Reactions of Hydroxyl Radical with Dimethyl Methylphosphonate and Diethyl Methylphosphonate. A Fundamental Mechanistic Study

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Dimethyl methylphosphonate (DMMP) and diethyl methylphosphonate (DEMP) were used as models for hazardous organophosphorus compounds to study their radiolytic reactions. Hydrated electrons and superoxide anion radicals do not appreciably react with the phosphonates. On the other hand, hydroxyl radicals degrade the model compounds and the associated rate constants were determined by competition kinetics with thiocyanate to be $(2 \pm 1) \times 10^8$ M^{-1} s^{-1} for DMMP and $(6 \pm 1) \times 10^8$ M^{-1} s^{-1} for DEMP. The initial products formed from an $^{\bullet}OH$ radical reaction with the phosphonates are mainly carbon-centered radicals created by H-abstraction. The initial products readily react with TNM to yield adducts, with characteristic absorbances at ∼300 nm, with rate constants of $(8.8 \pm 0.3) \times 10^7$ and $(3.5 \pm 0.3) \times 10^8$ M^{-1} s^{-1} for DMMP and DEMP, respectively. These hydrogen abstraction products react with oxygen to give the phosphonic acid monoesters at *G* values of 5.1 (5.3×10^{-7} mol J^{-1}) for methyl methylphosphonate and 4.7 (4.9×10^{-7} mol J^{-1}) for ethyl methylphosphonate. Thus, the hydrogen abstraction pathway constitutes a major route for $^{\bullet}OH$ radical reactions, which is also supported by the absence of electron abstraction and/or $^{\bullet}OH$ addition reactions.

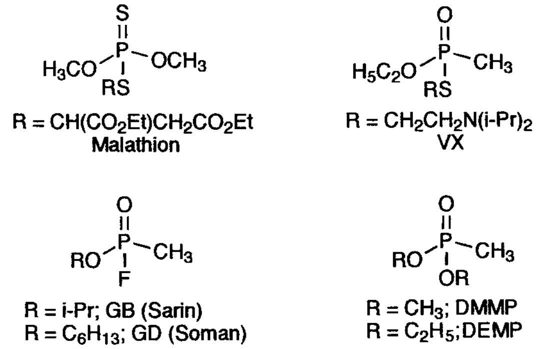
Introduction

Organophosphorus compounds represent a group of materials of biochemical and technical importance. The decontamination of large stockpiles of organophosphorus nerve agents is a serious concern and a timely problem.[1] Although organophosphorus compounds are less persistent than organochlorine compounds when used as pesticides, their widespread use and water solubility pose a significant threat to the environment. While the decontamination of organophosphorus compounds can be readily achieved employing hydroxyl radical generating techniques, such as advanced oxidation processes (AOPs), the mechanistic details for reactions of hydroxyl radicals with these substrates have not been clearly established.[1−11]

In an attempt to develop a better fundamental understanding of the reactions between radicals formed during radiolysis and organophosphorus compounds in aqueous media, we have chosen to conduct γ and pulse radiolysis studies of DMMP and DEMP, models for pesticides and nerve agents. Structures are shown in Scheme 1.

While considerable attention has been paid to the effects of high-energy radiation on organophosphorus compounds, the majority of these studies involve the radiolysis of pure liquid phosphates and phosphonates. In addition, the mechanistic conclusions are based on esr spectra obtained in matrixes at 77 K and/or product studies in nonaqueous media.[12] However, a limited number of studies have been made on the radiolysis of alkyl phosphonates and alkyl phosphates in aqueous solutions.[13] Schuchmann et al. have recently reported some elegant studies in which they determined rate constants for the reaction of hydroxyl radicals with alkyl phosphates, relevant to the radiation chemistry of DNA in aqueous solutions.[14]

SCHEME 1: Structures of Pesticide, Nerve Agents, and Model Compounds



Reaction pathways for the degradation of DMMP and DEMP have been investigated by TiO_2 photocatalysis and provide evidence for the processes being hydroxyl radical mediated.[2−4] While TiO_2 photocatalysis is known to produce hydroxyl radicals, direct electron transfer from the substrate to the valence band hole of the photoexcited semiconductor should, however, also be considered. The involvement of the valence band hole to yield a radical cation in the degradation of organophosphorus pesticides by TiO_2 photocatalysis has been proposed by Tanaka.[5,6] Knowledge of the reactivity of DMMP and DEMP toward radiolytically generated radicals, such as hydroxyl radicals, hydrated electrons, and superoxide radical anions, will be useful to elucidate the kinetic and mechanistic aspects of

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the decontamination of organophosphorus compounds. We report herein the results of γ and pulse radiolysis studies.

