ELSEVIER

Chemical Engineering Journal 128 (2007) 135–140

Chemical Engineering Journal

www.elsevier.com/locate/cej

Study on photolytic and photocatalytic decontamination of air polluted by chemical warfare agents (CWAs)

Guo-Min Zuo, Zhen-Xing Cheng*, Guo-Wen Li, Wen-Ping Shi, Ting Miao

The No. 3 Department, Institute of Chemical Defence, P.O. Box 1048, Beijing 102205, China

Received 20 March 2006; received in revised form 11 September 2006; accepted 7 October 2006

Abstract

Photolytic and photocatalytic reactions of sarin (GB), soman (GD), sulfur mustard (HD), cyanogen chloride (CK) and perfluoroisobutylene (PFIB) vapors in air were carried out. It was shown that vapors of GB, GD, HD and PFIB could be efficiently eliminated by UV light from germicidal lamp through either photolysis or photocatalysis, but CK could hardly be done through photodegradation. It was demonstrated that GB, GD and HD might possibly undergo a photo-induced polymerization under UV light irradiation. Photocatalytic reaction would lead to a cleavage of these molecules into small inorganic compounds at TiO_2 surface. The experimental results strongly suggested that both photolysis and photocatalysis of GB vapor at static conditions were kinetically slowed down and possibly limited by a low diffusion rate of GB molecule. It has been testified that the static photolysis approach could be applicable for decontamination of GB vapor in an indoor space. And that, a dynamic photocatalysis approach for decontamination of GB vapor was proved to be much more efficient than that through photolysis, and it was also considered to be feasible for decontamination of air polluted by GB vapor.

Keywords: Chemical warfare agents; Photolysis; Photocatalysis; Gas-phase; Decontamination

1. Introduction

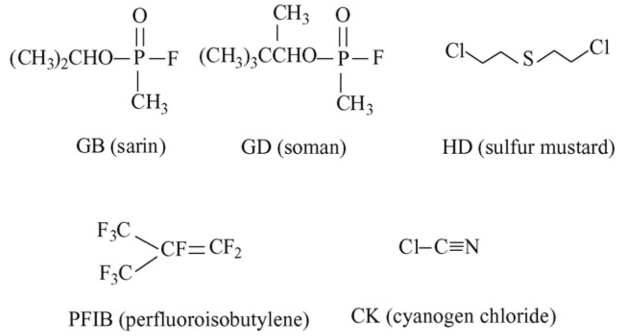
Decontamination of air polluted by chemical and biological warfare agents in an indoor space is of great importance to the chemical and biological defense as well as the counterterrorism field. Military chemists have always been trying to develop some new methods to safely and conveniently eliminate these pollutants [1]. It was early recognized that the adsorption method, typically using activated carbon, could successfully remove sarin (GB), soman (GD) and sulfur mustard (HD) vapors in air through physical adsorption. And that, cyanogen chloride (CK) and hydrogen cyanide (AC) could be catalytically eliminated by activated carbon impregnated with copper, chromium compounds and other additives [2–4]. Besides, the catalytic oxidation of chemical warfare agents (CWAs) over metals and metal oxides at a temperature over 200 °C has also attracted extensive attention in recent years. Particularly, the decomposition of dimethyl methylphosphonate (DMMP, a widely used simulant for nerve agent) was frequently reported [5–11], and high DMMP conversion was observed at the beginning of the reaction having CO_2 and H_2O as the major products. Thermocatalytic transformations of HD simulant [12] and CK [13,14] were also studied, and small molecules like CO_2, SO_2, Cl_2 were detected. Klabunde and co-workers [15–18] have extensively developed nanoparticulate metal oxide materials for decontaminating CW and BW agents at ambient temperature, which were demonstrated to be much more reactive than common oxides.

