Photocatalytic decomposition of DMMP on titania

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Abstract

The photocatalytic decomposition of gas-phase dimethyl methylphosphonate (DMMP) on TiO_2-coated glass substrate was studied using a single-pass reactor. The disappearance of DMMP and the appearance of products were monitored for several DMMP concentrations between 1 and 90 ppmv in air. Intrinsic reaction rates were determined, products were identified and reaction chemistry has been postulated. The main reaction products identified were carbon dioxide and carbon monoxide in the gas-phase, and methylphosphonic acid and phosphate on the catalyst. It was found that due to build-up of surface phosphorus-containing species, the catalyst de-activated relatively rapidly. One of the interesting results of this study is that the catalyst activity was completely recovered by washing with water and partially recovered by exposure to UV (UVA; ~ 352 nm) light. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: DMMP; Titania; Photocatalysis; Organophosphorus; Photo-oxidation; Nerve gas

1. Introduction

The decomposition of organophosphorus compounds has been of interest for several years, primarily for the destruction of chemical warfare agents and pesticides, as well as other phosphorus-containing hazardous waste. With approximately 25 000 tons of chemical weapons stockpiled in the US alone, there is interest in developing methods alternate to incineration for safely destroying these stockpiles. In addition to large-scale disposal, destroying trace quantities of such pollutants in enclosed spaces is important for storage and transport applications. Photocatalysis has emerged over the last two decades as a low cost and environmentally benign method to destroy low concentrations of pollutants in air and aqueous feed streams. In this study we report the photocatalytic oxidation of dimethyl methylphosphonate (DMMP); a widely used simulant for nerve gas (e.g., iso-propyl methylphosphonofluoridate or GB).

One of the main difficulties in the catalytic decomposition of phosphorus-containing compounds is poisoning or degradation of the catalyst. Several studies have been reported on the thermal decomposition of DMMP on various substrates, including Ni (1 1 1), Pd (1 1 1), Rh (1 0 0), Al_2O_3, Mo (1 0 0), Fe_2O_3, SiO_2, and Pt [1–8]. In most of the above studies, with the exception of Mo (1 0 0), the catalytic

reaction was not sustained due to the accumulation of products on the catalyst surface. In contrast to the thermally catalyzed reactions of DMMP reported above, we have studied the photocatalytic decomposition of DMMP on titania at room temperature. The use of titania for the oxidation of organophosphonates and pesticides in aqueous solutions has been documented in recent studies [9–15]. As opposed to liquid-phase reactions, we report here the photocatalytic reaction of DMMP in the gas-phase on a titania-coated glass support. The goals of the study were to determine intrinsic oxidation rates, identify reaction products, and demonstrate rejuvenation of the de-activated catalyst.

2. Experimental

2.1. Materials

DMMP was purchased from Aldrich and used without further purification. Titania, P-25 was purchased from Degussa. Nitrogen from an in-house source and oxygen (Matheson; 99.999%) were used in all experiments.

2.2. Intrinsic rate apparatus

A glass-plate photocatalytic reactor was used to generate intrinsic oxidation rate data. A complete description of the reactor and its operation is presented elsewhere [16]. Ultraviolet (UV) illumination was provided by a pair of black-

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light lamps (352 nm peak intensity, SpectroLine XX-15A). UV-intensity at the catalyst surface was measured by a UVA power meter (Oriel UVA Goldilux). DMMP was generated by vaporizing DMMP in a temperature-controlled-water bath. Control of the DMMP generation rate was effected through selection of the water bath temperature and the length and diameter of a feed tube leading from a DMMP containment vial; the DMMP effluent from the vial was swept away by a flow of nitrogen gas. High-purity nitrogen gas passed through a water bubbler to set the desired water vapor level. An oxygen gas flow was combined with the nitrogen and DMMP flows to produce the desired carrier gas mixture (10% oxygen and 90% nitrogen).

