Adsorption and reactions of CH_2Br_2 on TiO_2 : Effects of H_2O and O_2

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ABSTRACT. The adsorption, thermo- and photo-reactions of CH_2Br_2 on powdered TiO_2 as well as the effects of H_2O and/or O_2 have been studied by Fourier-transform infrared spectroscopy. CH_2Br_2 is adsorbed molecularly on the surface at 35°C , interacting with the surface OH groups. It is completely desorbed or decomposes to form $\text{CH}_3\text{O}_{(\text{a})}$ and $\text{HCOO}_{(\text{a})}$ in a vacuum by 250°C , probably via dioxymethylene ($-\text{OCH}_2\text{O}-$). The presence of adsorbed H_2O accelerates the formation of $\text{CH}_3\text{O}_{(\text{a})}$ and $\text{HCOO}_{(\text{a})}$ from CH_2Br_2 dissociation. Adsorbed CH_2Br_2 decomposes to form $\text{CO}_{(\text{a})}$, $\text{HCOO}_{(\text{a})}$, $\text{CO}_{3(\text{a})}$, and/or $\text{CO}_{2(\text{a})}$ under 400 nm irradiation, depending on whether the presence of H_2O and/or O_2 . The presence of O_2 increases the photoreaction rate of $\text{CH}_2\text{Br}_{2(\text{a})}$ and the photodecomposition is further accelerated with addition of H_2O .

1. INTRODUCTION

Photocatalysis mediated by semiconductors is a promising approach to destroy environmentally harmful chemical compounds [1]. TiO_2 is often used because of its chemical stability, absorption frequency overlapping with solar spectrum, and economic consideration. CH_2Br_2 is one of halogenated compounds which are used as reagents and solvents widely, but can cause ozone layer depletion and damage to human health. Photocatalytic degradation of CH_2Br_2 by TiO_2 dispersed in aqueous solutions in the presence of He or O_2 has been studied by Calza et al. [2]. Formaldehyde and formic acid was found by chromatography to be the reaction intermediates during CH_2Br_2 photodecomposition. Calza et al. deemed that the photodegradation of CH_2Br_2 proceeded with both oxidative and reductive steps. The presence of O_2 enhanced the CH_2Br_2 photodegradation rate, while depressed the formation of formaldehyde and formic acid. However, the subject for the interaction between CH_2Br_2 and TiO_2 surface, including adsorption, thermal transformation, and surface intermediates and products formed during CH_2Br_2 photodissociation has not been examined. In the present study, these surface topics are investigated by Fourier-transform infrared spectroscopy for CH_2Br_2 vapor- TiO_2 surface system. The effect of H_2O or O_2 on the CH_2Br_2 thermal reaction and photoreaction are also studied.

2. EXPERIMENTAL SECTION

The details of the stainless steel IR cell with two CaF_2 windows for IR transmission down to 1000 cm^{-1} used in the present study has been reported previously [3]. In our system, the IR cell was

connected to a gas manifold which was pumped by a 60 L/s turbomolecular pump with a base pressure of $\sim 1 \times 10^{-7}$ Torr. The TiO_2 powder was supported on a tungsten grid ($\sim 6\text{ cm}^2$). The preparation method has been described [4]. In brief, TiO_2 powder (Degussa P25, $\sim 50\text{ m}^2/\text{g}$, anatase 70%, rutile 30%) was dispersed in water-acetone solution to form a uniform mixture which was then sprayed onto a tungsten mesh. After that, the TiO_2 sample was mounted inside the IR cell for FTIR spectroscopy. The TiO_2 sample in the cell was heated to 450°C under vacuum for 24 hr by resistive heating. The temperature of TiO_2 sample was measured by a K-type thermocouple spotwelded on the tungsten mesh. Before each run of the experiment, the TiO_2 sample was heated to 450°C in vacuum for 2 hr. After the heating, 10 Torr O_2 was introduced into the cell as the sample was cooled to 70°C . When the TiO_2 temperature reached 35°C , the cell was evacuated for gas dosing. The TiO_2 sample after the annealing treatment still possessed residual surface hydroxyl groups [4, 5]. O_2 (99.998%) and CH_2Br_2 (99%) were purchased from Matheson and Aldrich respectively. CH_2Br_2 was purified by several cycles of freeze-pump-thaw before introduction to the cell. Pressure was monitored with a Baratron capacitance manometer and an ion gauge. In the photochemistry study, both the irradiation and IR beams were set 45° to the normal of the TiO_2 sample. The irradiation light source used was a combination of a 350 W-Hg arc lamp (Oriel Corp), a water filter, and a band pass filter with a band width of $\sim 100\text{ nm}$ centered at 400 nm (Oriel 51670). The power at the position of TiO_2 sample was $\sim 0.14\text{ W/cm}^2$ measured in the air by a power meter (Molelectron, PM10V1). Infrared spectra were obtained with a 4 cm^{-1} resolution by a Bruker FTIR spectrometer with a MCT detector. The entire optical path was purged with CO_2 -free dry air. The spectra presented here have been

