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Isotope studies of photocatalysis TiO_2-mediated degradation of dimethyl phenylphosphonate

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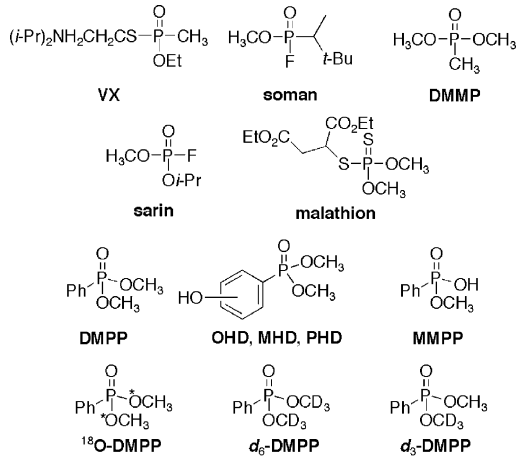
Abstract

The initial step of TiO_2-mediated photocatalytic degradation of dimethyl phenylphosphonate (DMPP), labeled with ^{18}O or deuteria in the methoxy groups, results in products due to ring hydroxylation and demethylation. The ^{18}O labeling experiments clearly demonstrate that the methyl group is lost, rather than a methoxy group, resulting in a labeled phosphonic mono-acid. Results from deuterium isotope experiments are more ambiguous.

Keywords: Photocatalytic degradation; Titanium dioxide; Phosphonate

1. Introduction

The oxidative degradation of phosphates and phosphonates has received significant attention because of the presence of these groups in chemical warfare agents and pesticides [1–12]. Among the relevant compounds are sarin, soman, VX, and malathion. Because of the hazards associated with these compounds, most study has been done with model compounds, such as dimethyl methylphosphonate (DMMP). Our primary interest is in TiO_2-mediated photocatalytic degradation and indeed detailed lists of compounds observed in the degradation of DMMP are now available [1,2,6].



Exposure of DMMP and related simple phosphonates to TiO_2-mediated photocatalytic conditions results first in the loss of one of the methyl esters. An important unsettled point is the mechanism by which the methyl is removed. The question is whether attack occurs at the methyl or at the phosphorus or both. As originally pointed out by O'Shea, one potential mechanism for the dealkylation of a phosphonate diester to the monoester is by an addition-elimination mechanism in which a hydroxyl radical adds to the phosphorus center to yield a transient 9-electron radical, as illustrated in Scheme 1. (Although illustrated as an oxygen-centered radical, it must be understood that the axial X-P-X system is a 3-centered-4-electron bond, or, in this hypothetical radical, a 3-centered-3-electron bond.) Subsequent loss of HO or CH_3O should be approximately equally favorable, especially if the phosphorus center has sufficient lifetime to undergo Berry pseudorotation to place the alkoxyl group in the axial position. This mechanism is of particular interest because of the well known chemistry in which hydroxyl radicals add to dimethyl sulfoxide at the sulfur center, causing expulsion of a methyl radical [13]. Furthermore, there is fundamental interest because of the question of the relationship between conventional free hydroxyl radicals and the adsorbed hydroxyl radical species presumed to be involved in photocatalysis.

Another mechanism occasionally invoked in discussions of photocatalysis, but not discussed by O'Shea, is that local generation of a proton as a result of water oxidation leads to acid catalyzed hydrolysis of the phosphonate, again by attack at phosphorus. Either of these mechanisms might

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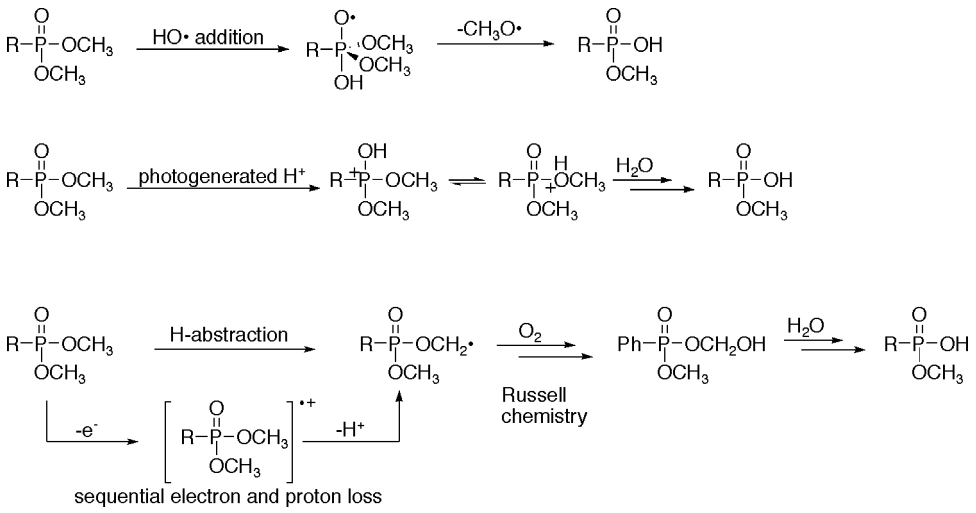


Scheme 1. Potential phosphonate dealkylation mechanisms.

be characterized by the observation of methanol production early in the degradation, as reported by Obee and Satyapal [7] under moist gas phase conditions.

