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# Photocatalytic decomposition of organophosphonates in irradiated $TiO_2$ suspensions

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## Abstract

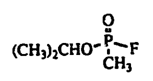
Kinetic analyses of the $TiO_2$-catalyzed photodegradation of dimethyl methylphosphonate (DMMP) and diethyl methylphosphonate (DEMP) in oxygenated aqueous solutions are described. The effects of substrate concentration and solution pH are investigated. A number of kinetic models appear to be applicable in accordance with the initial kinetic parameters. The major products formed from the photocatalytic decomposition of DMMP are methylphosphonic acid, phosphoric acid, formaldehyde and formic acid. © 1997 Elsevier Science S.A.

*Keywords:* Irradiated $TiO_2$ suspensions; Organophosphonates; Photocatalytic decomposition

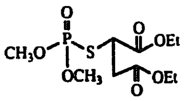
## 1. Introduction

The photocatalytic degradation of organic and inorganic substances in semiconductor suspensions has been shown to be a promising method for the treatment of wastewater and the destruction of chemical waste [1]. Over the past decade, it has been shown that the photocatalyst $TiO_2$ can be used to decompose a variety of environmentally threatening materials. Vigorous research has demonstrated that essentially all chlorinated aliphatics, chlorinated aromatics, several pesticides, herbicides, surfactants and dyes are completely oxidized to innocuous products, such as water, carbon dioxide and mineral acids [1–5]. Although extensive studies have been conducted by both chemists and engineers on a variety of hazardous materials, only a limited number have appeared on the photocatalytic degradation of organophosphorus compounds [6–10].

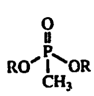
We have chosen to study the degradation of dimethyl methylphosphonate (DMMP) and diethyl methylphosphonate (DEMP) as models to estimate the reactivity of hazardous pesticides and chemical warfare agents towards $TiO_2$ photocatalysis. For comparison, the simulants, warfare agents and pesticides are shown below.



Warfare Agent - Sarin



Pesticide - Malathion



Simulants - R = $CH_3$, $CH_2CH_3$

The phosphorus–fluorine and phosphorus–sulfur bonds associated with sarin and malathion should be more labile than the phosphorus–carbon and phosphorus–oxygen bonds in the simulants. The simulants are therefore expected to be less reactive than the warfare agents and pesticides, and provide a conservative estimate for the potential of $TiO_2$ photocatalysis for the decontamination of hazardous organophosphorus compounds. The $TiO_2$-catalyzed photodecompositions of DMMP and DEMP were studied in an attempt to determine the feasibility of such a process for the controlled destruction of toxic organophosphorus compounds, such as pesticides and nerve gases. The kinetic analyses, product studies and effects of pH are reported herein.

## 2. Experimental section

### 2.1. Materials

DMMP, DEMP, 2,4-dinitrophenylhydrazine, heptafluorobutyric acid, heptabutylammonium hydroxide and methylphosphonic acid were purchased from Aldrich Chemical

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Company. Aqueous solutions were prepared from water distilled from an all-glass Corning distillation apparatus. The gases, oxygen and nitrogen, were UHP grade from Trigas. $TiO_2$ was donated by Degussa (P25, lot RV2186). All reagents were used as received unless noted otherwise.

### 2.2. *Instrumentation*

Gas chromatography (GC) analyses were performed on a Hewlett-Packard 5890A instrument equipped with a flame photometric detector (FPD) model 19256A (HP) with a 393 nm wavelength filter and a 30 m × 0.530 mm DB-5 Megabore bonded phase column (J&W Scientific). Irradiation of the semiconductor suspensions was conducted in a Rayonet photochemical reactor (Southern New England Ultraviolet) fitted with 16 "black light" phosphor (350 nm) lamps, a Rayonet merry-go-round (model RMA-500) and a cooling fan. pH measurements were conducted on a Corning pH meter (model 245).

### 2.3. *General photolysis procedure*

$TiO_2$ (5 mg) was added to a solution of phosphonate in 50 ml of distilled water. The solution was agitated in an ultrasonic bath for 20 min to ensure thorough mixing. The solutions were saturated with oxygen (or nitrogen where indicated) prior to photolysis. Magnetically stirred reaction mixtures in Pyrex tubes were irradiated in a Rayonet reactor. Samples (5.0 ml) were taken at various time intervals and the $TiO_2$ was removed from the samples by 0.45 μm filtration. The filters were rinsed with 5.0 ml of water to give a total volume of 10.0 ml of solution. The resulting solution was extracted in chloroform prior to GC analysis. The concentrations of DMMP and DEMP were determined by GC using internal standards.