Recently, it was revealed that the photocatalysis technique had a favorable potential to mineralize a range of toxic substances, and was regarded as a most promising technology to purify the polluted air [19,20]. Attempts to use the photocatalysis technique to detoxify CWAs and their simulants demonstrated this method to be principally feasible [21–33]. The studies on photocatalytic degradation of DMMP indicated that both P–OCH_3 and P–CH_3 moieties could be destroyed through photocatalysis. Products like CO, CO_2 and methanol were detected in gas phase, and P-containing species including PO_4^{3-} were proved to form on TiO_2 surface [25,26]. Photocatalytic oxidation of HD simulant 2-chloroethyl ethyl sulfide (2-CEES) [30–33] was also widely studied. The experimental results indicated that photocatalytic degradation of 2-CEES mainly proceeds via oxi-

---

* Corresponding author. Tel.: +86 10 69760164; fax: +86 10 69760161.
E-mail address: chengzx04@tom.com (Z.-X. Cheng).

1385-8947/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2006.10.006



Scheme 1. The structures of the CWAs used in this study.

dation of S atom, cleavage of S–C bond and oxidation of C atoms. It should be noted that photolytic degradation of these substances were scarcely mentioned in these literatures.

In this work, photolytic and photocatalytic degradation of five CWAs (Scheme 1) vapors in air were studied, and those two reactions characteristics together with their reaction pathways were comparatively discussed. The applicability of decontamination methods for GB vapor based on photolysis and photocatalysis was also investigated in both static and dynamic conditions.

2. Experimental

The photocatalyst used was P25 TiO_2 supplied by Degussa. GB and GD have a purity >99%, and HD has a purity >95%. CK and PFIB were stockpiled in steel cylinders, both agents have a purity >99%. All solvents were of analytical grade or distilled before use. *Caution*: All the five agents (GB, GD, HD, CK and PFIB) have high toxicity, and they should be handled only by trained personnel using applicable safety procedures.

Static photolytic and photocatalytic reactions of CWAs vapors were conducted in a self-designed photoreactor, as illustrated in Fig. 1(a). It was composed of a quartz light window of approximately 100 cm^2 and a columnar stainless steel chamber with 10 cm diameter and 25 cm length, both of which were adhered together with thermomelting adhesive to form a space of approximately 3.3 L. The CWAs vapors were generated by a method of static vacuum, i.e. to degas the reactor, to inject toxic agent liquid (or vapor) into the chamber with a syringe, and then to introduce air upon complete vaporization. UV light from an 8 W germicidal lamp (254 nm) was introduced into the reactor through a quartz window. The UV light irradiation intensity was determined with an UV-B-254 ultraviolet irradiator (Photoelectric Instrument Factory of Beijing Normal University) close to the inner surface of the quartz window. For photocatalytic reactions, we firstly blended 0.3 g of P25 TiO_2 powder with small amount of distilled water, and then made a uniform coating of the mixture onto the inner surface of the quartz window to form a thin layer upon air-drying. It was measured that the quartz window only caused 10% loss of the UV irradiation intensity, while the irradiation intensity would decrease from 0.6 to 0.025 mW/cm^2 when the quartz window was coated with TiO_2 layer. This implied that most of the UV light was absorbed or reflected by TiO_2 coating, and it ensured vapors of CWAs in reactor to absorb little light. The photoreactions were carried out under the conditions of atmospheric pressure and room temperature of 20–25 °C.

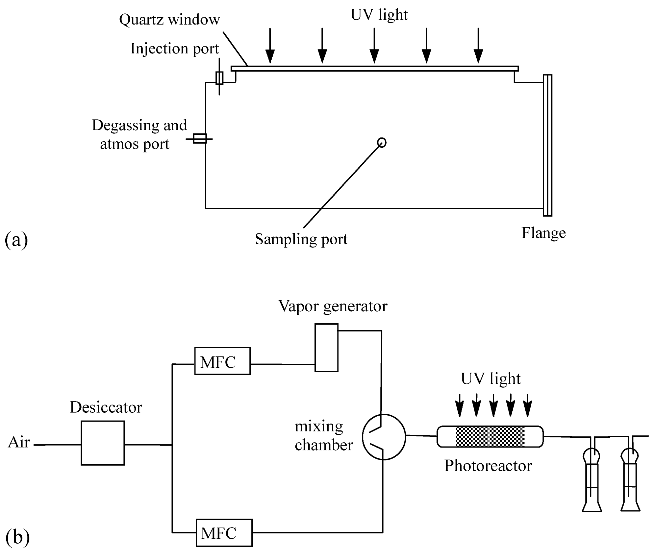


Fig. 1. Schematic drawing of the photoreaction setup: (a) static photoreactor and (b) dynamic photoreactor.