Experimental Section

Materials. DMMP, DEMP, ethyl methylphosphonate (EMP), and tetranitromethane (TNM) were obtained from Sigma-Aldrich. TNM was washed several times with distilled water until the water did not reveal any yellow color. Sodium azide, potassium thiocyanate, hydrochloric acid, and *tert*-butyl alcohol were reagent grade and used as received from Fisher Scientific. All the experiments were performed at room temperature using 18 MΩ deionized water.

Radiation Chemistry. Radiation of water produces ${}^\bullet$OH and ${}^\bullet$H radicals, hydrated electrons e_{aq}^-, the molecular products H_2 and H_2O_2 and solvated protons H_{aq}^+. Yields are given as G values that represent the number of species per 100 eV deposited energy.[13] The actual figures listed in reaction 1 refer to measured

$$H_2O \xrightarrow{\text{radiolysis}} 2.7{}^\bullet OH,\ 0.6{}^\bullet H,\ 2.6e_{aq}^-,\ 0.45H_2,\ 0.7H_2O_2,\ 2.6H_{aq}^+ \qquad (1)$$

yields in dilute substrate solutions and can be transferred into the SI unit system by multiplying with the factor 1.036×10^{-7} mol J^{-1}.

In aqueous, nitrous oxide (N_2O)-saturated solutions, the solvated electrons are selectively scavenged with a bimolecular rate constant of $k = 9.1 \times 10^9$ M^{-1} s^{-1} according to[15]

$$N_2O + e_{aq}^-/H_2O \rightarrow {}^\bullet OH + OH^- + N_2 \qquad (2)$$

thus, nearly doubling the amount of ${}^\bullet$OH available for reaction.

For selective monitoring of the reaction between hydrated electrons and a substrate, 1% v/v of 2-methyl-2-propanol (*tert*-butyl alcohol, *t*-ButOH) was added to the solution in order to scavenge ${}^\bullet$OH-radicals ($k = 6 \times 10^8$ M^{-1} s^{-1}) according to reaction 3.[16]

$$(CH_3)_3COH + {}^\bullet OH \rightarrow {}^\bullet CH_2(CH_3)_2COH + H_2O \qquad (3)$$

Superoxide with a yield of $G(O_2^{\bullet -}) = 3.2$ (3.3×10^{-7} mol J^{-1}) was produced using an air-saturated aqueous solution with 1% v/v *tert*-butyl alcohol to scavenge ${}^\bullet$OH according to reaction 3, thus allowing hydrated electrons and ${}^\bullet$H atoms to react with O_2 with rate constants of 1.9×10^{10} and 2.1×10^{10} M^{-1} s^{-1}, respectively.[13]

$$e_{aq}^-/{}^\bullet H + O_2 \rightarrow O_2^{\bullet -}/HO_2^\bullet \qquad (4)$$

Under experimental conditions of pH 7, the superoxide radical anion will predominantly exist in the anionic form since the pK_a of $HO_2^\bullet$ is 4.69.[17]

The rate constants determined in this paper were obtained by plotting the average of the data points and the standard deviation is included as error bars. Least squares linear regression was applied to fit the data points, with R^2 as a measure for the quality of the fit. $R^2 = 1$ denotes a perfect fit. All reported rate constants have an intrinsic error of no less than 10%.

Instrumentation. *Pulse Radiolysis.* A Model TB-8/16-1S linear electron accelerator, providing 5−50 ns pulses of 8 MeV electrons and generating radical concentrations of 1−3 μM per pulse in all investigated systems, was used for the pulse radiolysis experiments. A detailed description of the experimental setup at the Radiation Laboratory, University of Notre Dame,[18] as well as the basic details of the equipment and data analysis[19] have been given elsewhere. The dosimetry was based on the oxidation of 0.01 M thiocyanate anions (SCN^-) to $(SCN)_2^{\bullet -}$ in aqueous, N_2O-saturated solutions at pH 7. Absorptions are given in $G\epsilon$ units, referring to a $G\epsilon$ value of $(5.2 \pm 0.1) \times 10^{-4}$ m^2 J^{-1}.[20]

γ Radiolysis. The γ radiolysis experiments were performed in a Gammacell 220 Cobalt 60 source model GC-220R (Atomic Energy of Canada Limited) at a dose rate of 0.35 Gy s^{-1} (2.18×10^{15} eV g^{-1} s^{-1}). Dose rates were determined by comparison to Fricke dosimetry ($G(Fe^{3+}) = 15.45$ (16.00×10^{-7} mol J^{-1});[21] $\epsilon(Fe^{3+}) = 2197$ M^{-1} cm^{-1} at 304 nm and 25 °C; electron density correction = 1.024).

