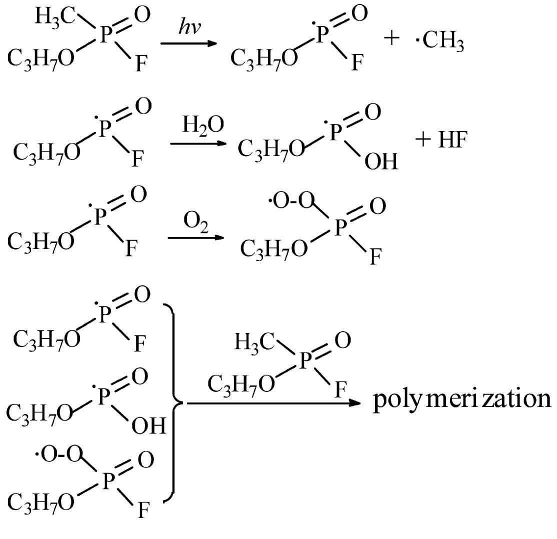


Fig. 9. LC/MS spectra of photoreaction products of sarin at dynamic conditions: (a) total negative chromatogram profile; (b) M–H$^+$ mass spectra for the observed peaks in (a).

and performed. Firstly, the photoreactions of sarin vapor in dry air and N_2 were carried out in the photoreactor using the same irradiation conditions. It was observed that the photoassisted elimination of sarin would similarly occur in dry air and N_2 atmosphere, despite slightly slower than that in air of 30% humidity. Table 2 presented the photoassisted elimination ratio of sarin vapor after being irradiated for 1 h in varied gas media. It implied that the photoassisted elimination of sarin vapor was not significantly influenced by the gas media, H_2O and O_2 in air was probably merely a promoter for the photoassisted reaction.

In addition, contribution of the wall contaminants was also experimentally examined. We firstly cleaned the inner surface of the reactor with acetone and deionized water for several times each, and then pretreated the reactor by UV light irradiation over 24 h. Photoreaction of sarin vapor was performed in the freshly cleaned reactor. It was observed that sarin vapor can also be destroyed under UV light irradiation. There was nearly 80% of the sarin vapor was eliminated after being irradiated for 1 h, which was approximately equal to that the cell was not cleaned. This indicated that sarin molecule could hardly be decomposed by the irradiated cell wall contaminants. Thus, it can be seen that sarin is probably the primary photon absorber, despite that it has a very weak absorption in UV region, the excited sarin molecules may undergo a photoreaction to destroy itself. The main photoremoval pathways may possibly including direct sarin photolysis and the reaction between sarin molecules of the excited and ground states.

For photodegradation of phosphates, the $n \rightarrow \pi^*$ transition of electrons in the P=O bond is commonly efficient to initiate the reaction, and a bond fission may possibly occur at the primary photoreaction step to generate free radicals [18]. As the weakest σ bond adjacent to P=O bond, P–C bond in sarin molecule is expected to be cleaved at the primary step. Subsequently, H_2O and O_2 might act in the next steps. And polymerization may finally occur with the free radicals as initiator, as evidenced by LC/MS and NMR analysis results. The commonly proposed mechanism is summarized as follows:



4. Conclusions

Sarin vapor can be destructively eliminated under UV light irradiation from the germicidal lamp. It was demonstrated that photoreaction of sarin molecules was the main pathway that lead to the elimination of sarin vapor. The elimination rate was kinetically dominated by the irradiation density and yet was somewhat influenced by the air humidity. The products analysis results strongly supported that sarin molecules were finally converted into a kind of nontoxic polymer under UV light irradiation.

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