Alternatively, a conventional photocatalytic mechanism can be written in which hydrogen abstraction occurs at the alkyl hydrogens, followed by O_2 trapping. Russell chemistry [14] then leads to an easily hydrolyzable group. Formaldehyde and formic acid have both been detected as products from degradation of DMMP [1,6]. A recent study using radiolysis to generate hydroxyl radicals [8] supports this pathway, in that (indirect) spectroscopic product studies indicated that carbon-centered radicals were formed. The same carbon-centered radical intermediate can, at least in principle, be obtained by sequential loss of an electron and a proton [6], a reaction considerably more likely with TiO_2 than under radiolysis conditions. Finally, there is also no reason not to believe that mechanisms of both types (attack at P or at CH) can occur simultaneously. This circumstance might explain some confusion among reports in the literature.

To address these issues, especially regarding the mechanism under conditions of TiO_2-mediated photocatalytic degradation, we report a study on the initial steps of degradation of a closely related compound dimethyl phenylphosphonate (DMPP). We use the phenyl group to clearly distinguish reactivity on the alkoxyl groups form that on the phosphonic acid side of the functionality. As expected, this introduces a new set of hydroxylated products: dimethyl *o*-, *m*-, and *p*-hydroxyphenylphosphonates (OHD, MHD, and PHD, respectively), but we are less concerned with these than the product of demethylation: monomethyl phenylphosphonate (MMPP). To answer definitively and directly whether a substitution reaction occurs, either alone or in combination with other mechanisms, DMPP was prepared with ^{18}O labels in the alkoxyl positions (^{18}O-DMPP); to probe for kinetic isotope effects (KIEs), the degradation of d_6-DMPP and d_3-DMPP was also studied.

2. Experimental

2.1. General instrumentation

NMR data were obtained on a Varian DRX-400 MHz spectrometer. ^{31}P- and ^{13}C NMR spectral data were obtained with ^{1}H decoupling, but ^{31}P coupling remains in the ^{13}C- and ^{1}H NMR spectral data. HPLC data were collected with an HP 1050 liquid chromatograph with diode array UV/VIS absorption detection. LC/MS data were collected on Shimadzu LC/MS-2010 by electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI). An ODS Hypersil reverse phase column (5 μm, 200 mm × 2.1 mm, Hewlett Packard) was used with a 50/50 mixture of acetonitrile and water used as eluent. GC data were obtained on HP 5890 gas chromatograph with a 30 m (0.25 mm i.d. × 2.5 μm) DB-5 column and an FID detector. Mesitylene was used as the internal standard when necessary. The GC/MS data were obtained on a VG Magnum ion trap, a Finnegan TSQ700 triple quadruple mass spectrometer, or a Micromass GCT time-of-flight (TOF) mass spectrometer, as indicated. Isotope enrichments and ratios were checked on at least two different MS instruments and always gave results well within experimental error of one another. Centrifugation was accomplished using an Eppendorf 5415 C Microcentrifuge. UV data were obtained on a Shimadzu UV-2101 PC.

2.2. Degradation and analysis procedures

2.2.1. Standard degradation procedure

Suspensions were prepared containing 5 mM DMPP and 50 mg TiO_2 in 100 ml water. When $^{18}O_2$-DMPP was used, this scale was dropped ten-fold. When regulated, the initial pH of the solution was controlled by using HCl (pH = 3), 10 mM phosphate buffer (pH = 7) or 10 mM carbonate

buffer (pH = 10). The resultant mixtures were treated in an ultrasonic bath for 5 min to disperse large TiO_2 aggregates immediately prior to photolysis. The photodegradation was performed in a Rayonet miniature photochemical reactor with 8×4 W "black light" bulbs whose emission is centered at 350 nm. A fan kept temperatures at ambient levels. Solutions were purged with O_2 for several minutes in advance of and during photolysis. Samples for analysis were taken out at desired time intervals. The TiO_2 was separated by centrifugation, followed by filtration through a syringe-mounted 0.2 μm Whatman filter. These solutions were analyzed directly when HPLC was used. For GC analysis, additional treatment was necessary. The water was removed in vacuo from the 5 ml aliquots. The samples were then silylated by dissolving in 0.5 ml pyridine, followed by treatment for a few minutes with 0.1 ml 1,1,1,3,3,3-hexamethyldisilazane and 0.05 ml chlorotrimethylsilane. After the pyridinium salts were separated by centrifugation, the samples were analyzed by GC/MS. All reported degradations were carried out to low conversion (≤10%) to minimize secondary reactions, except as noted and in kinetic runs.

2.2.2. H_2O_2 photodegradations

Solutions were prepared as above, leaving out the TiO_2. Immediately before photolysis, 1.0 ml of H_2O_2 (30% in water) was added. Photolysis and analysis were carried out in the ordinary way.

2.2.3. Fenton reactions

Reactions were conducted at room temperature. Normal conditions were 4 mM DMPP, 8 mM $FeSO_4$ and 80 mM H_2O_2 in aqueous solution. The pH was controlled at 7 by using 0.1 M phosphate buffer. After 15 min, the resultant mixture was filtered through 0.2 μm Whatman filters without otherwise quenching the reaction. Ordinary analysis procedures were then used.

2.2.4. Persulfate oxidations

A solution at room temperature containing 10 mM DMPP and 3 mM $K_2S_2O_8$ was purged with Ar to remove O_2. The resulting solution was held at 90 °C under Ar for 14 h. After cooling, it was extracted with methylene chloride, and the residue that remained after evaporation was silylated and analyzed as usual.