Solutions were in septa-capped vials, which were purged for ∼30 min with the respective gas, i.e., N_2, O_2, N_2O, or N_2O/O_2 (4:1). A blank vial for each condition was not subjected to γ irradiation. The applied irradiation doses D were used to calculate radiolytic product concentrations according to[22]

$$D = \frac{[\text{radiolytic product}]}{G\rho}(9.65 \times 10^9 \text{ Gy g mol}^{-1}) \qquad (5)$$

with G values of 5.35 (5.54×10^{-7} mol J^{-1}) or 2.6 (2.7×10^{-7} mol J^{-1}) depending on the experimental conditions and ρ as the density of the solution. Irradiation doses were varied to obtain 0−20% degradation of the starting material (1 mM DMMP or 1 mM DEMP). All respective doses were calculated using eq 5. The application of higher doses (degradation >20%) may lead to formation/detection of products from reactions between the initial radicals, (e.g. ${}^\bullet$OH, hydrated electrons, ${}^\bullet$H and superoxide radical anions) and already reacted starting material (early products).

Gas Chromatography (GC). A Hewlett-Packard 5890 series II instrument equipped with a flame photometric detector (FPD) model 19256A (BP), a 393 nm wavelength filter and a 30 m × 0.530 mm DB-5 Megabore bonded phase column (J & W Scientific) was employed. Concentrations of DMMP were determined from calibration curves using DEMP as the internal standard and vice versa.

Ion Chromatography (IC). The analyses were performed on a Dionex DX 500 equipped with a suppressed conductivity detector and an Anion Self-Regenerating Suppressor-1 (ASRS-1, 4 mm ID) in autosuppression recycle mode. The instrument contained an AG12A, 4 × 50 mm guard column and an Ionpac AS12A, 4 × 200 mm analytical column. The eluent employed was degassed 2.7 mM Na_2CO_3/0.3 mM $NaHCO_3$ at a flow rate of 1.5 mL/min.

Results and Discussion

***γ* Radiolysis.** Individual samples of 2.65×10^{-4} M DMMP were prepared at three different conditions: (a) N_2O saturation at pH 7, (b) air saturation at pH 7, and (c) 1% v/v *tert*-butyl alcohol solution at pH 7 purged with N_2. Samples were γ irradiated for different time intervals at 21 Gy min^{-1}. The disappearance of the starting material, our model compound, was monitored by gas chromatography (Figure 1).

No degradation was observed under condition (c), where aqueous electrons are the reactive species. However, in both the absence (a) or presence (b) of oxygen total degradation of the model compound was observed. An increased decay rate for nitrous oxide saturation (a) when compared to air-saturated solution, (b) suggests that ${}^\bullet$OH radicals are the main source of DMMP degradation.

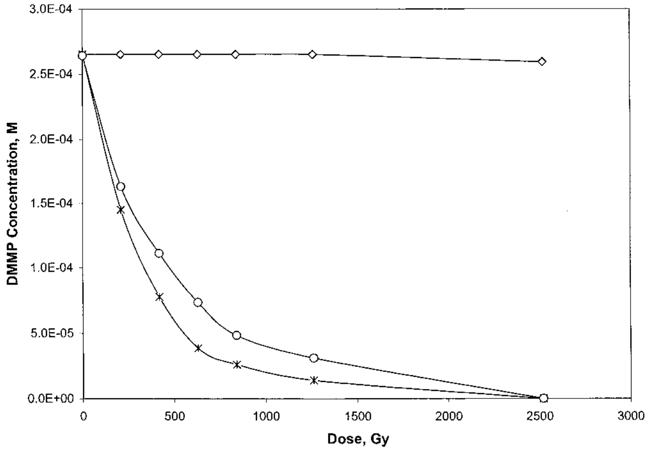


Figure 1. Degradation of DMMP analyzed by GC versus γ irradiation time at a rate of 21 Gy min^{-1}. Three conditions were monitored: (◇) solution purged with N_2 contained 1% v/v *tert*-butyl alcohol, (○) air-saturated solution, and (*) solution purged with N_2O.