An opaque film of Degussa P-25 titania was deposited on flat 25 mm wide microscope glass slides using a wash-coat process. The wash-coat was 5% by weight of titania in distilled water. A titania film was prepared by dipping the glass slide in the wash-coat several times, air-dried between dippings, and then oven-dried at 60°C. This process was repeated until a 0.90 mg/cm^2 film (one side) was attained. A fresh titania-coated slide was used in each DMMP experiment. The photocatalytic activity of each catalyst slide was determined from the photo-oxidation of 1-butene, which has been previously studied in this laboratory.

2.3. Analysis of reaction products

The concentrations of water vapor, carbon dioxide, and carbon monoxide were measured using a photo-acoustic detector (Brüel and Kjær 1302). The concentrations of DMMP and 1-butene were measured using a gas chromatograph (HP-5890 II) equipped with an FID detector and a megabore column (Restek RTX-502.2). Gas standards (Matheson) were used to calibrate the detectors for carbon dioxide, carbon monoxide, and 1-butene. A standard for DMMP was provided by vaporizing DMMP in a temperature-controlled oven (Metronics 230 Dynacalibrator). Formaldehyde and methanol were not detectable with the photo-acoustic detector due to overlap of DMMP absorption bands in the IR region.

After reaction with DMMP, the titania slides were immersed in distilled deionized water and the reaction products were extracted using ultrasonication. The extracted products were analyzed by ion chromatography using a Dionex AS4A-SC anion exchange column and a Na$_2$CO$_3$/NaHCO$_3$ buffer. Standards of methyl phosphonic acid (MPA) and phosphate (phosphoric acid) were used to identify the products.

In order to collect gas-phase products, a cold-trap (dry ice/acetone at ~-78°C or ethanol/liquid nitrogen maintained at ~-80°C) was used to trap volatile products at the exit of the titania reactor. The concentrated products were then identified by GC/GCMS/IR. The primary gas-phase products that we attempted to detect with the mass-spectrometer included methanol, formaldehyde, formic acid, and methyl formate.

3. Results and discussion

3.1. Preliminary reactivity measurements

Control experiments verified that under UV-illumination, no change in DMMP level or evolution of carbon dioxide or carbon monoxide was observed with uncoated slides. It was also shown that both oxygen and UV-light were required for photocatalytic decomposition of DMMP on TiO$_2$. There was no significant loss of DMMP due to adsorption/reaction on non-catalytic surfaces in the apparatus.

In a study of film loading by Jacoby et al. [17], the oxidation rate of trichloroethylene increased with film loading up to a titania (Degussa P-25) loading of 0.5 mg/cm^2 and remained constant for all higher loadings. This finding suggested that the oxidation rate maximized at a film loading of 0.5 mg/cm^2 and that additional film loading added nothing to the oxidation rate. This conclusion should not depend on the specific contaminant used, and hence, can be applied in the present study. The titania film in the present study was determined to be opaque to UVA by placing a coated plate between the UV black-light lamps and the UVA power meter. This finding coupled with the conclusion drawn from Jacoby et al's. finding [17] suggested that the UV-radiation was being maximally utilized in the oxidation process reported herein.

Oxygen was maintained at a constant level of 10% by volume for all rate measurements. Jacoby et al. [17] and Dibble and Raupp [18] have found that for the oxidation of trichloroethylene the rate was zero-order for oxygen levels above 1%. In view of the reported findings, and since the experiments performed in the present study used contaminant levels that were lower than the levels used by Jacoby et al. [17] and Dibble and Raupp [18], it is likely that the oxidation rates herein were independent of oxygen level for oxygen levels above 1%.

3.2. DMMP oxidation rates

For the data generated with the glass-plate reactor, the oxidation rate was defined as

$$r = 2.45(X_{in} - X_{out})Q/A \qquad (1)$$

where r (μ mol/cm^2 h) is the oxidation rate, X_{in} (ppmv) and X_{out} (ppmv) are the inlet and outlet contaminant (DMMP or 1-butene) concentrations, respectively, Q (lpm), the volumetric flow rate, and A (cm^2), the area of the titania-coated glass-plate; the numerical coefficient accounts for the units change.