Photochemical degradations were also carried out using persulfate. These solutions contained 10 mM DMPP and 100 mM $K_2S_2O_8$. The concentration of $K_2S_2O_8$ was so high because the extinction coefficient at 254 nm is about one-tenth that of DMPP. Photolysis of this mixture at 254 nm caused it to turn dark yellow. Samples were analyzed as usual. Control experiments, in which the persulfate was left out, showed that direct photolysis caused degradation on a much slower timescale than in the presence of persulfate. It was thus assumed that the photochemical degradation was due almost entirely to persulfate chemistry because of the higher relative quantum yield of persulfate photolysis and the filter effect of the high concentration persulfate on the light absorption by DMPP.

2.2.5. Competition experiments

Competition experiments between DMPP and d_6-DMPP were carried out like all other degradations, save that mixtures of the two isotopologs were used. The same total concentrations were used. MS analysis of the resultant mixtures allowed quantification of the MMPP and d_3-MMPP produced. After accounting for the concentration ratios of the starting materials (usually 1:1), selectivities were obtained from these data. Mass spectral integrations were carried out from either GC-TOF data or ion trap data and were well within experimental error of one another.

2.2.6. Adsorption experiments

Either 5 or 25 mg TiO_2 was added to 10 ml solutions of DMPP or other substrate at various concentrations. The resulting suspensions were stirred for a minimum of 4 h to allow equilibration. The TiO_2 was removed by centrifugation and filtration as earlier, and the concentration of the organic compound in the supernatant was determined by quantitative UV spectroscopy. DMPP $\varepsilon(264\,\text{nm}) = 905\,\text{M}^{-1}\,\text{cm}^{-1}$; MMPP $\varepsilon(263\,\text{nm}) = 452\,\text{M}^{-1}\,\text{cm}^{-1}$; MHP $\varepsilon(283\,\text{nm}) = 2401\,\text{M}^{-1}\,\text{cm}^{-1}$.

2.3. Materials

DeGussa P25 TiO_2 was used as received. Water was obtained from an ultrapurification unit from Millipore and had resistivity $\geq 17\,\text{M}\Omega\,\text{cm}^{-1}$. Dry THF was obtained by distillation under argon from THF solution dried by sodium and benzophenone. Dried benzene was obtained by distillation under argon from CaH_2. Phenylphosphonic acid was purified by recrystallization from ethyl acetate. Other solvents and reagents were used as received. Flash SiO_2 column chromatography or preparative TLC with 2 mm thickness of silica gel on a 20 cm × 20 cm glass plate was usually used to purify the products.

2.3.1. Dimethyl phenylphosphonate (DMPP) [15]

To a stirred solution of pyridine (6.57 ml, 0.081 mol) and methanol (3.14 ml, 0.078 mol) in 80 ml of methylene chloride at 0 °C under argon, phenylphosphononyl dichloride (5 ml, 0.035 mol) was added dropwise. The mixture was stirred for 5 h at room temperature. The resultant solution was washed with cold water, cold 1 M HCl, cold saturated $NaHCO_3$ solution, and again with cold water, in that order. After drying over anhydrous $MgSO_4$ and subsequent removal of the methylene chloride in vacuo, crude DMPP (6.05 g, 93% yield) was obtained. DMPP was purified by SiO_2 column chromatography with ethyl acetate solvent to yield a clear viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (2H, dd, $J = 13.6$, 7.5 Hz), 7.50 (1H, t, $J = 7.5$ Hz), 7.40 (2H, td, $J = 7.5$, 4.0 Hz), 3.68 (6H, d, $J = 11.2$ Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 132.7 (d, $J = 12$ Hz), 131.9

(d, $J = 39$ Hz), 128.6 (d, $J = 60$ Hz), 126.9 (d, $J = 750$ Hz) and 52.7 (d, $J = 22$ Hz); and ^{31}P NMR (161.5 MHz, $CDCl_3$) δ: 22.2; MS (EI, 70 eV, with TOF ion detector) *m/z* (relative intensity), 187 (5), 186 (64), 185 (100), 155 (27), 141 (57), 91 (54), 77 (38).

2.3.2. d_6-Dimethyl phenylphosphonate (d_6-DMPP)

The preparation of d_6-DMPP was the same as that of the DMPP except that methanol-d_4 was used instead of methanol. d_6-DMPP: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (2H, dd, $J = 13.6$, 7.5 Hz), 7.53 (1H, t, $J = 7.5$ Hz), 7.43 (2H, td, $J = 7.5$, 4.0 Hz); ^{13}C NMR ($CDCl_3$) δ: 132.7 (d, $J = 12$ Hz), 131.9 (d, $J = 39$ Hz), 128.6 (d, $J = 60$ Hz), and 126.9 (d, $J = 750$ Hz); and ^{31}P NMR (161.5 MHz, $CDCl_3$) δ: 22.2; MS (EI, 70 eV, ion trap) *m/z* (relative abundance), 193 (9), 192 (100), 191 (91), 162 (40), 142 (40), 94 (78), 94 (78), 77 (10).