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ratioed against a clean TiO_2 spectrum providing the background reference.

3. RESULTS AND DISCUSSION

Figure 1 shows the IR spectra of TiO_2 in contact with ~ 1.5 Torr of CH_2Br_2 at 35°C , followed by evacuation at this temperature and the indicated higher temperatures for 1 min. In the spectrum with ~ 1.5 Torr of CH_2Br_2 over TiO_2 in the cell, the bands at 1099, 1192, 1393, 2987, and 3070 cm^{-1} are assigned to CH_2 vibrational modes of twisting, wagging, scissoring, symmetric stretching, and antisymmetric stretching, respectively, based on the similar frequencies of the corresponding modes of CH_2Br_2 in gas or liquid phase as shown in Table 1. When the gaseous CH_2Br_2 is pumped out the cell, the absorption peaks in the 35°C spectrum are still close similar to those of gaseous CH_2Br_2 , but the band intensities are all reduced, clearly indicating the CH_2Br_2 is adsorbed on TiO_2 in a vacuum. Raising the temperature to 50°C causes the reduction of adsorbed CH_2Br_2 by $\sim 28\%$. This decrease is likely due to thermal desorption, because no surface new bands are detected. After increasing the temperature to 100°C , the amount of adsorbed CH_2Br_2 is largely diminished by $\sim 86\%$, but with enhanced absorptions at 1122 and 2880 cm^{-1} . These two bands are assigned to C-O stretching and CH_x stretching [7]. There are four possible surface intermediates with these two functional groups from CH_2Br_2 decomposition on TiO_2 : monobromomethoxy ($-\text{OCH}_2\text{Br}$), dibromomethoxy ($-\text{OCHBr}_2$), dioxymethylene ($-\text{OCH}_2\text{O}-$), and dioxymethylene ($-\text{OCHBrO}-$). The adsorbed CH_2Br_2 amount continues to decrease after the surface is heated to 150°C . New bands appear at 1367, 1387, 1557, 2841, and 2936 cm^{-1} . Based on the similar frequencies observed in the previous studies of dissociative adsorption of formic acid and methanol on TiO_2 , the first three bands are assigned to $-\text{COO}-$ symmetric stretching, CH bending, and $-\text{COO}-$ antisymmetric stretching of adsorbed HCOO and the last two are assigned to symmetric and antisymmetric CH_3 stretching of adsorbed CH_3O [8-11]. The band intensities of adsorbed HCOO and CH_3O increase after further heating the surface to 200°C . Note that the thermal transformation of $\text{CH}_2\text{Br}_2(\text{a})$ to $\text{HCOO}(\text{a})$ and $\text{CH}_3\text{O}(\text{a})$ is a surface process. Since the surface heating was carried out in a vacuum, readsorption of any gas phase product to form $\text{HCOO}(\text{a})$ and $\text{CH}_3\text{O}(\text{a})$ was unlikely to occur. In terms of the number of hydrogen attached to the carbons, the formation of $\text{HCOO}(\text{a})$ and $\text{CH}_3\text{O}(\text{a})$ from CH_2Br_2 decomposition on TiO_2 can be viewed as an oxidation and reduction process respectively. Previously, in the study of CH_2O adsorption on TiO_2 Busca et al. have observed dioxymethylene surface intermediate below 35°C [8]. This intermediate disproportionates to form $\text{HCOO}(\text{a})$ and $\text{CH}_3\text{O}(\text{a})$ as