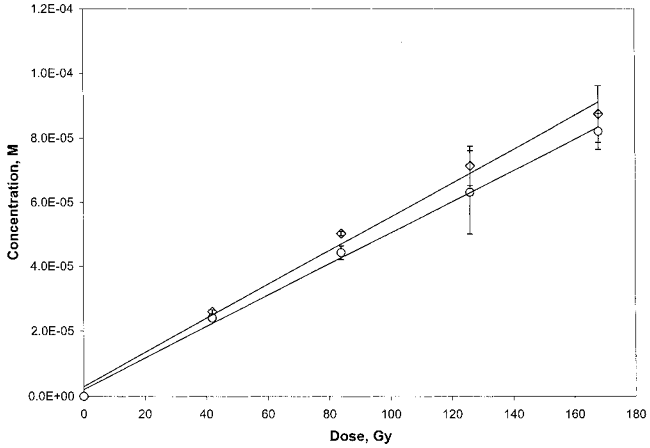


Figure 2. Linear fit of monoester MMP (◇) and EMP (○) concentrations as a function of dose. The initial phosphonate concentrations were 1 mM. Linear equations: DMMP $Y = 5.24 \times 10^{-7}X + 3.01 \times 10^{-6}$, $R^2 = 0.992$; DEMP $Y = 4.83 \times 10^{-7}X + 2.08 \times 10^{-6}$, $R^2 = 0.997$.

The formation of products during γ radiolysis was monitored by ion chromatography. The following conditions were utilized: (a) N_2O saturation at pH 7, (b) saturation with N_2O/O_2 at a ratio of 4:1 at pH 7, (c) 1% v/v *tert*-butyl alcohol solution at pH 7 purged with N_2, (d) air-saturated 1% v/v *tert*-butyl alcohol solution at pH 7, and (e) 1% v/v *tert*-butyl alcohol solution at pH 7 purged with O_2. No products were detected except in N_2O/O_2-saturated solutions (b).

Under condition b, a peak with the same retention time for irradiated DMMP and DEMP solutions was observed, each of which increased with increasing irradiation dose (Figure 2). For irradiated DEMP solutions, this peak was identified as ethyl methylphosphonate (EMP monoester) by comparison of the retention time to commercially available material. In the case of irradiated DMMP solutions, a reference material for methyl methylphosphonate (MMP monoester) was not available, but on the basis of the retention time similarity and mechanistic implications described in a later section, the peak is assumed to be the MMP monoester.

The linear relationships observed in Figure 2 between the concentration of the MMP and EMP monoesters as a function of dose confirm that they are the primary products of the reaction between the starting material and radicals formed during irradiation. According to eq 1, the slopes in Figure 2 can be used to calculate the generated yields for the monoesters. *G* values of 5.1 (5.3×10^{-7} mol J^{-1}) and 4.7 (4.9×10^{-7} mol J^{-1}) are obtained for MMP and EMP, respectively. Although, the determined *G* values are lower than the maximum yield of 5.35 (5.54×10^{-7} mol J^{-1}) for $^{\bullet}$OH radicals under condition b,[23] the formation of monoesters constitutes a major reaction pathway. Besides the formation of MMP and EMP under condition b, trace levels of methylphosphonic acid (MPA) and phosphate were identified by ion chromatography using commercially available materials.

Addition of $^{\bullet}$OH to the phosphorus atom in the pesticides had been proposed by Pignatello and Sun[11] and would constitute a similarity to the addition of an $^{\bullet}$OH to sulfur in organic sulfides.[24,25] However, in case of N_2O-saturated phosphonate solutions, condition a, no ions are detected by ion chromatography. This suggests that $^{\bullet}$OH addition products onto phosphorus are, in fact, not formed. Any such formation would lead to phosphonic acids, which could either be directly observed or, if unstable, their decay products should be easily detectable. Similarly, oxidation of phosphonates via electron abstraction by $^{\bullet}$OH radicals would ultimately lead to ionic products.

The absence of any products for conditions c−e indicates that the reactions between the phosphonates and aqueous electrons or superoxide radical anions are also unlikely. A reaction, if any, would likely occur at the oxygen double bonded to phosphorus. These products are not likely to be stable, but their decay products would be ionic in nature and detectable by IC.

Pulse Radiolysis. *Rate Constants Determination.* The rate constants for the reaction of the hydroxyl radicals with DMMP and DEMP in N_2O-saturated solutions were obtained by pulse radiolysis. Direct detection methods could not be employed to monitor the growth of intermediates due to the lack of absorptions in the UV−visible range of 25−750 nm. Therefore, to monitor a reaction of $^{\bullet}$OH with DMMP or DEMP, a competition method has to be employed. Thiocyanate, as a competitor reacts with $^{\bullet}$OH radicals and its product, $(SCN)_2^{\bullet-}$, shows an absorption with a maximum at 472 nm. In the presence of phosphonates, this absorption is lowered by the fraction of $^{\bullet}$OH that reacts with phosphonates. This established competition method can be expressed mathematically:[22]

$$\mathrm{Abs}_0((\mathrm{SCN})_2^{\bullet-})/\mathrm{Abs}((\mathrm{SCN})_2^{\bullet-}) = 1 + (k_{\mathrm{phosphonate}+^{\bullet}\mathrm{OH}}[\mathrm{phosphonate}]/k_{\mathrm{SCN}^-+^{\bullet}\mathrm{OH}}[\mathrm{SCN}^-]) \quad (6)$$