2.3.3. ^{18}O-labeled phenylphosphinic acid [16,17]

Dichlorophenylphosphine (0.6 ml, 0.0042 mol) in 5 ml THF was added over 15 min to water (0.3 ml; 10% ^{18}O) in 10 ml of THF under Ar. The mixture was stirred for 5 h, followed by removal of the solvent in vacuo to produce phenylphosphinic acid, which was recrystallized from ethyl acetate to obtain the product (0.599 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (2H, dd, $J = 14$, 7.5 Hz), 7.69 (1H, t, $J = 7.5$ Hz), 7.53 (2H, t, $J = 7.5$ Hz), 7.52 (1H, d, $J = 569.6$ Hz); ^{31}P NMR (161.5 MHz, $CDCl_3$) δ: 22.8. HPLC/MS (APCI) 144 (20), 143 (100), 142 (90), 91 (7), 77 (6).

2.3.4. ^{18}O-labeled methyl phenylphosphinate [18]

Cold ethereal diazomethane, prepared from the Aldrich diazald kit immediately before use, was added to the above phenylphosphinic acid (0.599 g) until the yellow color persisted in the solution, and further stirred for 0.5 h at 0 °C. Solvent was removed in vacuo to generate reasonably methyl phenylphosphinate (0.661 g, 95.8%) that was sufficiently pure to be carried on to the next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.78 (3H, d, $J = 12$ Hz), 7.70 (2H, t, $J = 10$ Hz), 7.59 (1H, d, $J = 7.2$ Hz), 7.51 (2H), 7.54 (1H, d, $J = 566$ Hz); ^{31}P NMR (161.5 MHz, $CDCl_3$) δ: 27.8. GC/MS (EI, 70 eV, with ion trap) *m/z* 158 (18), 157 (100), 156 (90), 141 (20), 126 (20), 91 (30), 77 (90), 51 (80).

2.3.5. ^{18}O-labeled dimethyl phenylphosphonite

This compound was prepared based on the procedure of Quin et al. [19]. To the above crude methyl phenylphosphinate (0.661 g, 0.0042 mol), methyl trifloromethanesulfonate (0.65 ml, 0.0055 mol) was added dropwise. The reaction mixture was stirred for several minutes at room temperature, then cooled down to about −20 °C. Triethylamine (1.38 ml, 0.0099 mol) in 20 ml dry benzene was added. The mixture was warmed up to ambient temperature, whereby two layers were formed. The top layer contained the desired dimethyl phenylphosphonite. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64–7.58 (2H, m), 7.47–7.38 (3H, m), 3.54 (6H, d, $J = 10.4$ Hz); ^{31}P NMR (161.5 MHz, $CDCl_3$) δ: 161.3; GC/MS (EI, 70 eV, with ion trap) M/Z (relative abundance), 170 (60), 155 (100), 139 (17), 109 (21), 93 (47), 77 (44), 63 (20), 51 (22). After removal of solvent, the resulting product mixture (0.524 g) contained a 2:1:3 mixture of dimethyl phenyl phosphonite, methyl phenylphosphinate and methyl methyl-phenylphosphinate, ^{31}P NMR (161.5 MHz, $CDCl_3$) δ: 44.8. Because dimethyl phenylphosphonite is easily hydrolyzed, this mixture was carried forward to the next synthetic step, where purification was more straightforward.

2.3.6. ^{18}O-labeled dimethyl phenylphosphonates ($^{18}O_2$-DMPP) [15,20]

t-Butyl hydroperoxide (3.0 M in isooctane,1.02 ml, 3.1 mmol) was added to the above product mixture (0.524 g). The mixture was stirred for 0.5 h. The solvent was removed in vacuo, and the residue (0.40 g) was obtained and purified by preparative TLC with ethyl acetate to yield $^{18}O_2$-DMPP (0.159 g, 20% from dichlorophenylphosphine). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (2H, d, $J = 7.5$ Hz), 7.50 (1H, t, $J = 7.5$ Hz), 7.40 (2H, td, $J = 7.5$, 4.0 Hz), 3.68 (6H, d, $J = 11.2$ Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 132.8 (d, $J = 12$ Hz), 131.9 (d, $J = 40$ Hz), 128.7 (d, $J = 60$ Hz), 127.0 (d, $J = 750$ Hz) and 52.7 (d, $J = 22$ Hz); ^{31}P NMR (161.5 MHz, $CDCl_3$) δ: 22.37; GC/MS (EI, 70 eV, TOF) *m/z* (relative abundance), 188 (15), 187 (30), 186 (71), 185 (100), 156 (38), 155 (32), 141 (64), 91 (78), 77 (53).

2.3.7. $^2H_3$-labeled dimethyl phenylphosphonate (d_3-DMPP)

d_3-DMPP was prepared using a sequence of reactions closely related to the preparation of ^{18}O-DMPP. d_3-Methyl phenylphosphinate was prepared from dichlorophenylphosphine and deuterated methanol in 90% yield using the method of Lei et al. [18]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.7–7.8 (2H, m) 7.45–7.60 (3H, m), 7.51 (d, $J = 564$ Hz). MS (EI, 70 eV, ion trap), *m/z* 160 (100), 142 (27), 94 (38), 77 (98), 51 (73). This material was then methylated and oxidized as described immediately above to yield d_3-DMPP. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.7–7.8 (m, 2H), 7.45–7.6 (m, 3H), 3.73 (3H, d, $J = 14.8$ Hz). IR (neat, cm^{-1}) 3060, 2955, 2852, 2256, 2201, 2137, 2078, 1593, 1439, 1252, 1045. GC/MS (EI, 70 eV, ion trap) *m/z* (relative abundance), 191 (100), 160 (22), 158 (20), 142 (83), 94 (66), 77 (63), 51 (62).