In order to exemplify the potential application of the photolytic and photocatalytic approach, the photoreactions of GB vapor were also studied under dynamic condition. The dynamic photoreaction was carried out in a quartz tube with an inside radius of 2 cm and length of 15 cm as photoreactor, as illustrated in Fig. 1(b). Mass flow controller (MFC) was used to control the airflow. A stable and low concentration of GB contaminated airflow was obtained by diluting GB vapor from a self-designed evaporator. The photocatalyst used was prepared by coating P25 TiO_2 onto the quartz-sands of 20–40 meshes with a proportion of 1%.

In addition, the static photolytic decontamination of air polluted by GB was also tried in a cubic glass-tank of 1 m^3, where a germicidal lamp of 20 W was placed at the central position.

Vapor concentrations of GB, GD and HD were determined by a colorimetric method, i.e. to purge the reactor with fresh dry air, to absorb the sweep gas by cooled ethanol. GB and GD in ethanol were quantitatively measured by a colorimetric method based on a Schöenemann reaction, and HD was measured based on a color reaction between HD and thymolphthalein [34]. Concentrations of CK, PFIB and CO_2 were determined by a direct sampling mass spectrometer (OmniStar^{TM} of Balzers).

3. Results and discussion

3.1. Photolysis and photocatalysis of several CWA vapors

It was experimentally shown that concentration of GB vapor would gradually decrease after it was generated in the static photoreactor. This could mainly be associated with the hydrolysis of GB molecules [35]. Once the GB vapor was directly exposed to the irradiation of germicidal lamp, its concentration was observed to sharply decrease. Nearly 99% of the GB vapor was eliminated after irradiation for 2 h, as shown in Fig. 2.

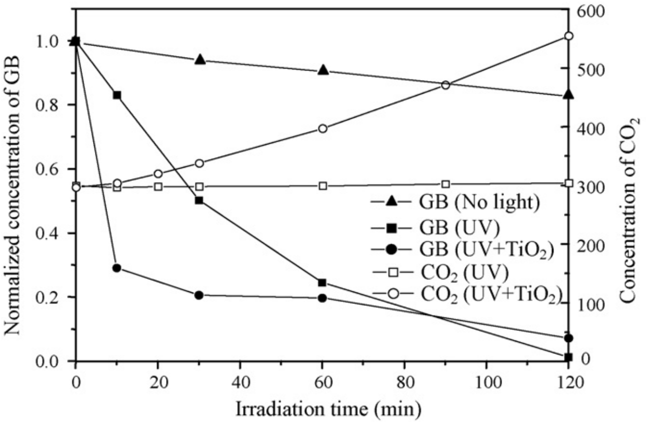


Fig. 2. Concentrations of GB and CO_2 as a function of irradiation time during photolysis and photocatalysis of GB vapor. The initial concentration of GB is 1.7 mg/L, the irradiation intensity is 0.6 mW/cm^2, the relative air humidity is 30–50%, and 0.3 g of TiO_2 is used for the photocatalytic reaction.

Under the same experimental conditions except for coating a thin layer of TiO_2 onto the inner surface of the quartz window, one could observe that the initial degradation rate of GB was greatly enhanced by the presence of TiO_2, and yet the degradation rate slowed down after around 30 min. This was possibly due to the slow diffusion rate of GB vapor and also the deactivation of active sites on the catalyst by some polar species. Obee et al. [26] had also found that the catalyst deactivated relatively rapidly during photocatalytic degradation of DMMP due to build-up of surface phosphorus-containing species. As one of the expected final products of photocatalysis, CO_2 was quantitatively monitored. It can be seen that concentration of CO_2 remarkably increased during the reaction, while there was nearly no change of CO_2 concentration during photolysis of GB vapor. About 90% of GB vapor was eliminated after photocatalysis for 2 h, and it could be calculated from the amount of generated CO_2 that only about 25% of the degraded molecules of GB were mineralized into CO_2.

