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Photocatalytic Oxidation of Dimethyl Methylphosphonate in Aqueous Suspensions of ${\rm TiO}_2$

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Abstract

Heterogeneous photocatalysis using simulated solar irradiation in the presence of titanium dioxide was studied using dimethyl methylphosphonate (DMMP) as a surrogate for organophosphorus compounds including pesticides and chemical warfare agents. A reduction in solution pH accompanied DMMP degradation with the pH approaching the pKa of DMMP. Addition of peroxide before reaction increased the amount of DMMP degraded. Nearly complete destruction of DMMP was only achieved with the largest addition of peroxide. Photoreaction of DMMP in a pH 10 solution and a pH 10 carbonate buffer degraded a similar percent of the solute, with a more gradual reaction observed for the buffered solution. Variations in reaction conditions were studied to evaluate the effect of potential spill conditions. The presence of fulvic acid in the solution slightly enhanced the oxidation of DMMP and the absence of dissolved oxygen inhibited DMMP oxidation. DMMP solutions prepared in simulated sea water reached similar degradation percentages as pure solutions, however, reacted more slowly.

Keywords: Photocatalysis; Titanium dioxide; DMMP; Oxidation; pH influence

Introduction

Heterogeneous photocatalysis using titanium dioxide (TiO₂) is a well-studied oxidation process that can degrade a broad range of wastewater contaminants, including chlorinated compounds, aromatics, pharmaceutical active ingredients, hydrocarbons and dyes [1]. Despite growing scientific understanding of the photocatalytic oxidation of wastes, industrial-scale applications continue to face practical challenges [2,3]. There is considerable interest in applying this oxidation technology to organophosphorus compounds widely used in agriculture and which have been found at increased concentrations in both surface and ground water [4]. Similarly, there is interest in understanding the effectiveness of this oxidation technology in safeguarding the water supply from potential threats. Dimethyl methylphosphonate (DMMP) has been used as a surrogate compound for hazardous organophosphate materials such as Sarin (a chemical warfare agent), Malathion (an agricultural and residential pesticide) and phosphate-based detergents. The structure of DMMP and two representative hazardous compounds are shown in Figure 1. Oxidation studies performed with DMMP are expected to provide a conservative estimate of the degradation rate obtainable with the target compounds [5,6]. In addition, DMMP is known to yield lower photoreaction rates than other potential surrogate compounds, including trimethyl phosphate, triethyl phosphate and diethyl phosphoramidate [7].

Other proposed processes for destruction of DMMP include catalyzed thermal decomposition [8], sonolysis [9,10], photolysis, and heterogeneous photocatalysis. Photocatalytic oxidation of DMMP using metal oxides including WO₃ [11] and amorphous manganese oxide [12] has been studied, however TiO₂ is the predominant photocatalyst. Previous studies have shown that TiO₂ and UV irradiation can completely degrade DMMP from 2 mM solutions and that the reaction proceeds via oxidation of the methoxy groups followed by oxidation of the methyl group [13]. Oxidation of DMMP to methylphosphonic acid, formaldehyde, formic acid and phosphate with TiO₂ in an air-purged system under 350 nm light and solar irradiation was observed to be sensitive to substrate concentration as well as catalyst type and loading. This was attributed to the availability of active sites and competitive adsorption of reactants and products on the catalyst surface [9,14].

Using a high-pressure mercury lamp with irradiance of 5x10⁻⁵ E/min and an open system, DMMP and total organic carbon (TOC) removal were more effective for lower initial concentrations of DMMP [7]. More recently, DMMP was used as a test compound for a kinetic study which included effects of several reaction parameters to develop a predictive model for reaction rate [15]. Using an air sparge, a 1.6 mM DMMP solution and 3700 W/m² irradiance, Almquist observed a 70% reduction in TOC after 60 minutes of irradiation. Sonication has also been used to accelerate the photoreaction due to the enhanced transport within the liquid phase [9,16].

Since photocatalytic reaction rates are sensitive to the details of the experimental system, this work further addresses the impact of reaction conditions on photocatalytic degradation of DMMP solutions using TiO_2 and simulated solar irradiation. The parameters varied include initial solution pH, dissolved oxygen, addition of H_2O_2 , presence of organic matrix compounds and salinity.