Intrinsic rate determinations were performed at a 4 lpm flow rate. To check for gas-side mass-transfer influence, the flow was doubled to 8 lpm. The subsequent oxidation rate remained unchanged indicating that the oxidation rates obtained at the 4 lpm flow were free of gas-side mass-transfer influence [19].
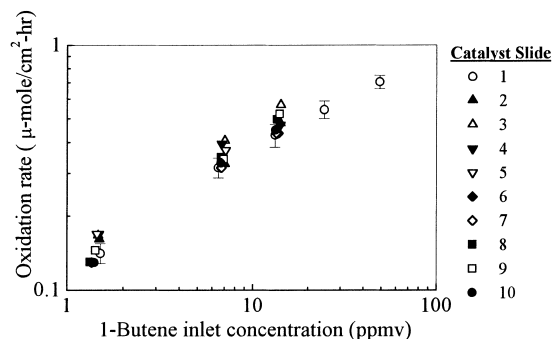
Fig. 1. Variance in photocatalyst activity of separate catalyst slides using 1-butene photo-oxidation: 1.96 mW/cm^2 UV; 5700 ppmv humidity.

Fig. 3. Photo-oxidation of DMMP: UVA 1.96 mW/cm^2; water vapor 5700 ppm; 48 ppm DMMP influent.

The relative fractional change in the DMMP (or 1-butene) concentration through the reactor was maintained below 0.1 through the selection of an appropriate catalyst (slide) length. This ensured that the reactor was being operated in a differential mode during rate determinations.

In all photo-oxidation experiments the following protocol was used: first, the gas flows and water vapor levels were set. After the reactor inlet/outlet water vapor levels reached equilibrium, DMMP (or 1-butene) was introduced. When the inlet/outlet DMMP (or 1-butene) concentration reached steady-state and was of equal magnitude, the UV-lamp was illuminated.

As discussed below, the photo-oxidation of DMMP resulted in the deactivation of the catalyst. As a result, a new titania-coated slide was used in each DMMP experiment. Prior to most DMMP experiments, the photo-activity of the subject catalyst slide was first determined by the photo-oxidation of 1-butene at several 1-butene influent concentrations. A sample of the resultant 1-butene rate determinations is shown in Fig. 1, in which each symbol in Fig. 1 represents a distinct slide allocated for a subsequent DMMP experiment. A variance of about 5% in the relative 1-butene oxidation rate was found from all the slides so far examined. Catalyst de-activation by 1-butene was not observed in any long-term exposure, as shown, for example, in Fig. 2. Importantly, in repeat DMMP experiments, the same DMMP result of oxidation rate dependence with time
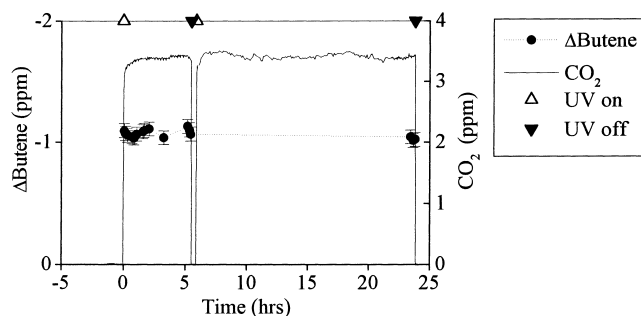
was found whether or not the subject catalyst was previously exposed to 1-butene.

Evidence for DMMP photocatalytic oxidation is shown in Fig. 3. A decrease in the reactor DMMP effluent, that is, a negative DMMP differential change (ΔDMMP in Fig. 3) through the reactor, was seen after the UV-lamp was illuminated. Concomitant with the decrease in DMMP concentration was the appearance of CO_2 and CO. After the UV-lamp was extinguished, ΔDMMP, CO_2, and CO returned to zero. The appearance of ΔDMMP when the UV-lamp was illuminated was interpreted as a photo-oxidation process. A carbon balance of the moment the UV-lamp was extinguished indicated that only about 20% of the carbon was being released as gas-phase CO_2 and CO.