Figure 1. Infrared spectra of TiO_2 taken after being in contact with ~ 1.5 Torr of CH_2Br_2 at 35°C followed by evacuation at 35, 50, 100, 150, and 200°C for 1 min. All of the spectra were measured at 35°C with 50 scans.

well as loses hydrogen to form $\text{HCOO}(\text{a})$ at higher temperatures. Therefore, it is proposed that the reaction of CH_2Br_2 on TiO_2 generating $\text{HCOO}(\text{a})$ and $\text{CH}_3\text{O}(\text{a})$ is via dioxymethylene. The dioxymethylene can not be detected in this study, because it is not stable as CH_2Br_2 dissociates on TiO_2 at temperature larger than $\sim 100^\circ\text{C}$ [8].

Figure 2 shows the effect of adsorbed H_2O on the adsorption and reaction of CH_2Br_2 on TiO_2 . The spectra of Figure 2(a), 2(c), and 2(e) are obtained for TiO_2 after being in contact with ~ 1.5 Torr CH_2Br_2 for 0, 60, and 120 min at 100°C respectively. In Figure 2(a), the CH_2Br_2 bands appear at 1393, 2987, and 3070 cm^{-1} . The adsorption of CH_2Br_2 causes absorption changes over 3200 cm^{-1} . The negative bands in the $3600\text{--}3800\text{ cm}^{-1}$ region signify loss of isolated surface OH groups and the appearance of the broad band in the $3200\text{--}3600\text{ cm}^{-1}$ region reveals the formation of hydrogen bonding. Adsorbed CH_2Br_2 interacts with the surface isolated OH groups, leading to their intensity loss. Furthermore, the type of interaction, via $-\text{O}-\text{H} \cdots \text{BrCH}_2\text{Br}$ hydrogen bonding, accounts for

Table 1. Comparison of vibrational frequencies (cm⁻¹) of CH₂Br₂.

CH ₂ Br ₂ (l) (ref. [6])	CH ₂ Br ₂ (g) (ref. [6])	CH ₂ Br ₂ /TiO ₂ (this work)	Assignment
1095	–	1099	CH ₂ twisting
1192	1195	1192	CH ₂ wagging
1387	1382	1393	CH ₂ scissoring
2989	3009	2987	CH ₂ symmetric stretching
3061	3073	3070	CH ₂ antisymmetric stretching

Figure 2. Infrared spectra taken for TiO₂ surfaces, with or without pre-adsorbed H₂O, in contact with ~ 1.5 Torr of CH₂Br₂ after the indicated annealing times at 100 °C. The pre-adsorbed H₂O was prepared by shortly exposing a clean TiO₂ surface to ~ 0.2 Torr of H₂O vapor, followed by evacuation at 35 °C.

the formation of the broad band in 3200–3600 cm⁻¹. However, the hydrogen bonding interaction has no significant effect on the CH₂ absorption frequencies of the adsorbed CH₂Br₂, because they are very close to those of free CH₂I₂ (see Table 1). In spite of the -O-H...BrCH₂Br interaction, another interaction between CH₂Br₂(a) and surface Ti⁴⁺ Lewis acid sites via the lone-pair electrons of Br can not be ignored. Holding the TiO₂ temperature at 100 °C for prolonged time