### 2.4. *Analysis of byproducts*

#### 2.4.1. *Formaldehyde*

An indirect method was used after a pre-column derivatization reaction with 2,4-dinitrophenylhydrazine [11,12]. A Hewlett-Packard HPLC model 1090 equipped with a 1040 M (HP) diode array UV–visible detection system was used for the determination of the formaldehyde derivative.

#### 2.4.2. *Carbon dioxide*

Air was passed from the reaction vessel through a saturated solution of $Ba(OH)_2$ in 1.0 M NaOH. The carbon dioxide produced during photolysis was trapped as solid $BaCO_3$ and measured gravimetrically.

#### 2.4.3. *Formic acid*

A Dionex 4000i ion chromatograph, equipped with an ICE-AS5 column (Dionex) and an AMMS-ICE micromembrane suppressor, was employed to analyze formic acid. Heptafluorobutyric acid at a concentration of 1.6 mM was used as eluent. The flow rate was 0.5 ml $min^{-1}$ at a pressure of 1300 lbf $in^{-2}$. Heptabutylammonium hydroxide at a concentration of 5 mM and a flow rate of 2 ml $min^{-1}$ was employed as regenerant. Formic acid was detected using a conductivity detector (Dionex). Samples to be analyzed were injected as aqueous solutions.

#### 2.4.4. *Phosphate and methylphosphonic acid*

A Dionex 4000i ion chromatograph, equipped with an ICE-AS9 column (Dionex) and an AMMS-ICE micromembrane suppressor, was employed to analyze phosphates and methylphosphonic acid. The flow rate was 0.5 ml $min^{-1}$ at 1300 lbf $in^{-2}$. The eluent solution was composed of 1.8 mM $Na_2CO_3$ and 1.7 mM $NaHCO_3$. As regenerant a 0.25 N solution of $H_2SO_4$ was used at a flow rate of 2.0 ml $min^{-1}$. The chromatograph was fitted with a conductivity detector. The samples were analyzed as aqueous solutions.

## 3. Results and discussion

### 3.1. *Degradation kinetics*

The photoexcitation of $TiO_2$ generates an electron–hole pair, creating the potential for both reduction and oxidation processes to occur at the surface of the semiconductor. Although a number of possible degradation pathways can be envisioned, the formation and subsequent reactions of hydroxyl radicals, generated from the oxidation of water molecules by photoexcited $TiO_2$, are generally accepted as the predominant degradation pathways of organic substrates in aqueous solutions.

DMMP and DEMP are readily decomposed on irradiation in oxygen-saturated aqueous suspensions of $TiO_2$. Appropriate controls verified that the decomposition is the result of photoexcited $TiO_2$ and not direct photolysis or ground state $TiO_2$-catalyzed reactions. The initial degradation rates were determined from the first 10% disappearance of the starting material to minimize the effects of products on the initial kinetic parameters. The disappearance of each substrate was monitored by GC analysis and extreme care was taken to ensure uniform experimental conditions. The initial rates of degradation as a function of substrate concentration are summarized in Table 1.

### 3.2. *Kinetic models*

An important consideration in the $TiO_2$-photocatalyzed reactions of substrates is the adsorption onto the surface of the semiconductor particle. Although it has been reported that adsorption is critical for the generation of reactive intermediates, there is still uncertainty as to the role adsorption plays and how it ultimately affects the reaction pathways [13,14] (i.e. Lawless et al. [15] have reported direct observation of hydroxyl radicals bound to the surface of $TiO_2$, but whether

Table 1
Initial degradation rates of phosphonates as a function of concentration by $TiO_2$ photocatalysis in aqueous solution

| Substrate | [Concentration [a] ( $\times 10^3$ M)], rate ( $\times 10^5$ M $min^{-1}$) |
|---|---|
| DMMP [b] | [0.10], 0.85; [0.19], 1.3; [0.52], 3.2; [1.38], 6.8; [2.72], 8.4 |
| DEMP [c] | [0.12], 0.51; [0.19], 0.53; [0.57], 1.6; [2.06], 5.6; [2.74], 6.4 |

[a] The concentrations were determined from a standardization curve constructed from aqueous extractions.

[b] The relative error in the determination of the initial rates is ±7% based on quadruplicate runs.

[c] The initial rates were reproducible within 5% based on duplicate runs at each concentration.

subsequent reactions occur at the surface or in solution remains unclear [16]).