At a relatively high UV-irradiation, a high initial rate of catalyst de-activation was seen following the activation of the UV-lamp, but which decreased as the influent DMMP was decreased (Fig. 4(A)). At the highest DMMP inlet concentrations in Fig. 4, catalyst de-activation was evident when the UV-exposure was observed over a time interval as short as a few hours following the activation of the UV-lamp. At a lower UV-irradiation, the catalyst de-activation rate was also lowered (Fig. 4(B)).

The oxidation rate, defined by Eq. (1), was considered meaningful when the adsorbate, DMMP, was in equilibrium with its gas-phase. If the oxidation process had reached a steady-state, then such a state of equilibrium would indeed exist. If stringently applied, the requirement of a state of equilibrium was not reached with DMMP, since the oxidation of DMMP de-activated the titania catalyst. However, if the rate of catalyst de-activation was sufficiently slow, then a pseudo steady-state of equilibrium may be envisioned to exist, and the oxidation rates may then be considered dependent, as an approximation, on the attendant DMMP gas-phase concentration.

The photocatalytic oxidation of gaseous contaminants on titania was shown to follow Lagmuir–Hinshelwood (L–H) kinetics in many studies [16,18,20–24]. L–H kinetics expresses a dependent relationship between the oxidation rate of a contaminant and its attendant gas-phase concentration, and furthermore, requires that a state of equilibrium exists between the adsorbate (i.e., contaminant) and its gas-

Fig. 2. Stability of 1-butene photo-oxidation: UVA 0.94 mW/cm^2, 13.9 ppm 1-butene influent, 5500 ppm water vapor.

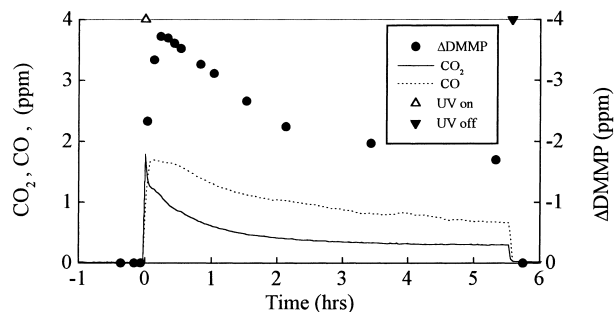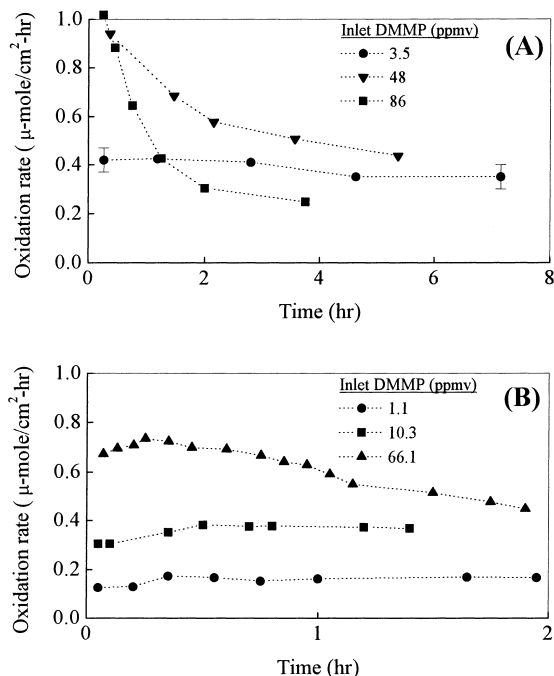Fig. 4. Influence of DMMP concentration on catalyst de-activation (UV-lamp activated at 0 h): (A) 1.96 mW/cm^2 UV, 5700 ppmv humidity; (B) 0.94 mW/cm^2 UV, 5600 ppmv humidity.

Fig. 6. Influence of UVA irradiation on DMMP initial oxidation rate: 8.1 ppmv DMMP inlet, 6000 ppmv water vapor.

phase [25]. To examine if the DMMP rate data followed a L–H rate form, an initial oxidation rate, defined herein as the highest measured oxidation rate at a given influent DMMP concentration, was used for the dependent variable.