induces the decomposition of CH₂Br₂, as shown in Figure 2(c) and 2(e). Its decomposition products are HCOO_(a) at 1360 and 1548 cm⁻¹, CH₃O_(a) at 2837 and 2935 cm⁻¹, and the species responsible for the 2882 cm⁻¹ band. The spectra of Figure 2(b), 2(d), and 2(f) are obtained for H₂O-preadsorbed TiO₂ after being in contact with ~ 1.5 Torr CH₂Br₂ for 0, 60, and 120 min at 100 °C. The 1618 cm⁻¹ band shows the presence of adsorbed H₂O. Additionally, there are absorption bands at 3417 and 3651 cm⁻¹ as well as negative bands in ~ 3680–3800 cm⁻¹. Previously, IR band assignments for TiO₂ hydroxyl groups have been reported in the literature. Primet et al. have found that surface hydroxyl groups absorb at 3410, 3655, and 3685 cm⁻¹ on rutile TiO₂ as well as at 3665 and 3715 cm⁻¹ on anatase TiO₂ [12]. The 3685 and 3715 cm⁻¹ are assumed to be isolated hydroxyls and the others are reasoned to result from hydroxyl groups bonded to each other by hydrogen bridges. Tanaka and White have assigned the bands at 3676 and 3715 cm⁻¹ on anatase TiO₂ to isolated hydroxyls bonded to Ti ions with different coordination or on different anatase faces [13]. In comparison of Figure 2(a) and 2(b), the presence of adsorbed water reduces the band intensities of CH₂Br₂ by ~ 28%. This is very likely due to H₂O_(a) site-blocking effect on CH₂Br₂ adsorption. Furthermore, the HCOO_(a) bands are barely visible in Figure 2(b), indicating the decomposition rate of CH₂Br₂ increases as H₂O is present on the surface. Like the case without H₂O_(a), HCOO_(a) and CH₃O_(a) continue to increase with annealing time at the expense of CH₂Br₂ as shown in Figure 2(d) and 2(f). It is found that, in the presence of H₂O_(a), HCOO_(a) and CH₃O_(a) are formed more for a same annealing time, even the surface amount of CH₂Br₂ is less. Figure 3 shows the relative amounts of CH₂Br₂, HCOO_(a), and CH₃O_(a) as a function of annealing time at 100 °C. The maximum intensities of their characteristic bands during the annealing are scaled to be 1 for the relative concentration in Figure 3. In both cases with or without adsorbed H₂O, HCOO_(a) and CH₃O increase with annealing time due to continuous decomposition of CH₂Br₂. The presence of H₂O promotes the formation of HCOO_(a) and CH₃O_(a). This promotion may be due to the following reasons: (1) the nucleophilic attack of adsorbed CH₂Br₂ by surface H₂O or OH groups and (2) solvation effect of adsorbed H₂O especially as the transition state in the CH₂Br₂ reaction coordinate possesses ionic character.

Figure 3. Relative concentrations of CH_2Br_2 , $\text{HCOO}_{(\text{a})}$, and $\text{CH}_3\text{O}_{(\text{a})}$ as a function of annealing time at 100°C . The maximum amount of each species is scaled to 1.

Figure 4 shows the spectra taken before and after the indicated times during photoirradiation of CH_2Br_2 adsorbed on TiO_2 in a closed cell. The surface CH_2Br_2 is consumed by photoirradiation, leading to the formation of new bands at 1330 , 1360 , 1556 , 1576 , and 2123 cm^{-1} . The CH_2Br_2 is reduced by $\sim 29\%$ after 180 min. The bands at 1360 and 1556 cm^{-1} are attributed to adsorbed formate. The 2123 cm^{-1} band is attributed to adsorbed CO which has been reported previously [14]. The 1330 and 1576 cm^{-1} bands are attributed to adsorbed CO_3 [14]. These three products increase along with the exposure of the lights. There is no new band detected at $\sim 2560\text{ cm}^{-1}$ which is the absorption frequency of gaseous HBr [7]. Bromine is likely to be adsorbed on the surface during the photodecomposition of $\text{CH}_2\text{Br}_{2(\text{a})}$, however it can not be detected due to the limitation of our experimental set-up (cut-off frequency at $\sim 1000\text{ cm}^{-1}$). Since the TiO_2 temperature was raised to 55°C during the photoillumination, a thermal control experiment was carried out by holding a TiO_2 surface with adsorbed CH_2Br_2 at 55°C in a closed cell for 180 min but without photon exposure. The amount of $\text{CH}_2\text{Br}_{2(\text{a})}$ is reduced by $\sim 12\%$ after the 180 min annealing, however only negligible formate and carbon monoxide were detected in this thermal control experiment. This result indicates that, in Figure 4, the decrease of $\text{CH}_2\text{Br}_{2(\text{a})}$ is in part due to thermal desorption and due to photoreaction to form of $\text{CO}_{(\text{a})}$, $\text{CO}_{3(\text{a})}$, and $\text{HCOO}_{(\text{a})}$. Figure 5 shows the spectra taken before and after the indicated times during photoirradiation of adsorbed CH_2Br_2 in 10 Torr of O_2 . Similar to the case without O_2 , the $\text{CH}_2\text{Br}_{2(\text{a})}$ decreases due to desorption and photoreaction forming adsorbed CO_3 (1331 , 1564 cm^{-1}), HCOO (1360 and 1556 cm^{-1}), and CO (2123 cm^{-1}), however adsorbed CO is no more monotonically increased and gaseous CO_2 is formed at