A number of kinetic models, including the Langmuir–Hinshelwood (L–H), Eley–Rideal (E–R) and Freundlich (F) models, have been commonly employed to describe heterogeneous photocatalysis [17–19]. In previous studies, the models were used in an attempt to determine whether the reactions occur in the adsorbed state (L–H and F models) or in solution (E–R model). With this in mind, each of the kinetic models was employed using the initial degradation rates of the phosphonates. In all cases, the kinetic parameters from the different models are essentially the same for DMMP and DEMP (Table 2). The least-squares fit correlation coefficients $R$ are a measure of the goodness of the fit of the experimental results to each model.

Although these models were originally adopted to describe different physical processes, our experimental data are equally consistent with all of the different models. Extreme care should be used in the application of these models for mechanistic distinctions in semiconductor photocatalysis. The similarity of the fit of each model to the experimental results is consistent with the suggestions of Turchi and Ollis [20] that these kinetic models simply represent saturation kinetics. The resulting kinetic parameters represent "apparent" rate constants. Apparent, however, does not mean useless; reliable information can be determined from comparisons for a given set of experimental conditions. DMMP and DEMP have comparable reactivities to a variety of organic compounds determined under these conditions [21], implying that hydroxyl radical production is the rate-determining step for these reactions.

### 3.3. Product studies

Product studies were used to establish the course of photodegradation and to determine the formation of intermediate products during degradation. The $TiO_2$-catalyzed photolytic degradation of DMMP yields phosphoric acid and $CO_2$ as the final products (Scheme 1). Methylphosphonic acid and formic acid, identified using ion chromatography, and formaldehyde, identified as the 2,4-dinitrophenylhydrazine derivative, are formed during $TiO_2$ photocatalysis.

Comparisons of $TiO_2$ photocatalytic and radiolytic studies have been used to provide insight into the mechanisms involved in the $TiO_2$-catalyzed photodegradation of a variety of organic substrates [3,15,22]. We have demonstrated that radiolytic and $TiO_2$ photocatalytic degradations of DMMP yield the same major products [23]. Although both processes generate hydroxyl and superoxide anion radicals, the radiolysis studies indicate that the hydroxyl radical is the predominant oxidizing species in the degradation of DMMP and DEMP.

### 3.4. Mechanistic considerations

A number of reaction mechanisms can be envisioned to explain the formation of the major products: methylphos-

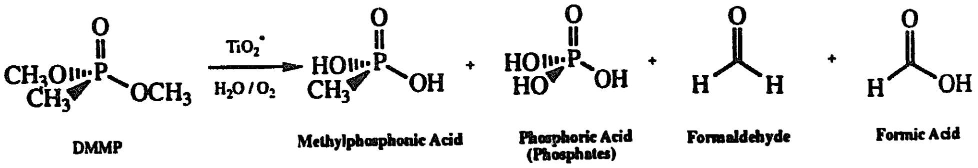
Table 2
Kinetic parameters of various models

| Substrate | Langmuir–Hinshelwood [a] | | | Eley–Rideal [b] | | Freundlich [c] | | |
|---|---|---|---|---|---|---|---|---|
| | $K$ ($M^{-1}$) | $k$ (M $min^{-1}$) | Fit ($R$) | $k$ ($min^{-1}$) | Fit ($R$) | $n$ ($min^{-1}$) | $k_rK$ | Fit ($R$) |
| DMMP | 790 | 11.1 | 0.994 | 0.03 | 0.955 | 0.74 | 7.6 | 0.992 |
| DEMP | 640 | 6.3 | 0.958 | 0.02 | 0.994 | 0.87 | 11.3 | 0.993 |

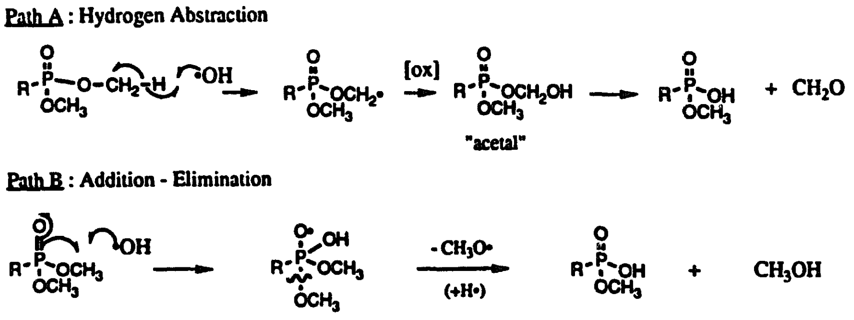
[a] $k$ and $K$ are defined as the reaction rate and adsorption equilibrium constant respectively.