where $\mathrm{Abs}_0((SCN)_2^{\bullet-})$ is the absorption of the thyocianate radical anions in the absence of phosphonates and $\mathrm{Abs}((SCN)_2^{\bullet-})$ is that in the presence of various concentrations of phosphonates. The concentrations ranged from 0.44 to 8.1 mM for DMMP and 0.17 to 2.19 mM for DEMP with a constant thyocianate concentration of 11 mM. Although the formation of $(SCN)_2^{\bullet-}$ involves a second SCN^- ion, this mathematical treatment is justified because at the SCN^- concentrations employed the formation of $(SCN)_2^{\bullet-}$ is only controlled by the primary competition of SCN^- and DMMP/DEMP for $^{\bullet}$OH. Thus, a plot of the absorption ratio $\mathrm{Abs}_0((SCN)_2^{\bullet-})/\mathrm{Abs}((SCN)_2^{\bullet-})$ versus the concentration ratio [phosphonate]/[SCN^-] yields the rate constant ratio $k(\text{phosphonate} + {}^{\bullet}\text{OH})/k(SCN^- + {}^{\bullet}\text{OH})$ as a slope.

The linear plots of the $(SCN)_2^{\bullet-}$ absorption ratio versus the concentration ratio [phosphonate]/[SCN^-] shown in Figure 3 yield *y* intercepts of 0.998 and 0.996 for DEMP and DMMP, respectively, which are very close to the theoretical value of 1.0. The rate constants for the reaction of hydroxyl radicals with the solutes equal the slope times 1.1×10^{10} M^{-1} s^{-1}, the rate constant for the reaction of hydroxyl radicals with SCN^-.[13]

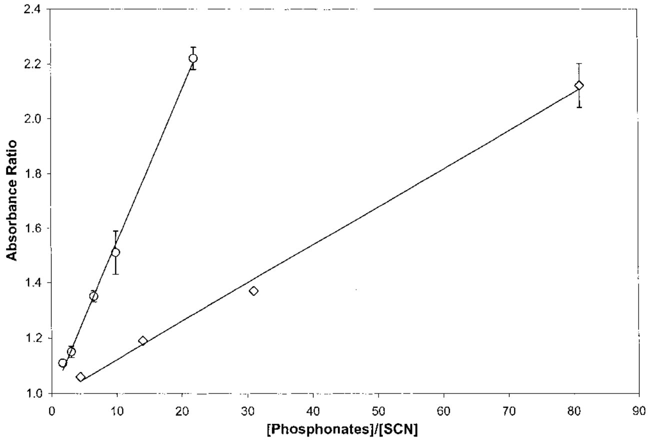


Figure 3. KSCN competition kinetics: plot of absorbance ratios $Abs_0((SCN)_2^{\bullet -})/Abs((SCN)_2^{\bullet -})$ at 472 nm versus concentration ratios of [phosphonates]/[SCN^-] upon pulse radiolysis of N_2O-saturated aqueous solutions at pH 7. The linear equations: DMMP (◇) $Y = 0.0139X + 0.9825$, $R^2 = 0.996$; DEMP (○) $Y = 0.0556X + 0.9902$, $R^2 = 0.998$.

Values derived this way for the $^\bullet$OH radical reactions with DMMP and DEMP amount to (2 ± 1) × 10^8 and (6 ± 1) × 10^8 M^{-1} s^{-1}. These rate constants are very similar to the reported ones for dimethyl and diethyl phosphate reacting with $^\bullet$OH radicals of 2.5 × 10^8 and 8.6 × 10^8 M^{-1} s^{-1}, respectively.[14] The difference in observed rates between the model compounds will be discussed later.

In an attempt to generate the radical cation of DMMP and DEMP, which may also be considered to be a possible transient in the $^\bullet$OH-induced reaction, we tried to oxidize these compounds via radiolytically formed $N_3^\bullet$ under neutral and $Cl_2^{\bullet -}$ under acidic conditions. With an excess of NaN_3 or HCl with respect to the phosphonates, $^\bullet$OH radicals preferably react with these scavengers, and oxidants are formed according to:

$$N_3^-/2Cl^- + {}^\bullet OH \rightarrow N_3^\bullet/Cl_2^{\bullet -} + OH^- \tag{7}$$