2.3.8. Monomethyl phenylphosphonate (MMPP) [21]

To a solution of phenyl phosphonic acid (0.326 g, 0.0020 mol) in dry *N*,*N*-dimethylformamide (10 ml) at −20 °C, thionyl chloride (0.18 ml, 0.0024 mol) was added. The mixture was warmed to 0 °C and kept at that temperature for 20 min. Then methanol (0.123 ml, 0.0030 mol) was added. Afterwards, the mixture was warmed to room temperature and stirred overnight. About 20 ml saturated sodium bicarbonate was added to the resultant solution. The

aqueous solution was washed with ether (2 ml × 15 ml), and acidified with concentrated hydrochloric acid. The product was extracted with ethyl acetate. After drying over anhydrous $MgSO_4$ and subsequent removal of ethyl acetate, crude MMPP (0.24 g, yield 70%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (2H, dd, J = 13.6, 7.8 Hz), 7.51 (1H, t, J = 7.8 Hz), 7.41(2H, td, J = 7.8, 4.4 Hz), 3.67 (3H, d, J = 11.2 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 132.4 (d, J = 11 Hz), 131.5 (d, J = 40 Hz), 128.5 (d, J = 60 Hz), 128.3 (d, J = 770 Hz) and 52.5 (d, J = 22 Hz); ^{31}P NMR (161.5 MHz, $CDCl_3$) δ: 21.5. The purity of MMPP was determined by GCMS, but this required silylation for the compound to tolerate the GC conditions. MMPP (1 mg) was treated for a few minutes with 0.5 ml pyridine, 0.1 ml 1,1,1,3,3,3-hexamethyldisilazane and 0.05 ml chlorotrimethylsilane, followed by removal of pyridinium salts by centrifugation to yield the TMS derivative of MMPP in a mixture that could be shot directly on a GC column. The purity of the product is about 80% with DMPP (10%) and phenylphosphonic acid (10%) as the other major products. Attempts to further purify with preparative TLC were unsuccessful. The mass spectrum of the TMS derivative of MMPP: (EI, 70 eV, TOF) *m*/*z* (relative abundance), 244 (5), 229 (100), 199 (10), 153 (17), 121 (11), 89 (13), 75 (13).

2.3.9. d_3-Monomethyl phenylphosphonate (d_3-MMPP)

Methanol-d_4 was used instead of methanol in the above procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (2H, dd, J = 13.6, 7.8 Hz); 7.53 (1H, t, J = 7.8 Hz); 7.43 (2H, td, J = 7.8, 4.4 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 132.5 (d, J = 12 Hz), 131.6 (d, J = 40 Hz), 128.5 (d, J = 60 Hz), and 128.2 (d, J = 770 Hz); ^{31}P NMR (161.5 MHz, $CDCl_3$) δ: 22.0; mass spectrum of the TMS derivative (EI, 70 eV, with TOF ion detector) *m*/*z* (relative intensity) 247 (5), 232 (100), 200 (5), 156 (10), 121 (10).

2.3.10. Dimethyl (o-hydroxy)phenyl phosphonate (OHD), dimethyl (m-hydroxy)phenyl phosphonate (MHD), and dimethyl (p-hydroxy)phenyl phosphonate (PHD)

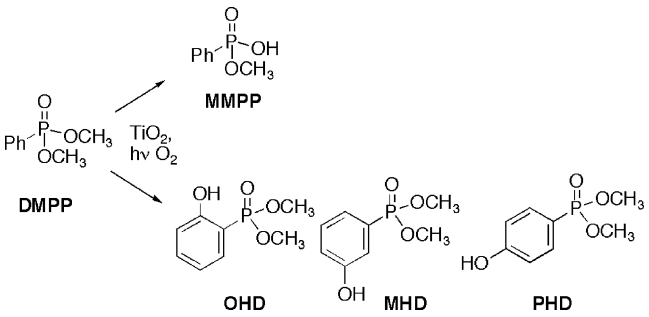
These compounds were prepared as noted in the literature [22]. They were purified by preparative TLC with developing solvents methylene chloride/EtOAc (6:1), EtOAc, and EtOAc/MeOH (4:1), respectively. OHD: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.1 (1H, s), 7.45 (1H, br t, J = 7.8 Hz), 7.34 (1H, ddd, J = 14.4, 7.6, 1.6 Hz), 6.97 (1H, br t, J = 7.6 Hz), 6.92 (1H, tdd, J = 7.8, 4.2, 1 Hz), 3.75 (6H, d, J = 11.6 Hz); ^{31}P NMR (161.5 MHz, $CDCl_3$) δ: 25.9; mass spectrum of its TMS derivative (EI, 70 eV, ion trap) *m*/*z* (relative intensity), 274 (22), 259 (100), 213 (10), 156 (9), 135 (10), 107 (10), 73 (18), 59 (19). MHD: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (1H, d, J = 15.2 Hz), 7.35 (1H, dd, J = 13.6 Hz), 7.15 (1H, dd, J = 12.8, 7.6 Hz), 7.10 (1H, d, J = 8 Hz), 3.77 (6H, d, J = 11.2 Hz); ^{31}P NMR (161.5 MHz, $CDCl_3$) δ: 22.9; mass spectrum of its TMS derivative (EI, 70 eV, ion trap) *m*/*z* (relative intensity), 274 (25), 259 (100), 91 (7), 73 (10), 63 (8). PHD: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.1 (1H s), 7.61 (2H, dd, J = 12.4, 8.4 Hz), 7.01 (2H, d, J = 4.8 Hz), 3.71 (6H, d, J = 11.2 Hz); ^{31}P NMR (161.5 MHz, $CDCl_3$) δ: 24.8; mass spectrum of its TMS derivative (EI, 70 eV, ion trap) *m*/*z* (relative intensity), 275 (30), 259 (100), 109 (10), 91 (8), 73 (15), 63 (8).