[b] $k$ represents a measure of the reactivity.

[c] $k_rK$ represents the product of the reaction rate constant and the adsorbent capacity, and $n$ is indicative of the strength of adsorption; lower values indicate stronger adsorption.



Scheme 1. Major products from the $TiO_2$-catalyzed photolytic degradation of DMMP in aqueous solutions.



Scheme 2. Proposed hydroxyl radical-mediated degradation mechanisms of DMMP.

phonic acid, formaldehyde, formic acid and carbon dioxide. Although Gratzel et al. [6] reported the "dark hydrolysis" of a *p*-nitrophenyl-substituted phosphate in aqueous $TiO_2$ suspensions and Rose and Nanjundiah [8] reported significant surface-catalyzed reactions of dimethoxyfluorophosphonate, no appreciable "dark" reactions or hydrolysis were observed in our investigations at $pH \leq 7$ for DMMP even at exposures up to several days. This apparent discrepancy is undoubtedly related to the relatively poor leaving group ability of the methoxy group in DMMP compared with *p*-nitrophenol and the labile nature of the P–F bond in these previous studies.

Electron transfer from the phosphonate to photoexcited $TiO_2$ can lead to the formation of a phosphonate radical cation, which may subsequently react with water or oxygen to yield oxygenated products. Harada et al. [7] have proposed the involvement of such radical cation intermediates in the $TiO_2$ photocatalytic degradation of alkyl phosphates, but under the conditions of our investigations, using dilute aqueous solutions, the predominant degradation pathway probably involves the reactions of hydroxyl radicals. Probable mechanisms for the hydroxyl radical-mediated conversion of DMMP to methylphosphonic acid are shown in Scheme 2.

Path A involves the abstraction of a hydrogen atom from the methyl ester leading to a radical intermediate. Once the radical is formed, further oxidation can lead to the formation of an "acetal", either by direct reaction with another hydroxyl radical, which in aqueous solution will be converted to the partially hydrolyzed ester, or by the addition of oxygen to form a peroxy radical. The dimerization of two peroxy radicals followed by the extrusion of $O_2$ via a Russell mechanism can also be used to explain the product formation. Oxidation of the remaining methoxy group yields methylphosphonic acid.

An alternative mechanism, path B, in which the hydroxyl radical adds to the phosphorus atom [24], followed by the elimination of the methoxy group, will also yield methylphosphonic acid. If such a mechanism is operative, the production of methanol is expected. Under the experimental conditions of these investigations, methanol was not formed at detectable levels. While this observation suggests that the addition–elimination mechanism is not a predominant reaction pathway, such a mechanism cannot be completely eliminated.

The formation of methylphosphonic acid is consistent with hydroxyl radical-mediated pathways, but subsequent formation of the phosphate requires oxidation/cleavage of the C–P bond which is not easily rationalized via hydroxyl radical-mediated pathways. The process may involve direct oxidation of the carbon–phosphorus bond by $TiO_2^*$, the addition of superoxide anion radical or oxygen, a Baeyer–Villiger-type rearrangement and/or a combination of these oxidation pathways.

### *3.5. Influence of reaction products and pH on the degradation process*

Water quality can have a pronounced effect on the photocatalytic efficiency of irradiated $TiO_2$ suspensions. A number of factors must be considered in the degradation of DMMP and DEMP. Phosphoric acid (phosphate) is one of the final oxidation products of $TiO_2$ photocatalysis of organophosphorus compounds. Phosphate-buffered solutions are also commonly used in $TiO_2$ photocatalysis to maintain solution pH. Although Abdullah et al. [25] have reported that phosphates inhibit the $TiO_2$ photocatalysis of several organic substrates, no appreciable inhibition was observed in our studies, despite the formation of phosphates during photocatalysis. The time profile for the disappearance of DMMP and the formation of products during photocatalysis is illustrated in Fig. 1.