Materials and Methods

DMMP analysis

Dimethyl methylphosphonate, 97%, was purchased from Sigma and Degussa P25 TiO_{2^3} nominal primary diameter 21 nm, was provided by the manufacturer. DMMP peak areas for standard solutions were quantified using an HP6890 GC with an HP Wax column and FID and used to create a calibration curve. One µl volumes of calibration standards and samples were injected with a 9:1 split ratio and the column temperature ramped from 40 to 120°C at a rate of 10°C/ min. During reaction, the solution pH often dropped below 5.5, the

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Figure 1: Molecular structures of a) Sarin; b) Malathion and; c) Dimethyl methylphosphonate.

suggested minimum pH for the column. Therefore, solution pH was measured and if needed, small, measured additions of NH₄OH were used to adjust the pH before injection into the GC. The resulting peak areas were converted to concentration using the calibration curve and corrections were made to the concentration for any solution volume added for pH adjustment. Likewise, if the solution pH was above 8.5, the suggested maximum pH for the column, small additions of dilute citric acid solution were used to lower the pH and calculated concentrations were similarly adjusted. Reaction progress is reported as C/C_0 , where C_0 was determined by GC analysis of the initial solution. For experiments involving TiO₂, the sample solution was centrifuged and an aliquot was filtered through a 0.22 µm nylon filter prior to GC injection.

Adsorption and stability studies

Adsorption studies were performed using approximately 10 mM DMMP solution and with this solution adjusted to pH 10 with NH₄OH and adjusted to pH 3 with dilute citric acid solution. DMMP 50 mL solution were combined with 20, 40 and 80 mg of TiO₂ and stirred for 5 hours in reaction flasks under room light. The DMMP concentrations were measured before and after the allotted contact time.

Stability studies were performed to determine the potential degradation of DMMP in neat solutions over extended times. DMMP 5 mL and 10 mM DMMP solutions were stored under room light, irradiated in the light box or irradiated in covered tubes in the light box (dark control) and the DMMP concentration monitored over 70 hours. Since enhanced DMMP photodegradation has been reported under alkaline conditions [14], these tests were repeated for solutions adjusted to pH 10 with dilute NH₄OH. Finally, the stability of DMMP in the presence of an oxidizing agent was studied by adding 3 wt% H₂O₂ solution to 10 mM DMMP solution to achieve a 5:1 molar ratio of H₂O₂ to DMMP storing these under irradiation and dark control conditions.

Photoreactions

Reactions were performed using 5 or 10 mL of DMMP solution in 16.5 mL capacity glass vials with a measured mass of TiO₂. Initial DMMP concentrations ranged from approximately 5 to 10 mM. The DMMP solution pH was measured and for some experiments was adjusted to a desired value using small additions of NH₄OH solution. For some experiments, H₂O₂ solution was added to the reaction tubes. For one set of experiments, open reaction tubes were placed in a sample bag which was purged using nitrogen flow. The tubes were stored overnight under nitrogen pressure and sealed before withdrawal to deoxygenate the solution. The tube mouth was covered with either cleaned aluminum foil or Teflon tape before sealing the cap. Sealed reaction tubes were sonicated before reaction to completely disperse the TiO₂.

Photoreactions were performed in a light box using six UVA-340 lamps (Q-Panel) providing an incident irradiance of 17.5 W/m^2 as

measured with a radiometer. Using ferrioxalate actinometry the photon absorption rate inside the reaction tube was estimated to be 5.0×10^{-6} E/min. To prevent settling of the TiO₂, the vials were stabilized on the bed of an orbital shaker and shaken at 150 rpm during irradiation.

Further studies on the influence of reaction conditions on photodegradation of DMMP included attempts to mimic contaminated fresh water and saline water. The addition of 10 mg/L of Suwannee River Fulvic Acid Standard to the DMMP solutions used in photoreactions was used as a representative of organic matter in ground and surface fresh water. To represent the treatment of DMMP contaminated brackish water or sea water, a simulated sea water solution was prepared by mixing sodium and potassium salts and used to prepare the DMMP solutions.

Results and Discussion

Adsorption and stability results

For initial DMMP concentrations of 10 mM, there was no measurable adsorption from the neat solution (pH ~ 6.2) nor the solutions adjusted to pH 10 and pH 3 for even the highest mass of TiO₂ added.