Figure 4. Infrared spectra taken before and after the indicated times during photoirradiation of a TiO_2 surface covered with CH_2Br_2 . The CH_2Br_2 -adsorbed surface was prepared by exposing a clean TiO_2 surface to ~ 1.5 Torr of CH_2Br_2 followed by evacuation at 35°C . All of the spectra were measured with 5 scans.

2349 cm^{-1} in the presence of O_2 . The $\text{CO}_{(\text{a})}$ amount reaches a maximum after ~ 30 min photoirradiation and then declines. The previous study has shown that CO on TiO_2 is photooxidized to CO_2 in the presence of O_2 [14]. Likewise, photooxidation of $\text{HCOO}_{(\text{a})}$ on TiO_2 in O_2 produces CO_2 [11]. Figure 6 shows the spectra taken before and after the indicated times during photoirradiation of a TiO_2 surface with co-adsorbed CH_2Br_2 and H_2O in 10 Torr of O_2 . The photoproducts are the same as those in O_2 only, but the $\text{HCOO}_{(\text{a})}$ and $\text{CO}_{2(\text{g})}$ are promoted. Furthermore, compared to the case without O_2 and $\text{H}_2\text{O}_{(\text{a})}$ or only with O_2 , the intensity ratio of $\text{HCOO}_{(\text{a})}$ band at 1360 cm^{-1} to the $\text{CO}_{3(\text{a})}$ band at 1330 cm^{-1} is highly increased. The previous study has shown that rate of $\text{HCOO}_{(\text{a})}$ photooxidation to form $\text{CO}_{2(\text{g})}$ is increased in the presence of $\text{H}_2\text{O}_{(\text{a})}$ [11]. Note that thermal control experiments in contrast to Figures 5 and 6 were carried out. The results indicate that $\text{CH}_2\text{Br}_{2(\text{a})}$ decomposition to form the products during

the photon exposure are due to photoeffect, instead of thermal heating.

Figure 5. Infrared spectra taken before and after the indicated times during photoirradiation of a TiO_2 surface covered with CH_2Br_2 in 10 Torr of O_2 . The CH_2Br_2 -adsorbed surface was prepared by exposing a clean TiO_2 surface to ~ 1.5 Torr of CH_2Br_2 followed by evacuation at 35°C . All of the spectra were measured with 5 scans.

Figure 7 shows the relative amounts of $\text{CH}_2\text{Br}_{2(a)}$, $\text{CO}_{(a)}$, $\text{CO}_{2(g)}$, and $\text{HCOO}_{(a)}$ plus $\text{CO}_{3(a)}$ as a function of photoirradiation time for CH_2Br_2 on TiO_2 under the light exposure in the absence of both $\text{H}_2\text{O}_{(a)}$ and O_2 , in the presence of O_2 only, and in the presence of both $\text{H}_2\text{O}_{(a)}$ and O_2 . Note that the initial amounts of $\text{CH}_2\text{Br}_{2(a)}$ for the three different experimental conditions are not the same, however the effect of H_2O and O_2 on the CH_2Br_2 photodecomposition can still be analyzed. From Figure 1, it has been observed that some of the adsorbed CH_2Br_2 is desorbed at 50°C in a vacuum, therefore the variation of $\text{CH}_2\text{Br}_{2(a)}$ with the time of annealing at 55°C without both light illumination and the presence of O_2 and $\text{H}_2\text{O}_{(a)}$ in a closed cell is presented in the $\text{CH}_2\text{Br}_{2(a)}$ panel in Figure 7 as well to check the thermal effect due to TiO_2 photoillumination.