A pseudo steady-state condition was likely to be achieved in Fig. 4(B) and for the lowest DMMP concentration in Fig. 4(A). The existence of a pseudo steady-state may not have been reached for the two highest DMMP concentrations in Fig. 4(A), and subsequently, the initial oxidation rate, as a pseudo steady-state oxidation rate, would be poorly determined. The initial oxidation rates computed from the data in Fig. 4 are shown in Fig. 5. Included in Fig. 5, was a fit to a unimolecular L–H rate form [25] for the low UV-irradiation (0.94 mW/cm^2) case. An adequate L–H fit was possible through the lower DMMP concentrations. It was not
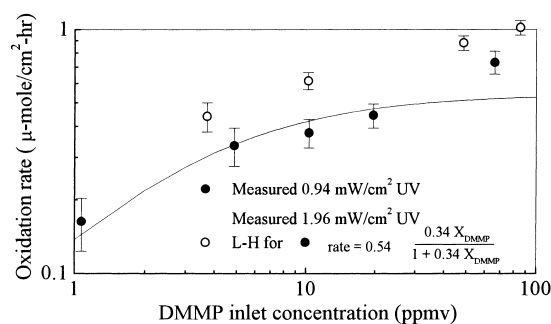
possible to also include the highest DMMP concentration, and it may be the result of not having achieved the pseudo steady-state condition, as discussed above.

The influence of UV-irradiation on DMMP initial oxidation rate is shown in Fig. 6. A low DMMP inlet concentration was used so that a pseudo steady-state rate could be established. The functional dependence of the oxidation rate on UV- intensity is well established both experimentally and theoretically [18,24,26], that is, UV-intensity raised to a power. The result (exponent in Fig. 6) is in agreement with those found by others [22,27] under similar UV-intensities.

3.3. Regeneration of depleted titania

One of the most interesting results of our study is that a de-activated titania catalyst may be easily regenerated by washing with water or by subjecting the catalyst in situ to UV-light in the absence of DMMP. The effect of these two regeneration strategies is shown in Fig. 7. The data shown in Fig. 7 was generated in a particular chronological order. First, a recently titania- coated slide was exposed to UV-illumination, following the stated experimental protocol, and allowed to de-activate (Fig. 7(A)). Next, the slide was exposed in situ to UV-light for 12 h in the absence of DMMP. Following this re-conditioning period, the slide was once again exposed to DMMP (Fig. 7(B)). By comparing Fig. 7((A) and (B)) some catalyst rejuvenation was achieved. This rejuvenation most likely resulted from oxidation of adsorbed DMMP and photodesorption of the adsorbed intermediates during the reconditioning period. The presence of adsorbed intermediates has been suspected to be a root cause of the titania catalyst deactivation [22]. The slide was then kept in the dark for 12 h in the absence of DMMP as another potential rejuvenation means. Following this reconditioning period, the slide was once again exposed to DMMP (Fig. 7(C)). A comparison of Fig. 7((B) and (C)), indicated that catalyst rejuvenation was not achieved, however. Next, the slide was removed, washed in distilled water (sequentially dipped in four fresh cylinders of distilled water and dried at approximately 35°C for roughly 10 min), and returned to the reactor. The slide was once again exposed to DMMP (Fig. 7(D)). A comparison of Fig. 7((A) and (D))