The pure DMMP solutions were stable in room light for 70 hours. However, for 5 and 10 mM DMMP solutions adjusted to pH 10, there was approximately a 20% loss in solute over 70 hours (Figure 2). For pH 10 solutions, the DMMP degradation was essentially the same for samples under room light, irradiation and dark control conditions and consistent with the reported hydrolysis of DMMP in alkaline aqueous solution [17]. DMMP solutions with the addition of H_2O_2 were stable over 70 hours under dark control conditions, yet under light box irradiation more than 50% of the DMMP degraded over the same time period.

Effect of alkaline solution pH on photocatalytic reaction

DMMP 10 mL of 9.35 mM solution was mixed with 10 mg of TiO, to give a reagent loading of 1.16 mg DMMP/g TiO, and an initial pH of 6.2. Under irradiation, only 30% of the DMMP degraded, the reaction was accompanied by a significant reduction in pH and the reaction terminated after approximately 5 hours (Figure 3). These observations are consistent with either a mechanism that involves the accumulation of a surface adsorbate or reagent depletion associated with the consumption of dissolved oxygen from the closed experimental system. The reduction in pH during the early stages of the reaction has been associated with the production of intermediate species including methylphosphonic acid and formic acid [6,14]. O'Shea [6] observed complete destruction of 100 µM DMMP concentrations within 4 hours using UV light and within 10 hours using solar light. This high percentage of oxidation may arise from both the low DMMP concentration and the replenishment of dissolved oxygen via an air purge during irradiation. Kozlova [7] used a closed photocatalytic system and observed that the percent destruction of DMMP decreased with initial DMMP concentration. This was attributed to the depletion of dissolved oxygen which plays a critical role as an electron scavenger for photocatalysis in aqueous solutions, and participates in hydroxyl radical production [18].

Based on stability test results which showed that higher solution pH promoted DMMP degradation, a series of photoreactions using an initial solution pH of 10 were performed with reagent loadings from 0.29 to 1.16 g DMMP/g TiO₂. Each reaction vial was loaded with 10 mg of TiO₂ and either 10 or 5 mL of 9.35 or 4.7 mM DMMP solution to achieve the desired reagent ratios. For a mass ratio of 1.16 mg DMMP/



Figure 2: Stability of DMMP under dark and irradiated conditions in pH 10 solution without addition of TiO₂.



mg TiO₂ and an initial pH of 10, the DMMP degradation (Figure 4a) was comparable to that for the same reagent loading and an initial pH of 6.2 (Figure 3). For solutions with an initial pH of 10, lowering the reagent ratio of DMMP to TiO₂ yielded much greater destruction of DMMP and a larger pH drop simultaneous with the drop in DMMP concentration (Figures 4a and 4b). Finally, control runs without TiO₂ confirm only slight degradation of DMMP without the photocatalyst. It was observed in this work that regardless of the initial pH, the initial DMMP concentration and the percent degradation, the final solution pH never dropped below 2.4, approximately the pKa of DMMP. Voronstov [13] reported a minimum pH of about 3 and suggested that the observed pH plateau in the presence of continued DMMP degradation and acid byproducts, consistent with the results reported here.

Solution pH plays a critical role in many stages of the photocatalytic reaction, affecting both the semiconductor surface charge and the protonation of dissolved species. Therefore, to eliminate the effect of solution acidification during reaction, one experiment was performed using a pH 10 carbonate buffer solution. For a reagent ratio of 0.58 g DMMP/g TiO₂, the irradiated buffered solution showed a more gradual decrease in DMMP concentration which continued beyond

the concentration plateau for the unbuffered solution (Figure 5). In the buffered system, the phosphate would be present in solution as $PO_4^{3^-}$ versus the $HPO_4^{2^-}$ that would prevail at lower pH and this could impact interactions between the anion and the semiconductor surface. However the small difference in DMMP degradation between the buffered solution and the initial pH 10 solution supports the hypothesis that the dissolved oxygen concentration may limit the photoreaction.

