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# Titanium dioxide photocatalysis to decompose isopropyl methylphosphonofluoridate (GB) in gas phase

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ABSTRACT

The adsorption and photocatalytic degradation of nerve agent, isopropyl methylphosphonofluoridate, Sarin (GB) as a real Chemical Warfare Agent (CWA) on powdery Titanium dioxide ($TiO_2$) film have been investigated using Gas chromatography/mass spectrometry (GC/MS) analysis in ambient atmosphere. We found that the ability to decontaminate GB molecules on $TiO_2$ photocatalyst can be estimated to be 42 molecules/nm$^2$, indicating that 1 g of $TiO_2$ photocatalyst can decontaminate 3.4 mmol of GB molecules as the limitation value to maintain the photocatalytic activity. We also elucidated a plausible photocatalytic decontamination mechanism of GB at the surface of $TiO_2$ photocatalyst on the basis of the results obtained in this study.

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## 1. Introduction

Decontamination of the environmental area contaminated by Chemical Warfare Agents, CWAs, has been studied. [1–5] Since titanium dioxide ($TiO_2$) has been shown to be an effective photocatalyst for the decomposition of a large number of organic compounds [6–15], use of $TiO_2$ as a photocatalyst has been greatly focused on the decontamination of the CWAs in terms of crisis management [16–44].

A lot of studies examined the reaction of CWA simulants in the gas and liquid phase have been reported. For CWAs simulant, dimethyl sulfide (DMS), diethyl sulfide (DES) and 2-chloroethyl ethyl sulfide (2CEES) as 2,2′-dichloro diethyl sulfide (sulfur mustard: HD) simulant as a blister agent [18–28], and dimethyl methyl phosphonate (DMMP) [34–43] and di-isopropylfluorophosphate (DFP) [44,45] as isopropyl methylphosphonofluoridate, Sarin (GB) and trimethylpropyl methylphosphonofluoridate, tabun (GD) simulant as a nerve agent have been known for major simulants. Complete decomposition of these simulants by $TiO_2$ photocatalysis and the detailed decomposition mechanism at the surface of $TiO_2$ photocatalyst are well elucidated and widely known. However, few studies on the photocatalytic decomposition for real CWA have been reported [46,47].

Recently, the photocatalytic adsorption and decomposition mechanism of GB has been investigated by ATR–FTIR technique, and the detailed adsorption and photocatalytic decomposition mechanism has been demonstrated by our research group [47]. The GB molecule is finally decomposed to phosphoric acid (PA), carbon dioxide and water molecules. The PA then adsorb on the Lewis acid like site such as $Ti^{4+}$, $Ti^{3+}$, and $Ti^{2+}$ with forming Ti–O–P–O–Ti bond at the surface of $TiO_2$. The formation of Ti–O–P–O–Ti bond occupies the Ti site to adsorb $O_2$ molecules, indicating that $O_2$ reduction in the $TiO_2$ photocatalysis will be inhibited. The deactivation by inhibiting the $TiO_2$ photocatalytic $O_2$ reduction with forming Ti–O–P–O–Ti bond has actually suggested as a consequence of forming methyl phosphoric acid with the large amount of DMMP adsorption at the surface of $TiO_2$ [35–37]. On the basis of these reports, the $TiO_2$ photocatalyst will be deactivated with decomposing real CWA continuously as a consequence of the PA accumulation, indicating that the $TiO_2$ photocatalyst have a limitation value to maintain the photocatalytic activity in the $TiO_2$ photocatalysis in decomposing the real CWA. Therefore, experimentally verifying the limitation value to maintain the photocatalytic activity in decomposing the real CWAs is necessary to pave the way to develop the photocatalytic decontamination systems.

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Herein, we focus on vaporized GB molecule as real CWA and report the limitation value to maintain the photocatalytic activity in decomposing the vaporized GB molecules. In this study, the adsorption and photocatalytic decomposition of the vaporized GB was analyzed by Gas chromatography/mass spectrometry (GC/MS) analysis in ambient.

## 2. Experimental

### 2.1.1. Samples

$TiO_2$ powder (P25, Nippon aerojil) was used as a photocatalyst [48]. P25 was suspended into MilliQ water and agitated by sonication for 15 min. The suspension was applied to a rubbed glass Plate 5 cm × 5 cm and was dried in air on a warm plate; finally powdery $TiO_2$ film was obtained [45]. The amount of $TiO_2$ applied to the glass plate was adjusted from 0.0001 to 0.01 g (1 mg) per 25 $cm^2$. Typically, the powdery $TiO_2$ film exposed to UV light (EFD 15 BLB, 15 W, Toshiba, center wavelength: 354 nm and the light intensity at 360 nm: 6.3 $mW/cm^2$ at 360 nm, TOPCON UVR-2(UD-36)) for 1 h under ambient air to remove surface pollutants [45].

Isopropyl methylphosphonofluoridate, GB (the purity was >97% according to the supplier) was obtained from TNO Prince Maurits Laboratory, Rijswijk, the Netherlands and used with the permission of the Ministry of Economy, Trade and Industry of Japan. The molecular structures are represented in Table 1.

### 2.1.2. GC–MS analysis

The change in the concentration of the vaporized GB with hexane (GB/hexane) in the $TiO_2$ photocatalysis was analyzed by GC/MS (Agilent 6890(HP-GC 6890), HP-MS mass selective detector 5973)) every 15 min. Hexane was then used as a solvent for adjusting the concentration of the vaporized GB. In this study, no intermediates such as vaporized isopropanol, acetone and so on were detected by our GC/MS.