The products of eq 7 are powerful one-electron oxidants and, in turn, produce radical cations upon reaction with a variety of organic substrates.[26] The phosphonate concentrations ranged from 0.1 to 1 mM in the case of 0.1 M NaN_3 and from 1 to 12 mM in the case of 0.01 M HCl. However, the decay of each of the two oxidants did not depend on the phosphonate concentration; i.e., the time traces with and without DMMP/DEMP present are virtually the same. It is, therefore, safe to assume that no significant reactions occur between these oxidizing species and our model compounds. A comparison of the one-electron reduction potentials for $Cl_2^{\bullet -}$ radicals $E(Cl_2^{\bullet -}/2Cl^-) = 2.09$ V[27] and azide radicals at neutral pH $E(N_3^\bullet/N_3^-) = 1.33$ V[28] with $^\bullet$OH radicals at neutral pH $E(^\bullet OH/OH^-) = 1.89$ V[29] indicates that electron transfer to $^\bullet$OH yielding OH^- and the radical cation is also unlikely, mainly due to the $^\bullet$OH radical being a less powerful oxidant when compared to $Cl_2^{\bullet -}$ radicals.

Tetranitromethane (TNM) and Phophonates. If hydrogen abstraction by $^\bullet$OH radicals occurs, it is likely to yield carbon-centered radicals, which are activated by α-positioned oxygen or phosphorus functionalities. Tetranitromethane (TNM) is known for selectively reacting with such carbon-centered radicals by formation of TNM adducts with an absorption maximum around 300 nm.[14,24,25,30] Such adducts will further decay into nitroform anions absorbing at 350 nm.[14] (eq 8).

$$C^\bullet + C(NO_2)_4 \rightarrow [C{-}TNM]^\bullet \rightarrow C^+ + C(NO_2)_3^- + NO_2^\bullet \tag{8}$$

The radicals formed from the reaction of our model compounds with the hydroxyl radical were, therefore, tested for their ability to react with and eventually reduce TNM.

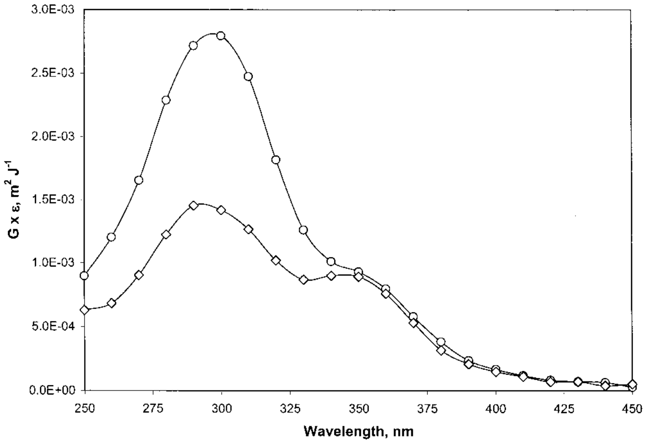


Figure 4. UV/vis absorption spectra of 5 × 10^{-3} M aqueous DMMP (◇) and DEMP (○) solutions with 1 × 10^{-4} M TNM, N_2O saturated, pH 7, 150 μs after the electron pulse.

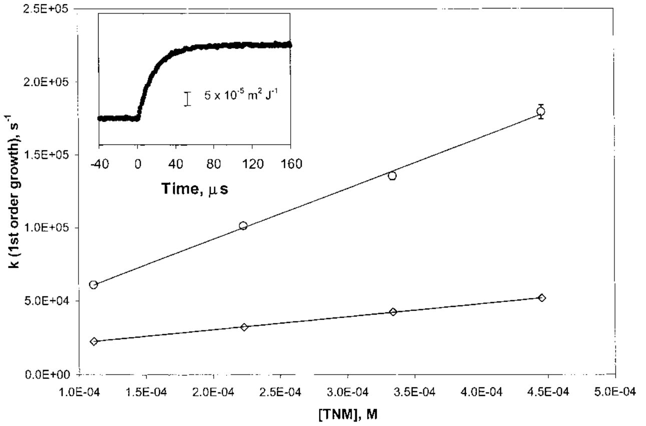


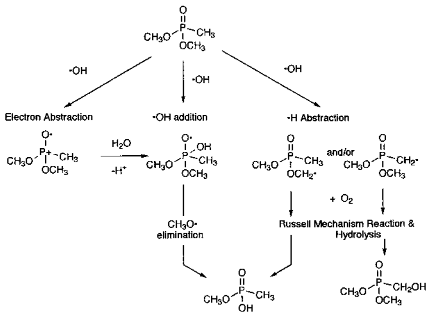
Figure 5. Dependence of pseudo-first-order rate constant for the absorption at 300 nm on the concentration of TNM for DMMP (◇) and DEMP (○) (40 mM DMMP or 30 mM DEMP, N_2O-saturated aqueous solution, pH 7). Linear equations: DMMP $Y = 8.8 \times 10^7X + 1.3 \times 10^4$, $R^2 = 0.9997$; DEMP $Y = 3.5 \times 10^8X + 2.2 \times 10^4$, $R^2 = 0.998$. Inset: growth of TNM adduct at 300 nm.