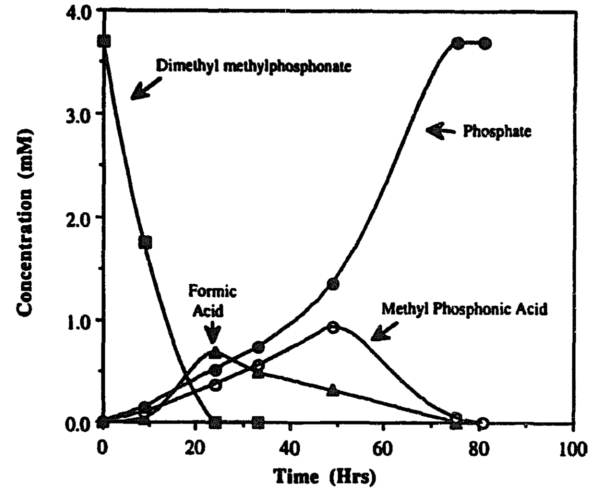
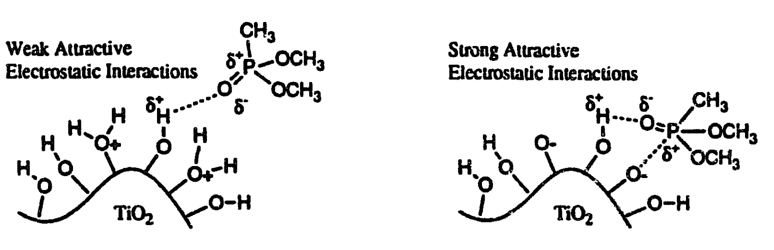


Fig. 1. Degradation of DMMP and the subsequent formation and disappearance of products as a function of irradiation time during $TiO_2$ photocatalysis.



Acidic Conditions Basic Conditions

Scheme 3. Adsorption of phosphonates and electrostatic interactions at the surface of $TiO_2$.

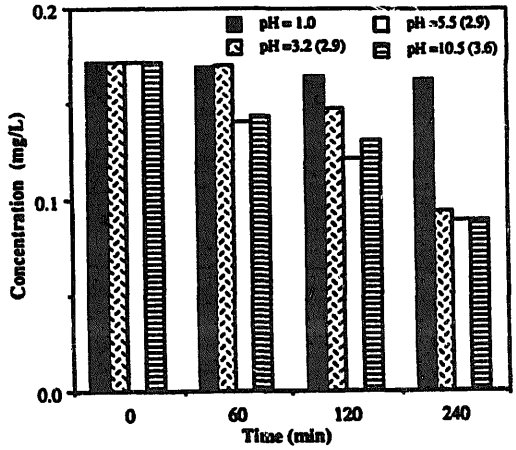


Fig. 2. Photocatalyzed degradation of DMMP as a function of the initial solution pH over 4 h of irradiation in aqueous suspensions of $TiO_2$. The numbers in parentheses are the solution pH values after 4 h of irradiation.

The extent and means by which phosphates can affect photocatalysis will undoubtedly depend on a variety of factors, i.e. phosphate adsorption at the active sites of $TiO_2$ will be influenced by the phosphoric acid/phosphate species and the surface charge of the $TiO_2$ particles. Investigations evaluating phosphate adsorption and inhibition as a function of solution pH and concentration are currently underway.

The solution pH can significantly influence the $TiO_2$ photocatalysis of substrates in aqueous solutions [26,27]. The surface of a $TiO_2$ particle is completely hydroxylated and has zero overall charge at pH ~6.6. As the pH is lowered, the number of protonated sites increases as does the overall positive charge on the particle. At high pH, the number of oxyanion sites increases and the particle becomes negatively charged. These surface changes will directly affect surface adsorption and subsequent reactivity.

The initial solution pH has a pronounced influence on the rate of degradation of DMMP, as shown in Fig. 2. The rate of disappearance increases at high initial pH and decreases at low pH.

The increase in the rate of disappearance at high pH may be the result of stronger adsorption and a significant contribution from surface-catalyzed reactions and direct hydrolysis [28]. At low pH ($pH < 2$), the decomposition is very slow, presumably as a result of a highly protonated surface, which leads to weak adsorption of the simulant onto the surface of the $TiO_2$ particles (Scheme 3).

Under basic conditions, the surface has a negative charge and stronger electrostatic interaction/adsorption are expected than under acidic conditions. As the reaction progresses, the solution becomes acidic because of the formation of acidic products. Despite the acidic nature of the reaction solution after 4 h of irradiation, effective degradation was still observed. Faster initial degradation rates are observed under basic conditions, but the overall degradation is comparable over the range pH ~ 3–10.

## 4. Conclusions

The phosphonates DMMP and DEMP are readily degraded by $TiO_2$ photocatalysis over a range of concentrations and solution pH. Saturation kinetics are observed and the final products are indicative of complete mineralization. Mechanistic considerations imply that hydroxyl radicals are involved in the degradation of DMMP to methylphosphonic acid. The involvement of additional oxidative pathways is suggested for the transformation/oxidation of the C–P bond, ultimately leading to phosphoric acid. Our studies suggest that $TiO_2$ photocatalysis should be an effective technique for the destruction of organophosphorus compounds in aqueous solutions.

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