Fig. 5. Influence of DMMP concentration on DMMP initial oxidation rate: (●) 0.94 mW/cm^2 UV; (○) 1.96 mW/cm^2 UV; all data at 5700 ppmv humidity.
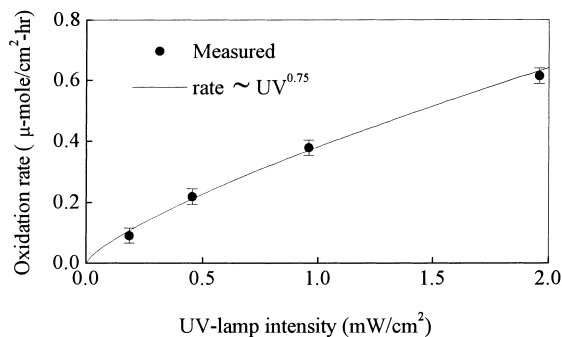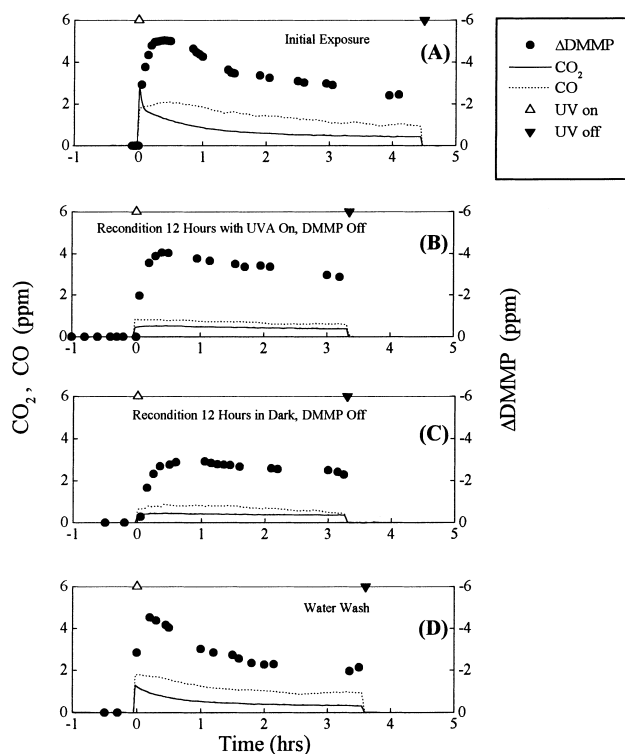
Fig. 7. Effect of catalyst regeneration strategies: water vapor 5700 ppm, 60 ppm DMMP influent; (A) initial exposure, UVA 0.94 mW/cm^2; (B) re-condition by 12 h with UVA on, DMMP off; (C) re-condition by 12 h in the dark, DMMP off; (D) re-condition by water wash.

indicated that catalyst rejuvenation was again achieved. The water wash and the UV-exposure rejuvenation strategies were repeated, but instead of exposing the catalyst to DMMP as a test for rejuvenation, the catalyst was exposed to 1-butene and UV-illumination. The crucial comparison was between the oxidation rate of 1-butene determined on a new titania-coated slide against the oxidation rate of 1-butene on the supposed rejuvenated slide. Again, the water wash strategy was found to completely rejuvenate the catalyst, while a 2 h exposure to UV-irradiation was found to partially rejuvenate the catalyst.

The washing of titania with water, as opposed to drying at 35°C, is believed to be responsible for rejuvenating the catalyst. Previous studies have shown that temperatures greater than 100°C are required to remove adsorbed water from the surface of titania [28]. This is due to the fact that the surface of the titania in a humid environment is hydroxylated and contains adsorbed water and hydroxyl groups. Water strongly adsorbs on the hydroxylated titania surface via hydrogen bonding to surface hydroxyl groups [28]. Other molecules that are also strongly bonded to the surface hydroxyl groups of hydroxylated anatase and rutile, via hydrogen bonding, include phenol, ammonia and pyridine [29]. In addition, adsorption on a dehydroxylated site can result in irreversible chemisorption [30]. Creation of a dehydroxylated site can result from the oxidation reaction itself. In the case of DMMP, methyl phosphonic acid and

phosphate, strong adsorption to the hydroxylated titania surface may take place via the phosphorus atom, and/or via the oxygen atom of either methoxy or hydroxyl groups. The low vapor pressures of these compounds also suggests that they remain on the de-activated catalyst during the brief, low temperature drying process.

3.4. Reaction pathways

The molecular structures of the nerve gas sarin (GB) and the simulant DMMP are shown below.