Optical absorption spectra, obtained upon pulse irradiation of a N_2O-saturated, aqueous solution containing 0.1 mM TNM and 5 mM phosphonate are shown in Figure 4.

The small absorbance at 350 nm is the result of nitroform formation from direct reduction of TNM by H atoms.[31] The strong absorption observed at 300 nm is indicative of TNM adducts formed from radicals derived from both phosphonates and compares favorably to similar absorptions of alkyl phosphate TNM adducts.[14] While a number of other TNM adducts decompose to form nitroform anions, we did not observe the formation of the latter on the time scale of our experiments (1.6 ms). This is reasonable, given that the stability of the TNM adducts formed from the reactions of TNM with different carbon-centered radicals varies significantly depending on substituents.[14,24,25,30−33]

Plots of the first-order rate constants for the growth of the absorbance at 300 nm versus [TNM] yields bimolecular rate constants of $k(DMMP^\bullet + TNM) = (8.8 \pm 0.3) \times 10^7$ M^{-1} s^{-1} and $k(DEMP^\bullet + TNM) = (3.5 \pm 0.3) \times 10^8$ M^{-1} s^{-1}, as shown in Figure 5. The very small positive intercepts for these lines suggest there is a minimal contribution from alternative reaction

SCHEME 2: Proposed Mechanisms of Hydroxyl Radical Reactions with DMMP



pathways (i.e., radical−radical reactions or other channels for the decay of the radicals).

The dependence of these reactions on [TNM] is a further indication that, indeed carbon-centered radical intermediates are produced when hydroxyl radicals react with DMMP or DEMP. A similar trend in rate constants has been reported for α-phosphatoalkyl TNM adducts by Schuchmann et al.[14] According to their observation, dimethyl and diethyl phosphate radicals react with rate constants of 8.0×10^8 and 2.0×10^9 M^{-1} s^{-1}, respectively.

Hydroxyl radicals reacting with DEMP by hydrogen abstraction mainly produce a secondary carbon radical $-^{\bullet}CH-CH_3$, which is more stable than a primary radical $-^{\bullet}CH_2$ formed from a similar reaction with DMMP. Secondary radicals are generally better reductants and are expected to reduce TNM faster than primary radicals due to a higher electron density at the radical site.[26,30] Accordingly, in addition reactions they may be expected to be stronger nucleophiles. This would mean that the radicals should preferentially interact with the carbon atom in TNM, which is a highly unlikely scenario for two reasons: (i) it would require a hypervalent carbon in the long-lived adduct radical and (ii) be inconsistent with the structure of the adduct deduced from earlier studies,[24,25,33] which indicate radical addition at an oxygen of one of the nitro groups. Therefore, it seems that other parameters are dominating the mode of adduct formation. From earlier studies it appears, in fact, that the most relevant parameter is the activation entropy for the adduct formation.[24,33]

Mechanism of •OH Reactions. Water radiolysis yields a variety of radicals that could react and thus degrade phosphonates. γ and pulse radiolysis results suggest that e_{aq}^- and superoxide radical anions are not involved in the mechanism. On the other hand, •OH radicals appear to have an active role in degrading DEMP and DMMP. Scheme 2 proposes reaction pathways for the hydroxyl radical mediated oxidation of DMMP. A similar mechanism can be deduced for DEMP.

Hydroxyl radical addition to the central phosphorus should yield an oxygen-centered phosphorenyl radical. This adduct radical, in analogy to the sulfoxide •OH adduct is prone to stabilization by alkoxy cleavage.[34−36] The molecular product expected from this process is phosphonic acid monoester, a product that can be identified by IC. However, no such product is observed during γ-radiolysis experiments in the absence of O_2.

It is also known that oxygen-centered radicals such as the ones proposed in the addition−elimination reaction ($CH_3O^{\bullet}$ and $CH_3CH_2O^{\bullet}$) are known to convert rapidly, within about 1 μs, via a water-assisted 1,2-hydrogen shift[31] to reducing α hydroxyl radicals $^{\bullet}CH_2OH$ and $CH_3CH^{\bullet}OH$. The rate constants for TNM reduction by $^{\bullet}CH_2OH$ and $CH_3CH^{\bullet}OH$ are 5×10^9 M^{-1} s^{-1},[30] i.e., more than 1 order of magnitude higher than the rate constants we report for the reaction of TNM with phosphonate intermediates. Furthermore, α hydroxyl radicals do not form TNM adducts of any appreciable lifetime. This evidence virtually eliminates the alkoxy radical elimination as a possible route to the observed TNM adducts.