3. Results and discussion

3.1. General characteristics of TiO_2-mediated partial degradations of dimethyl phenylphosphonate (DMPP)

Standard conditions for degradations were 100 ml aqueous suspensions containing 50 mg DeGussa P25 and 5 mM DMPP. The pH of the solution was either unregulated or set to 3 with HCl, 7 with 10 mM phosphate buffer, or 9–10 with carbonate buffer. All solutions were treated in an ultrasonic bath to disperse aggregates immediately before photolysis and purged with O_2 before and during photolysis. Irradiation was carried out using broadly emitting 350 nm fluorescent tubes. Samples were removed at appropriate intervals and analyzed after removal of the TiO_2. For HPLC analysis, no further processing was necessary, but for GC analysis, the water was removed and the resulting materials were exhaustively silylated with TMSCl and $(TMS)_2NH$. Control experiments showed that degradation in the absence of any one or more of the key elements (light, TiO_2, and O_2) was negligibly slow. Without regulation of pH, complete loss of DMPP could be achieved in about 22 h and complete mineralization was achieved in about 33 h. A maximum of phenolic products, as observed by an unstructured UV absorption at 285 nm was observed at about 10 h.

At early degradation times (e.g. 30–60 min), four primary degradation products were observed (Scheme 2). They result from hydroxylation of the arene ring in the *o*, *m*, and *p*-positions and from demethylation of the phosphonate. No phenol was observed. The *m*-hydroxylated product (MHD) was produced in about three times the concentration as the other isomers (which were formed in similar amounts), in keeping with the notion that hydroxylation by $HO^{\bullet}_{ads}$ is an electrophilic reaction. At low conversion, these four



Scheme 2.

Table 1
First order rate constants and initial rates for the oxygen-saturated TiO_2 photoinduced disappearance of DMPP

[DMPP] (mM)	k_{app} ($\times 10^{-5}\,s^{-1}$)	Rate (M/sec)
2.3	11.17 ± 0.1	2.7×10^{-7}
4.6	3.6 ± 0.3	1.6×10^{-7}
9.1	1.8 ± 0.1	1.6×10^{-7}

products summed to approximately quantitative yield, within the precision that could be determined.

The influence of pH on the initial rate of photocatalytic degradation of DMPP was briefly investigated. Degradations were carried out for 1 h at pH 3, 7, and 10, and the percentage DMPP remaining was assessed. The degradation was fastest at pH 10 (40% consumption), with 22 and 13% consumption at pH 7 and 3, respectively. This is in qualitative agreement with the observations of O'Shea et al. for MMPP [1,2].

The kinetics of the disappearance of DMPP could be fit to first order decays. The apparent rate constants for three concentrations in the mM range at pH 7 are shown in Table 1. The inverse relationship between [DMPP] and k_{app} is analogous to that observed by O'Shea et al. for DMMP [2], though here the relationship is sufficiently strong that even the absolute initial rate of decomposition is slower for the higher concentrations, in contrast to a simple interpretation using the Langmuir–Hinshelwood equation. O'Shea suggested that strong adsorption by intermediate products may be the cause of the lowering of apparent degradation rate constants, though that data did not slow in the initial absolute rates.

We thus investigated the adsorption of MHD, MMPP, and DMPP at pH 3, 7, and 10. At the high pH, where both the phenol and MMPP are mainly deprotonated, MHD adsorbs much more strongly than the other two in the concentration region investigated, as shown in Fig. 1. However, while the adsorption of MHD is marginally stronger at the lower pH values, it does not appear to be sufficiently so as to completely displace DMPP when [MHD] is low at any pH, unless it is the case that only very specific adsorption sites are

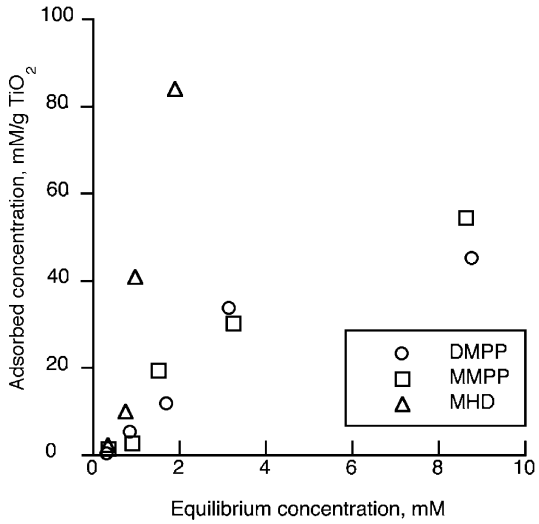


Fig. 1. Adsorption isotherm for DMPP, MMPP, and MHD at pH 10 with 25 mg TiO_2 per 10 ml.