In the same manner, photolytic and photocatalytic reactions of vapors of GD, HD, CK and PFIB were also investigated. Similar phenomena were observed along with the photolysis and photocatalysis of GD, HD and PFIB, while CK could hardly be degraded through either photolysis or photocatalysis even though the UV light irradiation intensity grew up to 10 mW/cm^2. Theoretically, a photoreaction could not always be a first-order reaction. However, a first-order reaction rate constant was still easily calculated for the photolysis and photocatalysis of the CWA vapors in order to compare the rate of different photoreactions studied, as presented in Table 1. It can be seen in reference to the reaction rate constant that photocatalysis rate of PFIB was more than four times that of photolysis. In spite that photocatalysis of GB and GD during the first 30 min went nearly two times as quickly as photolysis, it became slower than photolysis since that moment. Notably, the presence of TiO_2 slowed down the degradation of HD vapor during the photocatalytic reaction in comparison with photolytic reaction. This was probably because of a low diffusion rate of HD molecule and the deactivation of catalyst.

Table 1
The first-order reaction rate constant for the photolytsis and photocatalysis of several CWAs vapors

Vapor	Initial concentration (mg/L)	$k_1 \times 10^2$ (min^{-1})	
		Photolysis	Photocatalysis
GB	1.7	2.32	5.97
GD	0.94	4.09	7.25
HD	0.42	2.54	1.19
PFIB	4.9	0.36	1.61
CK	7.7	0	0

Both mass spectrometer and gas chromatograph were used to detect the gas-phase species during the photolytic and photocatalytic reaction of these vapors. The experimental results revealed that no products or intermediates were detected in the gas phase during photolytic degradation of the five vapors, and only CO_2 was detected during the photocatalytic reaction of GB, GD, HD and PFIB. But, one could clearly observe that some sticky substances adhered onto the inner surface of the quartz window after photolysis of GB, GD, or HD vapor. These substances were nonvolatile and difficultly soluble in solvents, which was quite similar to a kind of polymer. Another experiment has testified that the sticky substance formed during the photolysis of GB and GD vapor had no inhibition upon acetylcholinesterase, and the substance formed during photolysis of HD vapor has no positive reaction against thymolphthalein. This suggested that the final products generated by photolysis of GB had no neurotoxicity, and those of HD had no vesicant toxicity. Thus, the irradiation of UV light possibly could efficiently detoxify the molecules of GB, GD and HD via a photo-induced polymerization. By contrast, photocatalytic reaction of the four agents could possibly accomplish through oxidation by $^{\bullet}OH$ free radial, and the reactant may be cleaved into small pieces and finally be mineralized to CO_2, H_2O and other inorganic compounds.

3.2. *Factors affecting photolysis of GB vapor*

The above experimental results indicated that all the studied CWAs, except for CK, could be directly degraded through UV light irradiation. In order to find an efficient approach to accelerate the degradation rate, several factors such as vapor concentration, irradiation intensity and air humidity affecting the photolysis of GB vapor were investigated. The initial concentration of GB vapor can be adjusted by varying the volume of the injected GB liquid. The air humidity can be augmented by injecting water into the photoreactor. The irradiation intensity can be adjusted by changing the distance between the lamp and the quartz window.

Fig. 3 showed the influence of the initial concentration of GB vapor to the photodegradation rate. In order to have a kinetic comparison, the apparent first-order reaction rate constants were calculated, which were 0.067, 0.0464, 0.0232 and 0.0205 min^{-1}, respectively. It can be seen that the GB elimination reaction rate would increase along with decreasing the initial concentration of GB vapor. As presented in Fig. 4, the photolytic reaction rate was somewhat influenced by the air humidity, the apparent

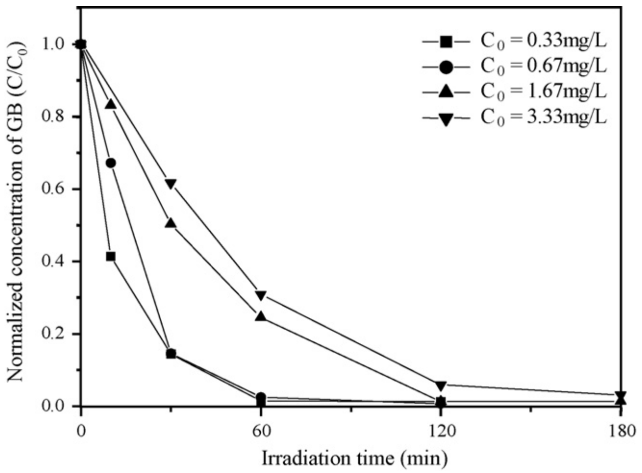


Fig. 3. Photolytic degradation of GB vapor of varied initial concentrations. The irradiation intensity is 0.6 mW/cm^2, the relative air humidity is 30–50%.