Effect of dissolved oxidizing species on photocatalytic reaction

Oxidation under light is expected to proceed through the generation of oxidizing species that react with solutes. It was previously noted by O'Shea that elimination of dissolved oxygen stopped the photocatalytic degradation of DMMP [6]. The dependence of the photocatalytic oxidation of organophosphorus compounds on dissolved oxygen concentration was explained by Vorontsov using a Langmuir-Hinshelwood model with competitive adsorption of oxygen and solute [7]. In this experiment, 9.35 mM DMMP solution, 9.35 mM DMMP solution adjusted to pH 10, and 9.35 mM DMMP solution with the addition of 0.1 mL of H_2O_2 were deoxygenated before use in photoreactions. Both solutions without added H_2O_2 showed little change in DMMP concentration with irradiation (Figure 6). However, the solution with added H_2O_2 gave approximately a 20% loss of DMMP concentration, indicating the formation of oxidizing radicals under these conditions (Figure 6).



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Further investigations with the addition of H_2O_2 in neutral DMMP solutions (Figure 7a) indicate that complete destruction of DMMP is possible with the addition of 0.5 mL of H_2O_2 solution to 10 mL of solution (4.7 volume percent H_2O_2 solution). The corresponding pH changes for these trials (Figure 7b) all coincide with a similar pH lower limit.

Effect of competing organic solutes on photocatalytic reaction

The presence of other organic and inorganic components in the solution can significantly impact the photooxidation of solutes. For example, both the partial reduction of dissolved oxygen to O_2^{-} and the oxidation of water to produce hydroxyl radicals [16] are potentially influenced by dissolved substances and the ionic strength of the solution. Whether these matrix effects promote or inhibit the reaction further depends on the particular matrix component and the mechanism of interaction between the solute and the photocatalyst [19].

To study the potential impact of natural organic matter (ubiquitously present in environmental surface waters) on DMMP degradation, a 9.35 mM DMMP solution was prepared using water that contained 10 mg/L fulvic acid. This solution was used with a reagent ratio of 1.16 g DMMP/g TiO2, and for comparison, this solution was also pH adjusted to 10 and used both with and without TiO₂. The presence of fulvic acid moderately increased the amount of DMMP degraded versus photoreactions with the same initial DMMP concentration, pH and TiO₂ loading (Figure 8a versus Figures 4a and 5). This may be attributed to participation of the organic compounds in charge transfer reactions that prevent electron-hole recombination or in the production of reactive oxygen species. The presence of fulvic acid caused a slightly lower initial pH than for solutions prepared in water, yet the final pH still reached the pKa threshold (Figure 8b). The solution that was pH adjusted to 10 before reaction had a measurably higher final pH than other solutions. Based on these observations, the photocatalytic treatment of groundwater contaminated with organophosphate compounds is not expected to be hindered by typical background organic contaminants.

Effect of salinity on photocatalytic reaction

Since it might be desirable to perform heterogeneous photocatalysis on contaminated brackish water or sea water without prior salt

removal, experiments were performed to study the impact of salinity on the reaction. Photoreactions performed using 1.16 g DMMP/g TiO_2 in pure water and simulated sea water solutions provided similar destruction of DMMP (Figure 9a) and similar pH decreases (Figure 9b). However an important difference is that simulated sea water solutions react more gradually with irradiation time compared to the

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Figure 8: Effect of fulvic acid on photoreaction of DMMP for C₀=9.35 mM and where present, 1.16 g DMMP/gTiO₂. a) C/C_0 ; b) Solution pH.





sharp plateau features observed for the solutions prepared from pure water. This difference might arise from the high ionic strength of the simulated sea water and its impact on the charged species involved in the photocatalytic reaction.

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Conclusions

Heterogeneous photocatalysis using simulated solar light and titanium dioxide was studied with dimethyl methylphosphonate as a model compound for aqueous organophosphorus contaminants. DMMP degradation was associated with a reduction in solution pH, with the pH approaching the pKa for DMMP for large amounts of DMMP reacted. Photoreaction of DMMP in a pH 10 solutions and a pH 10 carbonate buffer degraded a similar percent of the solute, with a more gradual reaction observed for the buffered solution. Addition of peroxide solution before reaction increased the percentage of DMMP oxidized and nearly complete destruction of DMMP was achieved with the addition of 5 volume percent of H₂O₂ solution. The presence of fulvic acid in the solution slightly enhanced the oxidation of DMMP whereas the absence of dissolved oxygen inhibited DMMP oxidation. DMMP solutions prepared in simulated salt water reached similar degradation percentages as for pure solutions, however, reacted more gradually. This enhanced understanding of background solution components on the photooxidation of DMMP provides valuable insight into practical applications of this technology.

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