DMMP   Sarin
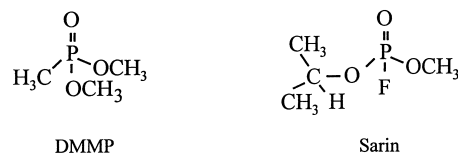
The decomposition of DMMP compared to nerve gas is predicted to be more difficult due to the absence of fluorine atoms which may act as a better leaving group than methyl or methoxy radicals.

Several recent studies in the literature are relevant to the results we report here [9–15]. Tanaka and co-workers, for example, have recently investigated the photocatalytic degradation of the insecticides DDVP (dimethyl-2,2-dichlorovinyl phosphate) and DEP (dimethyl-2,2,2-trichloro-1-hydroxyethyl phosphonate) in aqueous suspensions of TiO_2 [14]. The main products observed were Cl^- and PO_4^{3-}, with formaldehyde as an intermediate that disappeared under further reaction. In a study by Fox and co-workers [13], butylphosphonic acid, benzylphosphonic acid and phenylphosphonic acid were decomposed in aqueous TiO_2 suspensions. Kinetic data were found to be consistent with a Langmuir–Hinshelwood model [13].

According to the generally reported mechanism for photocatalytic decomposition using TiO_2, irradiation of TiO_2 promotes a valence band electron to the conduction band ([13,26] and references therein). This results in a conduction band electron (e_c^-) available for reducing species on the surface of the semiconductor, and a valence band hole (h_v^+) capable of oxidizing species adsorbed on the substrate. The actual mechanism of oxidation/reduction, is believed to involve the production of superoxide anions and hydroxide radicals as shown in Eqs. (3) and (4).

$$TiO_2 + h\nu \rightarrow e_c^- + h_v^+ \tag{2}$$

$$e_c^- + O_2 \rightarrow O_2^- \tag{3}$$

$$h_v^+ + H_2O \rightarrow H^+ + {}^{\bullet}IOH \tag{4}$$

The conduction band electron, e_c^-, is believed to be trapped by adsorbed O_2 to form a superoxide ion (Eq. (3)). The valence band hole, h_v^+, may be trapped by H_2O to form OH radicals; or by an adsorbed organic (e.g., DMMP or phosphonate intermediates) as discussed in the literature [13,31,32].

In Fox's study [13], evidence was found for cleavage of the carbon–phosphorus bond and a postulated mechanistic

route was reported as shown in Eq. (5).

$$\phi - CH_2 - P(=O)(OH)_2 + H_2O + h_v^+$$
$$\rightarrow \phi - CH_2^{\bullet} + H_3PO_4 + H^+ \qquad (5)$$
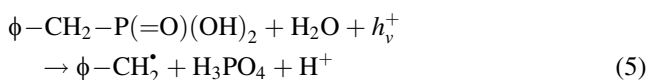
The benzyl radical was found to be an intermediate for the observed species ϕ–CH_2OH, ϕ–CHO, and ϕ–CH_2CH_2–ϕ. In our study, we believe that the more common route of P–O cleavage occurs before eventual P–C cleavage. This is due to the observance of methyl phosphonic acid, CH_3–

explaining the mass balance discrepancy based on gas-phase CO_2/CO alone. In contrast with the liquid-phase study [11], we have detected methyl formate ($HCOOCH_3$). Although, methyl formate may be formed directly on the TiO_2 surface, another possibility is the formation of methanol and formic acid which react readily to give methyl formate. We also observed methanol from a GC analysis of cold-trap constituents. The identification was based on the comparison of retention time with a methanol standard.