first-order reaction rate constants were, respectively calculated as 0.0232, 0.0259, 0.0306, and 0.0377 min^{-1}. It seemed that a high relative humidity would favor the photolytic reaction of GB vapor. Meanwhile, the elimination rate of GB vapor was greatly accelerated by strengthening the irradiation intensity, as shown in Fig. 5. The apparent first-order reaction rate constants were, respectively, 0.0012, 0.0024, 0.0232, and 0.0406 min^{-1}.

Thus, it can be seen that the degradation rate of GB vapor was significantly promoted by strengthening the irradiation density or lower the initial concentration, and yet was less significantly influenced by the air humidity. Generally, the rate of a photoreaction was dominated by the primary photochemical step, where the target molecules would be dissociated once they were excited via absorbing efficient photons. Accordingly, the GB molecule might be dissociated at the primary step, and the dissociation rate would greatly rely on the UV light irradiation intensity. Nevertheless, H_2O molecule would not be involved in the primary step, and affected the degradation rate slightly.

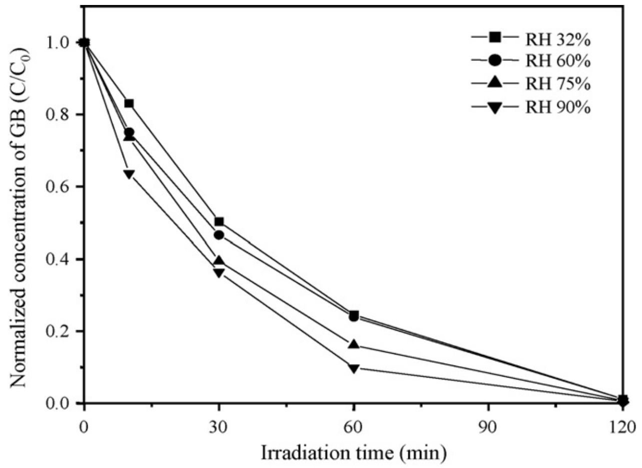


Fig. 4. Photolytic degradation of GB vapor under different relative humidity. The irradiation intensity of germicidal lamp is 0.6 mW/cm^2, and the initial concentration of GB is 1.7 mg/L.

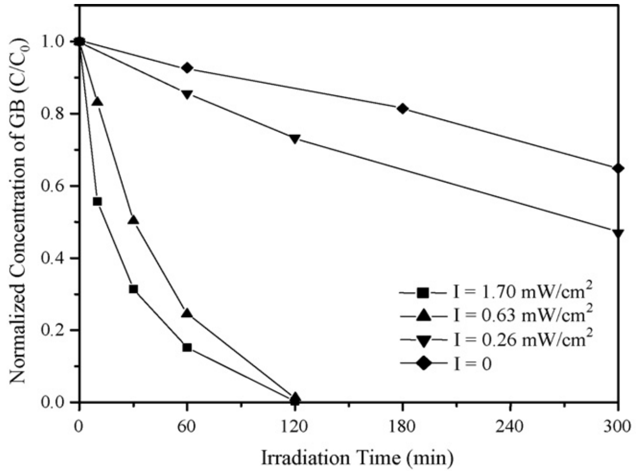


Fig. 5. Photolytic degradation of GB vapor under different UV light irradiation intensity. The initial concentration of GB vapor is 1.7 mg/L, the relative air humidity is 30–50%.