Figure 6. Infrared spectra taken before and after the indicated times during photoirradiation of a TiO_2 surface covered with CH_2Br_2 and H_2O in 10 Torr of O_2 . The TiO_2 surface covered with CH_2Br_2 and H_2O was prepared by exposing a clean TiO_2 surface to ~ 1.5 Torr of CH_2Br_2 followed by evacuation at 35°C and then shortly to ~ 0.3 Torr of H_2O followed by evacuation. All of the spectra were measured with 5 scans.

The thermal control data show that the $\text{CH}_2\text{Br}_{2(a)}$ decreases more rapidly in the early stage and then declines very slowly. In comparison of the thermal result to the photoirradiation case without both O_2 and $\text{H}_2\text{O}_{(a)}$, the light illumination enhances the consumption of the $\text{CH}_2\text{Br}_{2(a)}$. Furthermore, from the CO uptake curve for $\text{CH}_2\text{Br}_{2(a)}$ photodecomposition without both O_2 and $\text{H}_2\text{O}_{(a)}$, it has a larger formation rate in the early stage that is consistent with the CH_2Br_2 decreasing behavior. A similar consumption trend for $\text{CH}_3\text{O}_{(a)}$ photodecomposition on TiO_2 has been reported and reasoned to be electron accumulation on the surface for prolonged light illumination so that the lifetime of holes is decreased [15]. In photodecomposition of CH_2Br_2 in presence of only O_2 or both O_2 and $\text{H}_2\text{O}_{(a)}$, faster $\text{CH}_2\text{Br}_{2(a)}$ consumption rate is also observed in

Figure 7. Relative concentrations of $\text{CH}_2\text{Br}_{2(\text{a})}$, $\text{CO}_{(\text{a})}$, $\text{CO}_{2(\text{g})}$, and $\text{HCOO}_{(\text{a})}$ plus $\text{CO}_{3(\text{a})}$ as a function of photoirradiation time of CH_2Br_2 on TiO_2 in the absence of both $\text{H}_2\text{O}_{(\text{a})}$ and O_2 , in the presence of O_2 only, and in the presence of both $\text{H}_2\text{O}_{(\text{a})}$ and O_2 . The changes of $\text{CH}_2\text{Br}_{2(\text{a})}$, $\text{CO}_{(\text{a})}$, $\text{CO}_{2(\text{g})}$, and $\text{HCOO}_{(\text{a})}$ plus $\text{CO}_{3(\text{a})}$ for annealing $\text{CH}_2\text{Br}_{2(\text{a})}$ at 55°C without photoillumination and presence of both O_2 and H_2O in a closed cell are also displayed for comparison.

the early photoirradiation stage. In the presence O_2 , $\text{CH}_2\text{Br}_{2(\text{a})}$ is able to be continuously oxidized to a larger extent for prolonged photoillumination, as compared to the case without O_2 . After 180 min photoillumination for $\text{CH}_2\text{Br}_{2(\text{a})}$, the $\text{CH}_2\text{Br}_{2(\text{a})}$ is reduced by $\sim 29\%$ in the absence of both O_2 and $\text{H}_2\text{O}_{(\text{a})}$, $\sim 42\%$ in the presence of only O_2 , and $\sim 58\%$ in the presence of both O_2 and $\text{H}_2\text{O}_{(\text{a})}$. In the $\text{CO}_{(\text{a})}$ panel in Figure 7, the presence of O_2 enhances the CO formation in the early photoillumination stage, however due to the $\text{CO}_{(\text{a})}$ photooxidation to $\text{CO}_{2(\text{g})}$, the $\text{CO}_{(\text{a})}$ amount reaches maximum at ~ 30 min and then declines. In the $\text{CO}_{2(\text{g})}$ panel, it is formed only O_2 is present and further promoted by the addition of $\text{H}_2\text{O}_{(\text{a})}$. In the panel of $\text{HCOO}_{(\text{a})} + \text{CO}_{3(\text{a})}$, they are enhanced also in the presence of O_2 .