Hydrogen Abstraction
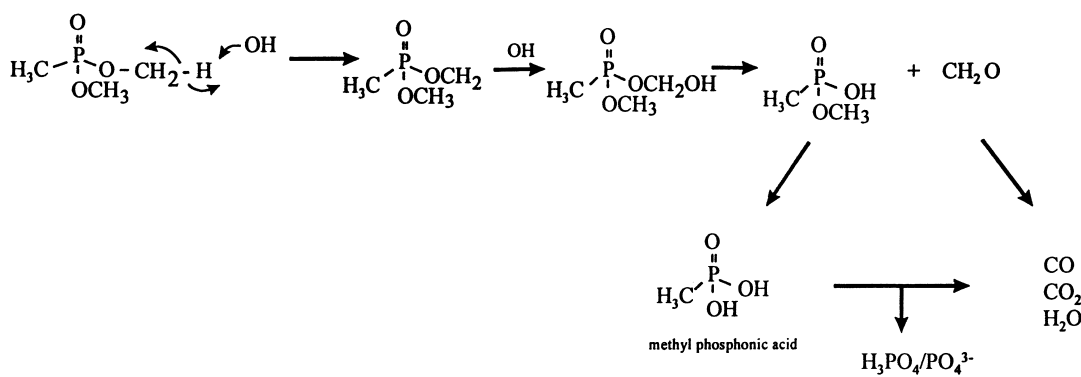
Addition - Elimination
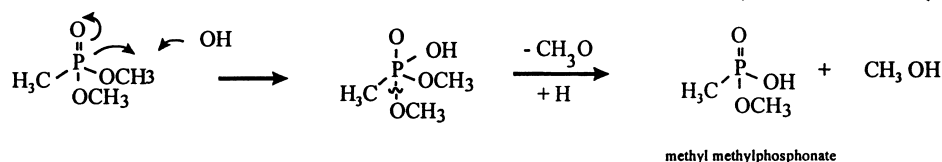
$P(=O)(OH)(OCH_3)$. We also observed phosphate (PO_4^{3-}) and CO_2, indicative of complete oxidation of DMMP.

In addition to direct oxidation by valence band holes as discussed above, hydroxyl radical attack provides another oxidation pathway for DMMP. The primary mechanisms for the photocatalytic oxidation of DMMP via hydroxyl radical attack, are hydrogen abstraction and addition–elimination [11]. Further oxidation to produce CO/CO_2 and H_2O from methanol and formaldehyde is anticipated as a result of the high reactivity of these compounds on titania. A previous investigation of the photocatalytic oxidation of DMMP in an aqueous solution of titania [11] found that methanol was not observed, thereby suggesting that the addition–elimination mechanism is not significant under aqueous conditions. It is not possible at this time, to determine the importance of the hydroxyl radical mechanism as compared to the direct valence hole mechanism.

In our investigation, complete conversion of any methanol or formaldehyde that may be formed, to produce CO_2 and CO appears to be the dominant reaction. Phosphates remain on the surface along with methyl phosphonic acid which retains a portion of the carbon content of DMMP, thereby

To investigate the formation of methyl formate, we injected a mixed gas-phase sample of formic acid and methanol into the GC–MS. The standard protocol of cryo-trapping to increase sensitivity was employed, and a GC–MS peak corresponding to methyl formate was observed. Therefore, any gas-phase methanol and formic acid may react during the process of detection via the GC–MS. In addition, methyl formate may be synthesized in the cold-trap during the process of collecting products from the titania reactor. It should also be noted that in the study of liquid-phase DMMP decomposition on titania, formic acid was detected as an intermediate, while neither methanol nor methyl formate were reported [11]. In contrast to the liquid-phase study which followed the accumulation of products over several days in a closed reactor [11], our reactor was not a batch system. The distribution of reactants, intermediates and products in equilibrium would therefore be different in both cases. It is also clear that in aqueous solution the role of water, acidity and basicity, and the ability to strip organic/inorganic phosphates from the surface of the catalyst, play a critical role.

4. Conclusions

In conclusion, we have determined the intrinsic rates for the photocatalytic decomposition of gas-phase DMMP on titania at room temperature. The products we detected were carbon dioxide, carbon monoxide, methylphosphonic acid and phosphate. There also appears to be methanol and methyl formate; the latter most probably originates from the reaction of methanol and formic acid. Finally, we have determined that washing of de-activated catalyst with water is sufficient for complete regeneration of the catalyst with respect to both DMMP and butene reactivity. The solubility of methyl phosphonic acid and phosphates in water aids in removing these species from catalytically active sites.

Acknowledgements

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