3.3. Application of the photolysis and photocatalysis approach for decontamination of GB vapor in air

GB vapor in air could be efficiently eliminated through either photolysis or photocatalysis in a static reactor. The elimination rate of GB through photolysis seemed to be faster than that through photocatalysis under the static conditions. Then the photolysis approach was expected to be applicable for decontamination of air polluted by GB in an inclosed space. Thereby, a large space of 1 m^3 volume was used to testify whether photolysis would be an efficient approach to decontaminate air polluted by GB. As presented in Fig. 6, when GB vapor was introduced into the glass tank with an initial concentration around 3×10^{-3} mg/L, concentration of GB would keep lowing mainly due to adsorption of GB molecule on the glass wall, it would achieve a relatively stable concentration around 5×10^{-4} mg/L after 7 h. Once germicidal lamp was lighted on, the concentration of GB vapor would sharply decrease to 4×10^{-6} mg/L in 100 min, but it will recover to

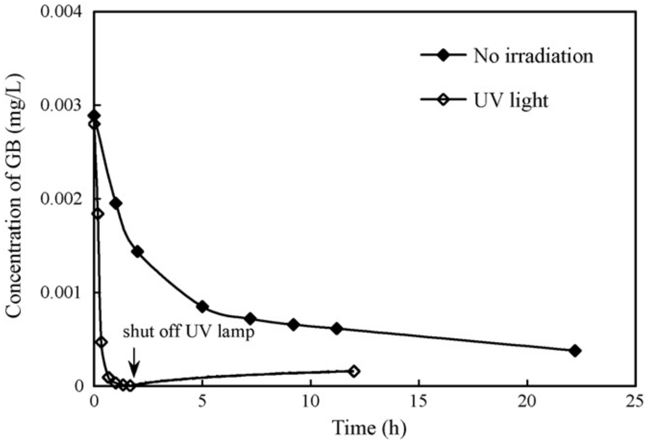


Fig. 6. Photolytic decontamination of GB vapor in a glass tank of 1 m^3. A germicidal lamp of 20 W as light source is placed in it. The initial concentration of GB vapor is 3 mg/m^3, and the relative air humidity is 30–50%.

Table 2
The dynamic elimination efficiency of GB vapor through photolysis and photocatalysis

Photolysis		Photocatalysis	
Initial concentration (mg/L)	Elimination ratio (%)	Initial concentration (mg/L)	Elimination ratio (%)
1×10^{-4}	9.2	5×10^{-3}	>99.9
8×10^{-4}	30.2	7×10^{-2}	>99.9
5×10^{-3}	42.0	7×10^{-1}	9.8

The flow rate of the decontaminated air was 200 mL/min for photolytic reaction and 2000 mL/min for photocatalytic reaction.

around 1.6×10^{-4} mg/L after stewing for 12 h. This would suggest that the elimination rate of GB through photolysis was quite rapid, but it was greatly slowed down by the diffusion rate of GB in gas phase and from the glass wall.

The experiments carried out in static conditions have strongly suggested that both photolytic and photocatalytic reactions of GB were greatly influenced by the diffusion rate, then one would quickly arise the question what would be at dynamic conditions. Then, a flow reactor was applied to study the dynamic photolysis and photocatalysis of GB vapor. The intensity of UV light irradiated the flow reactor was adjusted closely to that in the static study. As presented in Table 2, the conversion ratios for elimination of GB vapor through photolysis in the absence of TiO_2 catalyst were all lower than 50% when the inlet concentration of GB varied from 5×10^{-3} to 1×10^{-4} mg/L. The apparent first-order reaction rate constant was evaluated as 2.4 min^{-1} at these dynamic conditions and much larger than that at static conditions (2.3×10^{-2} min^{-1}). One can observe that the ratio for elimination of GB through photocatalysis would still remain larger than 99.9% in spite of a very short contact time 1.5 s (2000 mL/min airflow) for at least 8 h when the inlet concentration of GB was less than 7×10^{-2} mg/L, and it would sharply fall down to about 10% when the inlet concentration of GB vapor increased up to 7×10^{-1} mg/L. It seemed that at dynamic conditions photocatalysis could be an approach much better than photolysis, but its disposable capability to detoxify GB in air was limited certainly by the concentration of active sites in catalyst; once the catalyst was overcharged by GB molecule, the catalyst bed would quickly be broken through. The apparent first-order reaction rate constant was evaluated as 40 min^{-1} for this dynamic photocatalytic reaction, and it was nearly 700 times as big as that for static photocatalytic reaction. Thus, it can be seen that at dynamic conditions elimination of GB contaminated airflow through photocatalysis was much more efficient and quick than that through photolysis and basically is feasible for decontamination of air polluted by GB. Therefore, not only photolysis but also photocatalysis of GB vapor at static conditions were kinetically slowed down and possibly limited by a low diffusion rate of GB molecule in air.