In the studies of photoreactions of CH_2Cl_2 and CH_2Br_2 catalyzed by TiO_2 dispersed in aqueous solutions, Calza et al. found that the CH_2Cl_2 rate of degradation was highly enhanced in the presence of O_2 , compared to the case in the presence of He, while CH_2Br_2 showed a less increase in degradation rate [2, 16]. They suggested that, for the photodecomposition of CH_2Br_2 , oxidative steps were favored, but some reductive steps might still take place. They assumed that radical species such as $\cdot\text{CHBr}_2$, $\cdot\text{CH}_2\text{Br}$, $:\text{CBr}_2$ were generated in the CH_2Br_2 photodecomposition. Photogenerated electrons are possible initiation species for reductive dissociation of CH_2Br_2 . Dissociative elec-

tron attachment of CH_2Br_2 in gas phase or solutions has been well investigated, forming Br^- and possibly $\cdot\text{CH}_2\text{Br}$ [17, 18]. For the oxidative degradation of $\text{CH}_2\text{Br}_{2(\text{a})}$, the possible reaction initiation species include photogenerated hole, $\equiv\text{Ti}-\text{O}\cdot$ [19], or $\text{OH}\cdot$ as $\text{OH}_{(\text{a})}$ or $\text{H}_2\text{O}_{(\text{a})}$ is present on the surface during TiO_2 photoirradiation. Interaction of hole with $\text{CH}_2\text{Br}_{2(\text{a})}$ can proceed via electron transfer from the occupied CH_2Br_2 orbitals to the empty TiO_2 valence band edge, if the former energy levels are higher than the latter ones. On the other hand, if the HOMO of $\text{CH}_2\text{Br}_{2(\text{a})}$ is lower than the TiO_2 valence band edge, the overlap between the $\text{CH}_2\text{Br}_{2(\text{a})}$ occupied orbitals with the empty TiO_2 valence band orbitals may cause the dissociation of $\text{CH}_2\text{Br}_{2(\text{a})}$, as demonstrated in the theoretical calculation of CH_4 photodecomposition on TiO_2 [20]. $\text{OH}\cdot$ and $\equiv\text{Ti}-\text{O}\cdot$ may abstract H from $\text{CH}_2\text{Br}_{2(\text{a})}$ to start the $\text{CH}_2\text{Br}_{2(\text{a})}$ decomposition process. The presence of O_2 increases the $\text{CH}_2\text{Br}_{2(\text{a})}$ degradation. O_2 may capture photo-generated electrons and retard the recombination of electron-hole pairs, so the lifetime of the hole species increases, enhancing the oxidative degradation rate. Meanwhile O_2^- , O_3^- , and O_3^{-3} have been observed by ESR study during TiO_2 photoexcitation at 77 K [21]. O_2^- survives at room temperature and may react with CH_2Br_2 . Reactions of CH_2Br_2 and CH_2Cl_2 with O_2^- in solutions have been reported [22, 23]. Additionally, O_2 may take part in the photoreactions of CH_2Br_2 , because

it may recombine with the radical species formed during photoillumination. As H₂O_(a) is added in the presence of O₂, CH₂Br_{2(a)} is consumed more and the photoproducts of CO_{2(g)} and HCOO_(a) are correspondingly enhanced. It is believed that photoholes can react with H₂O_(a) or OH_(a) to form OH· radicals. If the OH· are the active species for CH₂Br₂ photodegradation, the present of H₂O is expected to increase the consumption of CH₂Br_{2(a)}. In recent chemiluminescence study, it is found that the steady-state O₂[−] concentration for TiO₂-H₂O-air system is twice that for TiO₂-air system under UV illumination [24]. Enhanced O₂[−] formation can increase the lifetime of the hole species and direct reaction with CH₂Br_{2(a)}.

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