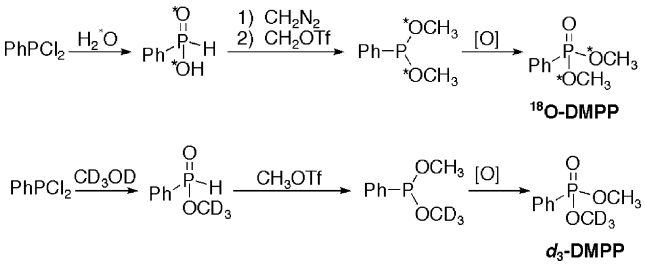
active. Macroscopic adsorption experiments such as these would not reveal the behavior at a small number of the most active sites in the presence of a much larger number of less active binding sites. This being said, it is by now understood that dark macroscopic adsorption properties do not always correlate with reactivity.

Initial product distributions under a few related conditions are shown in Table 2. The product mixtures are all similar for TiO_2 degradation and degradation carried out by direct photolysis of hydrogen peroxide, and TiO_2-mediated degradation in the presence of 10 mM NaF at low pH. These latter two conditions are expected to produce homogeneous hydroxyl radicals [23,24]. The distribution of products under Fenton conditions, which may result in reactions between the substrate and oxidizing iron complexes, is similar, but appears to be reproducibly different from the others. Persulfate oxidation does not produce hydroxylated products, at least at low conversion, consistent with the direct reaction of sulfate radical anions with DMPP.

Table 2
H/D isotope selectivities of DMPP demethylation under different experimental conditions and general product distributions at low conversion

Degradation conditions	H/D selectivity	MMPP	OHD	MHD	PHD
		Relative yields			
TiO_2, $h\nu$, O_2, pH unregulated	1.07 ± 0.04	67	2	24	7
TiO_2, $h\nu$, O_2, pH 3	1.05 ± 0.08				
TiO_2, $h\nu$, O_2, pH 7	1.05 ± 0.08				
TiO_2, $h\nu$, O_2, pH 10	1.01 ± 0.04				
H_2O_2, $h\nu$	0.99 ± 0.05	67	4	18	11
Fenton, pH 7	1.01 ± 0.13	81	6	8	5
$K_2S_2O_8$, 90 °C	0.99 ± 0.03	100[a]			
$K_2S_2O_8$, $h\nu$	1.05 ± 0.13	100[a]			
TiO_2, $h\nu$, O_2, NaF, pH 3	1.02 ± 0.02	70	3	23	4

Error limits are standard deviations from multiple runs.
[a] No other primary products were detected at levels above ~3% of MMPP.



Scheme 3. Preparation of labeled DMPP.

Table 3
^{18}O Enrichment in MMPP after formation by degradation of DMPP

	^{18}O enrichment in MMPP (%)[a]
Without control of pH	9.2 ± 0.2
pH = 3, TiO_2, $h\nu$	9.4 ± 0.3
pH = 7, TiO_2, $h\nu$	9.4 ± 0.1
pH =10, TiO_2, $h\nu$	9.3 ± 0.1
H_2O_2, $h\nu$	9.0 ± 0.2

[a] Errors limits are the standard deviations among triplicate or greater measurements. Enrichment of DMPP is 9.23 ± 0.06%.

3.2. Isotope labeling experiments on the demethylation of DMPP

In order to test whether substitution of a hydroxyl group for a methoxy group in DMPP goes by a mechanism that involves substitution of OH for CH_3O or by a mechanism in which the methyl group is degraded off, leaving the oxygen behind, experiments were carried out using two different types of isotopologs of DMPP.

The most critical of these is ^{18}O-DMPP. This compound was prepared by a synthetic route that unambiguously places the ^{18}O labels in the alkoxy positions, rather than at the phosphine oxide position (Scheme 3), so that any loss of ^{18}O label carried into the MMPP product detected by MS is directly attributable to a substitution type mechanism. Using labeled water nominally 10% in ^{18}O, ^{18}O-DMPP was obtained with (9.23 ± 0.06)% enrichment was obtained, such that approximately 18% of the DMPP molecules contained a single ^{18}O label, and only a small fraction were double-labeled.

Degradations were carried out in the usual fashion, save for a 10-fold drop in scale, at pH 3, 7, and 10, and also with H_2O_2 in lieu of TiO_2. The results of these experiments, shown in Table 3, are unambiguous, there is no significant loss of ^{18}O, and thus the mechanism of loss of the methyl group cannot involve direct attack by any species at the phosphorus center in such a way that expels $CH_3O^{\bullet}$ or CH_3O^{-}. Naturally, the ^{18}O is also retained in the hydroxylated products.

We thus sought to confirm that the product/rate determining step in the sequence that leads to MMPP is hydrogen abstraction. In previous work, we have reported an H/D selectivity[1] of approximately 3 for the demethylation of trimethyl cyanurate and anisole [25,26]. In the spirit of these previous experiments, we prepared d_6-DMPP from phenylphosphonoyl dichloride and deuterated methanol. Degradations were then carried out in which mixtures of DMPP and d_6-DMPP were employed. Usually the ratio of the two isotopologs was kept near 1.0, but several experiments were also run with other ratios. After compensating for the isotopolog ratios, the ratio of MMPP to d_3-MMPP is taken as the H/D selectivity for the demethylation reaction. To our surprise, the H/D selectivities were very near 1.0, i.e. essentially no selectivity (Table 2). This implied either that hydrogen abstraction is not the product/rate determining step or that an unusually small primary isotope effect was being observed.