4. Conclusions

It was experimentally shown that UV light of germicidal lamp could efficiently eliminate vapors of GB, GD, HD and PFIB through either photolysis or photocatalysis, but it was not effective for CK vapor. Vapors of GB, GD and HD may possibly undergo a photo-induced polymerization directly under UV light irradiation, while they may be cleaved into small inorganic compounds at TiO_2 surface through photocatalysis. The obtained results strongly suggested that both photolysis and photocatalysis of GB vapor at static conditions were kinetically slowed down and possibly limited by a low diffusion rate of GB molecule. It was testified that the photolysis approach was applicable for decontamination of GB vapor in an indoor space in static conditions, and the photocatalysis approach was proved to be much more efficient than photolysis under dynamic conditions.

References

[1] Y.-C. Yang, J.A. Baker, J.R. Ward, Decontamination of chemical warfare agents, Chem. Rev. 92 (1992) 1929–1943.

[2] Z. Barnir, C. Aharoni, Adsorption of cyanogen chloride on impregnated active carbon, Carbon 13 (1975) 363–366.

[3] P.J. Reucroft, C.T. Chiou, Adsorption of cyanogen chloride and hydrogen cyanide by activated and impregnated carbons, Carbon 15 (1977) 285–290.

[4] T. Sutikno, Analytical model for chemisorption of cyanogen chloride on impregnated carbon, Carbon 75 (1999) 207–212.

[5] V.S. Smentkowski, P. Hagans, J.T. Yates Jr., Study of the catalytic destruction of dimethyl methylphosphonate (DMMP): oxidation over molybdenum(1 1 0), J. Phys. Chem. 92 (1988) 6351–6357.

[6] M.A. Henderson, J.M. White, Adsorption and decomposition of dimethyl methylphosphonate on platinum(1 1 1), J. Am. Chem. Soc. 110 (1988) 6939–6947.

[7] M.K. Templeton, W.H. Weinberg, Adsorption and decomposition of dimethyl methylphosphonate on an aluminum oxide surface, J. Am. Chem. Soc. 107 (1985) 97–108.

[8] X. Guo, J. Yoshinobu, J.T. Yates Jr., Decomposition of an organophosphonate compound (dimethylmethylphosphonate) on the nickel(1 1 1) and palladium(1 1 1) surfaces, J. Phys. Chem. 94 (1990) 6839–6842.

[9] K.W. Lee, M. Houalla, D.M. Hercules, W.K. Hall, Catalytic oxidative decomposition of dimethyl methylphosphonate over Cu-substituted hydroxyapatite, J. Catal. 145 (1994) 223–231.

[10] M.A. Henderson, T. Jin, J.M. White, A TPD/AES study of the interaction of dimethyl methylphosphonate with iron oxide (alpha-Fe_2O_3) and silicon dioxide, J. Phys. Chem. 90 (1986) 4607–4611.

[11] M.B. Mitchell, V.N. Sheinker, E.A. Mintz, Adsorption and decomposition of dimethyl methylphosphonate on metal oxides, J. Phys. Chem. B 101 (1997) 11192–11203.

[12] J.A. Rossin, Complete catalytic oxidation of diethyl sulfide over a 1% Pt/Al_2O_3 catalyst, Ind. Eng. Chem. Res. 28 (1989) 1562–1564.

[13] A.A. Klinghoffer, J.A. Rossin, Catalytic oxidation of chloroacetonitrile over a 1% platinum alumina catalyst, Ind. Eng. Chem. Res. 31 (1992) 481–486.

[14] S.K. Agarwal, J.J. Spivey, D.E. Tevault, Kinetics of the catalytic destruction of cyanogen chloride, Appl. Catal. B: Environ. 5 (1995) 389–403.

[15] G.W. Wagner, L.R. Procel, R.J. O'Connor, et al., Reactions of VX, GB, GD, and HD with nanosize Al_2O_3. Formation of aluminophosphonates, J. Am. Chem. Soc. 123 (2001) 1636–1644.

[16] G.W. Wagner, O.B. Koper, E. Lucas, et al., Reactions of VX, GD, and HD with nanosize CaO. Autocatalytic dehydrohalogenation of HD, J. Phys. Chem. B 104 (2000) 5118–5123.