### 2.1.3. Photocatalytic reaction

Powdery $TiO_2$ film was placed on the special Teflon stage in the reactor and was capped by using Teflon O-ring. Teflon stage, O-ring and tube were used for all connections and inner wall of the reactor was treated by silane application in order to decrease adsorption of GB at the inner wall of experimental systems. In this study, the GB concentration was basically adjusted by diluting with hexane as solvent. Hexane is suitable to dissolve GB because the GB molecule is smoothly dissolved in hexane and stable in nonpolar solvent. The residual concentration of the vaporized GB in the photocatalytic reactor was then 0.5 μmol.

The GB/hexane solvent was injected into a glass tube (volume of 500 mL, GL science) equipped with a gas flow cock and was completely vaporized by heating the GB liquid spot in the tube with a heat blower from outside. Then, the temperature in the glass tube was usually 333.5–334 K. The vaporized GB/hexane in the glass tube was pumped into the photocatalytic reactor by an air cylinder at a flow rate of 200 mL/min for 2 min. The exhaust cock of the gas pipe in the reactor was then opened in order to keep the pressure of the photocatalytic reactor. After pumping, the inlet and exhaust cocks of the gas pipe in the photocatalytic reactor part were closed. The photocatalysis started after observing the adsorption of the vaporized GB at the surface of $TiO_2$ in the dark. UV irradiation was carried out by Black light (EFD BLB15W, center wavelength 352 nm, Toshiba) at a 6.3 $mW/cm^2$ light intensity passed through a window (TEMPAX Float®) of the reactor. Under the UV irradiation, the temperature in the reactor increased to 318 K. All of experiments were carried out in ambient air.

*Caution*: GB as CWAs is highly toxic by both inhalation and ingestion. The compounds should always be handled with special care in a special experimental room under reduced air pressure and should be immediately destroyed with sodium hypochlorite after use. Every experiment was performed by trained personnel and using applicable safety procedures in a special laboratory of NRIPS with the permission of the Ministry of Economy, Trade and Industry of Japan.

## 3. Physical and chemical properties of GB and DMMP

Table 1 shows the chemical and physical properties of GB. The vapor pressure of GB obey to $9.4–2700/T$ (K) as listed in Table 1 [3]. On the basis of the equation, GB molecule is easily evaporated into gas phase in room temperature. Thermal stability of GB is listed. The pure GB liquid is completely decomposed by heating at 150 °C for 2 h [49]. On the contrary, pure GB liquid is fairly stable in a steel container at 65 °C. Stability improves with increasing impurity [49]. Above boiling point of GB, pure GB liquid is decomposed to propen and methylphosphonofluoridic acid [50]. On the basis of the thermal stability of GB molecule, the GB molecule is not decomposed in our study [50].

## 4. Results and discussion

### 4.1. Dependency of the amount of $TiO_2$ photocatalyst to decompose GB molecules in gas phase

Fig. 1(a) shows the GB adsorption at the surface of the powdery $TiO_2$ film in the dark. The amount of $TiO_2$ is 0.01 g. The residual concentration of the vaporized GB in the photocatalytic reactor was observed to be 0.28 μmol and it decreased to be 0.026 μmol for 10 min. For 90 min, the concentration of GB remaining in the gas phase decreased to be 0.0015 μmol and the decrement stopped. Therefore, of GB molecules, 0.26 μmol totally adsorbed at the surface of the powdery $TiO_2$ film. The adsorption rate of GB at the surface of $TiO_2$ ($r_{\text{GB-ads}}$) is then estimated to be 0.22 ($r_{\text{GB-ads-first}}$) and 0.05 ($r_{\text{GB-ads-second}}$) μmol $min^{-1}$ as the first decay for 10 min and the second decay from 10 to 80 min as an adsorption by assuming the first order reaction. The number of GB molecule adsorbed at the surface of $TiO_2$ is estimated to be 0.54 molecules/$nm^2$ at 0.01 g of $TiO_2$ on the basis of the molecular size of GB as reported by Hoffmann and Reeves [50]. Fig. 1(b) shows the decrement of the concentration of GB by the $TiO_2$ photocatalysis as the same condition on the Fig. 1(a). The $TiO_2$ photocatalytic decomposition rate ($r_{\text{GB-dec}}$) is similar to that of adsorption as shown in Fig. 1(a) and the first decrement $r_{\text{GB-dec-first}}$ was then calculated to be 0.24 μmol $min^{-1}$ for 10 min. At 10 min, the decrement rate of vaporized GB slowed to be $r_{\text{GB-dec-second}} = 0.08$ μmol $min^{-1}$. By taking into account of the result of Fig. 1(a), the $r_{\text{GB-dec}}$ was controlled by the $r_{\text{GB-ads}}$. The plausible $r_{\text{GB-sub}}$ is calculated by subtracting $r_{\text{GB-ads}}$ from $r_{\text{GB-dec}}$ and then the $r_{\text{GB-sub-first}}$ and $r_{\text{GB-sub-second}}$ are estimated to be 0.024 μmol $min^{-1}$ for 10 min and 0.021 μmol $min^{-1}$ from 10 to 40 min. Therefore, the $r_{\text{GB-ads}}$ controls the $r_{\text{GB-dec}}$ in this condition.

Fig. 2 shows the decrement of the concentration of GB in the photocatalysis at 0.0005 g of $TiO_2$. The concentration of the vaporized GB in the reactor was stable in the dark, indicating that the adsorption of the GB molecules performed adsorption equilibrium at the interface of gas phase and surface of $TiO_2$. The residual concentration of the vaporized GB in the photocatalytic reactor was then observed to be 0.3 μmol. By the UV irradiation, the concentration of the vaporized GB was decreased and reached undetectable value at 100 min. The photocatalytic decomposition rate slowed with the UV irradiation after 30 min, indicating that the GB molecule adsorption spent a long time since the concentration of GB is thin. The

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