An electron abstraction by •OH radicals, if occurring, will produce radical cations. On the basis of electron densities and electronegativities, the electron should be abstracted from the phosphorus−oxygen double bond, resulting in a positive charge centered on phosphorus. Such species would probably undergo a rapid reaction with water to form the above-described phosphorenyl radical. We did not observe either phosphonate radical cations in the reaction with the more powerful oxidant $Cl_2^{\bullet-}$ or α hydroxyl radicals as the elimination products of the phosphorenyl radicals. Thus, we conclude that electron abstraction from phosphonates by •OH radicals is not a major reaction pathway.

Hydrogen abstraction at alkyl sites by •OH radicals produces carbon-centered radicals. Direct evidence for the existence of carbon-centered radicals during the reaction of •OH radicals with phosphonates is the formation of TNM adducts. These were observed for both phosphonates by strong absorbances with maxima around 300 nm (Figure 4) and by the determination of second-order rate constants for these reactions. The faster hydroxyl radical rate constant for DEMP relative to DMMP is further evidence of a carbon-centered radical pathway. Hydroxyl radicals react with DEMP by hydrogen abstraction to produce a secondary carbon radical, which is more stable than a primary radical formed from DMMP and hence a faster rate for DEMP is plausible. Similar trends have been reported for the formation of primary and secondary radicals from the reactions of hydroxyl radicals with alkyl phosphates.[14]

Product studies from electron beam treatment suggest the hydroxyl radical mediated degradation of DMMP involves the formation of a predominant intermediate product, prior to the production of methylphosphonic acid (MPA), which is further oxidized to phosphate.[4] We identified this predominant intermediate product by ion chromatography as the monoester of DMMP or DEMP, respectively.

The phosphonic acid monoester of DMMP, formed in oxygenated solutions can be envisioned as a result of hydrogen abstraction from the methoxy group, followed by oxygen addition, which generates the peroxyl radical $-P-O-CH_2OO^{\bullet}$. $CH_2OO^{\bullet}$-type peroxyl radicals typically undergo a bimolecular Russell decay[37] leading to the corresponding alcohol, here $-P-OCH_2-OH$, and aldehyde, here $-P-O-CHO$. Both of these products are expected to be readily hydrolyzed to produce phosphonic acid monoester under the experimental conditions of isolation and identification.[38] Unfortunately, we cannot assess the hydrogen abstraction pathway via $P-CH_2^{\bullet}$ and $P-OCH_2$-$CH_2^{\bullet}$, which our data indicate to be minor pathways for the degradation of phosphonates. However, they may account for the *G* value difference between the yield of the monoesters (5.1 (5.3×10^{-7} mol J^{-1}) for MMP and 4.7 (4.9×10^{-7} mol J^{-1}) for EMP) and the overall •OH radical yield of 5.35 (5.54×10^{-7} mol J^{-1}). One might further speculate that the lower EMP yield of 4.7 (4.9×10^{-7} mol J^{-1}) when compared to 5.1 (5.3×10^{-7} mol J^{-1}) for MMP is due to the presence of the ethyl substituent, which offers a second, less reactive hydrogen abstraction site.

Conclusions

DMMP and DEMP were used as models for hazardous organophosphorus compounds to study their radiolytic reactions. The results suggest that hydrated electrons and superoxide anion radical react slowly with the phosphonates. The hydroxyl radical rate constants are $(2 \pm 1) \times 10^8$ M^{-1} s^{-1} for DMMP and $(6 \pm 1) \times 10^8$ M^{-1} s^{-1} for DEMP. The involvement of radical cations upon reaction of our model compounds with hydroxyl radicals is unlikely, given no significant reaction is observed between the phosphonates and one-electron oxidizing agents such as $N_3^{\bullet-}$ and $Cl_2^{\bullet-}$. Product studies and the reactions of tetranitromethane during pulse radiolysis of N_2O-saturated aqueous solutions provide strong evidence that hydroxyl radical reactions yield a carbon-centered radical likely formed through hydrogen abstraction at the alkyl group of the ester chain. The observed reaction products indicate that the presence of O_2 should be beneficial in the decontamination of pesticides and/or chemical warfare agents, since the products obtained are less harmful than their precursors. A number of advanced oxidation processes (AOP) employ hydroxyl radicals as the predominant oxidant and are, therefore, also expected to be effective for the destruction of organophosphorus compounds. The kinetic parameters and mechanistic details presented in this work are useful in designing strategies and developing models for these degradation processes.

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