[17] G.W. Wagner, P.W. Bartram, O. Koper, K.J. Klabunde, Reactions of VX, GD, and HD with nanosize MgO, J. Phys. Chem. B 103 (1999) 3225–3228.

[18] P.K. Stoimenov, R.L. Klinger, G.L. Marchin, K.J. Klabunde, Metal oxide nanoparticles as bactericidal agents, Langmuir 18 (2002) 6679–6686.

[19] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, Chem. Rev. 93 (1993) 341–357.

[20] A.L. Linsebigler, G. Lu, J.T. Yates Jr., Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results, Chem. Rev. 95 (1995) 735–758.

[21] E.A. Kozlova, P.G. Smirniotis, A.V. Vorontsov, Comparative study on photocatalytic oxidation of four organophosphorus simulants of chemical warfare agents in aqueous suspension of titanium dioxide, J. Photochem. Photobiol. A: Chem. 162 (2004) 503–511.

[22] Y.-C. Oh, Y. Bao, W.S. Jenks, Isotope studies of photocatalysis TiO_2-mediated degradation of dimethyl phenylphosphonate, J. Photochem. Photobiol. A: Chem. 161 (2003) 69–77.

[23] S. Segal, S.L. Suib, X. Tang, S. Satyapal, Photoassisted decomposition of dimethylphosphonate over amorphous manganese oxide catalyst, Chem. Mater. 11 (1999) 1687–1695.

[24] C.N. Rusu, J.T. Yates Jr., Adsorption and decomposition of dimethylphosphonate on TiO_2, J. Phys. Chem. B 104 (2000) 12292–12298.

[25] C.N. Rusu, J.T. Yates Jr., Photooxidation of dimethylphosphonate on TiO_2 powder, J. Phys. Chem. B 104 (2000) 12299–12305.

[26] T.N. Obee, S. Satyapal, Photocatalytic decomposition of DMMP on titania, J. Photochem. Photobiol. A: Chem. 118 (1998) 45–51.

[27] A.V. Vorontsov, E.V. Savinov, L. Davydov, P.G. Smirniotis, Photocatalytic destruction of gaseous diethyl sulfide over TiO_2, Appl. Catal. B: Environ. 32 (2001) 11–24.

[28] A.V. Vorontsov, A.A. Panchenko, E.N. Savinov, et al., Photocatalytic degradation of 2-phenethyl-2-chloroethyl sulfide in liquid and gas phases, Environ. Sci. Technol. 36 (2002) 5261–5269.

[29] D.V. Kozlov, A.V. Vorontsov, P.G. Smirniotis, E.N. Savinov, Gas-phase photocatalytic oxidation of diethyl sulfide over TiO_2: kinetic investigations and catalyst deactivation, Appl. Catal. B: Environ. 42 (2003) 77–87.

[30] A.V. Vorontsov, C. Lion, E.N. Savinov, P.G. Smirniotis, Pathways of photocatalytic gas phase destruction of HD simulant 2-chloroethyl ethyl sulfide, J. Catal. 220 (2003) 414–423.

[31] D.A. Panayotov, D.K. Paul, J.T. Yates Jr., Photocatalytic oxidation of 2-chloroethyl ethyl sulfide on TiO_2-SiO_2 powders, J. Phys. Chem. B 107 (2003) 10571–10575.

[32] D.A. Panayotov, P. Kondratyuk, J.T. Yates Jr., Photooxidation of a mustard gas simulant over TiO_2-SiO_2 mixed-oxide photocatalyst: site poisoning by oxidation products and reactivation, Langmuir 20 (2004) 3674–3678.

[33] I. Martyanov, K.J. Klabunde, Photocatalytic oxidation of gaseous 2-chloroethyl ethyl sulfide over TiO_2, Environ. Sci. Technol. 37 (2003) 3448–3453.

[34] S. Franke, Lehrbuch der Militärchemie, Band 2, Militärverlag der DDR, Berlin, 1977, pp. 316–318, 324–326.

[35] N.B. Munro, S.S. Talmage, G.D. Griffin, et al., The sources, fate, and toxicity of chemical warfare agent degradation products, Environ. Health Perspect. 107 (1999) 933–974.