One alternative mechanism that would remove isotope-selective hydrogen abstraction as the rate determining step is a stepwise loss of an electron and a proton. The electron transfer step is postulated not to have any isotope selectivity. Subsequent loss of one of the methyl protons from the resulting radical cation would in principle be isotope-selective, but if every radical cation so-formed became a radical through loss of a proton (or deuteron, regardless of differing rate constant) the selectivity would not be observed.[2] We thus subjected mixtures of d_6-DMPP and DMPP to several other conditions that were thought to produce hydroxyl radicals and/or the possibility of electron transfer reactions, thinking that perhaps a pattern would arise that would be consistent with this hypothesis even though previous radiolysis studies with DMMP have not provided any evidence for such processes. Instead, as can be seen in Table 2, the H/D selectivity was near 1.0 for the whole set of conditions. While the numbers were almost all slightly greater than 1.0, we were not convinced that this represented a real, very small selectivity.

Among the chemical methods used, we did not expect an electron transfer mediated mechanism for Fenton chemistry or hydrogen peroxide photolysis, but persulfate chemistry can sometimes lead to direct 1-electron oxidation, along with oxidation by sulfate radical anion and/or hydroxyl radical. We attempted sub-band gap irradiation of TiO_2 suspensions (broad irradiation with cutoff filter having 50% transmittance at 435 nm) with the idea that successful degradation here would clearly indicate electron transfer via irradiation of a charge transfer complex. However, no degradation was observed, even after extended irradiation. By contrast, irradiation of low pH suspensions of TiO_2 in the presence of NaF are thought to produce free hydroxyl radicals [23,24]. In the end, we realized we could not absolutely rule out even that the hydroxyl radicals would react by this stepwise electron/proton transfer, though we thought it unlikely.

[1] We hesitate to use the term “kinetic isotope effect” since these are not strictly kinetic experiments, but product isolation studies after several chemical steps.

[2] Rapid degenerate electron transfer between DMPP molecules followed by comparatively slow loss of a proton/deuteron would show isotope selectivity.

Table 4
H/D selectivities observed for demethylation of d_3-DMPP and relative product distributions at the lowest conversions

Degradation conditions	H/D selectivity
TiO_2, O_2, $h\nu$	1.38 ± 0.08
H_2O_2, O_2, $h\nu$ (300 nm)	1.21 ± 0.14
Fenton	1.22 ± 0.13

Thus, we resolved to explore one last route to probing for such an isotope effect and considered the degradation of d_3-DMPP. Its preparation is shown in Scheme 3. For this compound, the observed ratio of d_3-MMPP to MMPP reflects the H/D selectivity, since it is the "other" methyl group that has been removed. A key difference between this intramolecular competition and the intermolecular competition is that if electron transfer is an irreversible primary step, there still remains the possibility for isotope selectivity in the deprotonation of the radical cation when d_3-DMPP is used. In contrast, for the competition experiments using mixtures of DMPP and d_6-DMPP, once the electron loss has occurred, the choice for H^+ or D^+ loss has already been made. The results of this set of experiments are shown in Table 4.

The H/D selectivities in Table 4 appear convincingly to be greater than 1.00, but are still quite small for a primary isotope effect. They are, in fact, what one might expect for a *secondary* isotope effect with attack at the methyl group. This might be imagined as a nucleophilic attack on the methyl group, producing a leaving group of a phosphonate that has been activated in some manner. While we cannot rule this out, it seems unlikely that hydrogen peroxide photolysis, Fenton chemistry, and TiO_2 in the presence of NaF would all react in this way, even if it could be imagined (e.g. as a variation on the acid catalyzed reactions postulated in Scheme 1) for TiO_2.

It is possible also that the H/D, KIE might simply be very small. A survey of the literature on the deprotonation of related radical cations (e.g. dimethyl aniline structure types and/or benzyl structure types) suggests that directly measured KIEs for radical cation deprotonations, while structure-dependent, are in the normal range for primary KIEs, i.e. 2–7, with a few very large ones that implicate H-atom tunneling [27–32]. We were unable to find any directly measured KIEs for radical cations more closely related to $DMPP^+$ than these. Though we have difficulty in rationalizing the observed magnitude of the H/D selectivity, the important point remains that there is a measurable isotope effect. This is at least consistent with the quite clear implication of the ^{18}O experiments that the mechanism of demethylation derives from attack at the methyl group, rather than attack at phosphorus.

4. Conclusions

The TiO_2-mediated photocatalytic degradation of phosphonates is understood to include removal of the alkyl ester portion of the compounds to produce phosphonic acid monoesters among the primary steps. While there is ambiguity in the interpretation of small H/D selectivity in the dealkylation of DMPP by TIO_2 photocatalysis and various other methods, the results of ^{18}O labeling are clear. They do not rely on any kinetic effect, and the retention of ^{18}O in the formation of MMPP clearly requires that the dealkylation mechanism involves degradation of the methyl group exclusively, and neither attack at phosphorus by $HO^{\bullet}_{ads}$ or a related species, nor by water or hydroxide in photoinduced hydrolysis.

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