# Detailed Investigation of the Radical-Induced Destruction of Chemical Warfare Agent Simulants in Aqueous Solution

Amberashley Abbott,<sup>†</sup> Tim Sierakowski,<sup>†</sup> James J. Kiddle,<sup>\*,†</sup> Kristin K. Clark,<sup>‡</sup> and Stephen P. Mezyk<sup>\*,‡</sup>

Department of Chemistry, Western Michigan University, 3425 Wood Hall, Kalamazoo, Michigan 49008, and Department of Chemistry and Biochemistry, California State University at Long Beach, 1250 Bellflower Boulevard, Long Beach, California 90840

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The persistence of delivered chemical warfare agents (CWAs) in a variety of environmental matrices is of serious concern to both the military and civilian populations. Ultimately understanding all of the degradation pathways of the various CWAs in different environmental matrices is essential for determining whether native processes would offer sufficient decontamination of a particular material or if active chemical decontamination is required. Whereas much work on base-promoted chemical degradation has been reported, additional remediation strategies such as the use of advanced oxidation or reduction process free radical treatments may also be a viable option. We have examined here the primary kinetics and reaction mechanisms for an extensive library of chemical warfare agent simulants with the oxidizing hydroxyl radical and reducing hydrated electrons in water. From these values, it is seen that the reductive destruction occurs primarily through a single mechanism, consisting of hydrated electron capture at the phosphorus group with subsequent elimination, whereas hydroxyl radical oxidation shows two separate reaction mechanisms, dependent on the aqueous  $pK_a$  of the leaving group.

## Introduction

The persistence of released organophosphorous compounds such as chemical warfare agents (CWAs) into the environment remains a worldwide concern. Over the past decade, scientists have focused their attention on the ability to detect,<sup>1</sup> decontaminate,<sup>2</sup> and destroy CWAs.<sup>3</sup> These agents exert their toxic effects through inhibition of acetylcholinesterase. Because of their extreme toxicity and restricted use, actual CWAs (Figure 1) such as Tabun (GA), Sarin (GB), Soman (GD), and VX are not regularly employed in studies at academic laboratories. Instead, simulants, which mimic the structural and electronic properties of actual CW agents, are mainly utilized. These stimulants have the general formula  $R^{1}R^{2}P(O)X$ , where X is a leaving group. Simulant chemicals also have a range of toxicities, from the hazardous (e.g., paraoxon, LD<sub>50</sub> rat: i.p. 0.54 mg/kg)<sup>4</sup> to the relatively nontoxic (e.g., diethyl methylphosphonate, DEMP LD<sub>50</sub> mouse: i.p. 2240 mg/kg,).<sup>5</sup>

Whereas base hydrolysis works well to destroy excess inventory of these types of chemicals, this approach may not be as readily utilized for real-world decontamination problems. One major concern would be the CWA contamination of water supplies. Whereas natural processes will deactivate CWAs through a variety of processes, active removal may also be necessary under some circumstances. However, standard water treatment processes such as activated charcoal absorption or phase transfer through aeration stripping may not result in quantitative removal and decontamination. One new group of technologies that can also be used for hazardous chemical removal from waters is advanced oxidation or reduction processes (AO/RPs). These processes are based on the production of radicals *in situ*, typically the oxidizing hydroxyl radical ('OH) and the reducing electron  $(e_{aq}^{-})$ . These generated radicals then react with and degrade the unwanted contaminant chemicals. However, these radicals will also react with other water constituents (O<sub>2</sub>, dissolved organic matter, bicarbonate) usually present at higher concentrations. Therefore, for the practical utilization of any AO/RP for CWA removal, its free radical chemistry (kinetics and reaction mechanisms) needs to be quantitatively established. Moreover, it is also important to ensure that no additional hazardous products are created through these radical-induced degradation mechanisms.

In previous work on simulants, it was shown that whereas oxidizing hydroxyl radicals degraded DEMP (Figure 1) and dimethyl methyl phosphonate (DMMP) in aqueous solution, reducing hydrated electrons and superoxide anion radicals were unreactive.<sup>6</sup> Although these two compounds have been widely used as CWA simulants, these phosphonate species show very low toxicity and do not have a good leaving group like those found in true CW agents.<sup>7</sup> In a preliminary investigation, six model simulants of the general form (EtO)<sub>2</sub>P(O)X that are better mimics of true CWAs were studied, and their rate constants were established for reaction with hydroxyl radicals and hydrated electrons.<sup>8</sup> Brönsted plots for these model compounds



 $\begin{array}{l} \textbf{Tabun: } {R}^1 = Et, {R}^2 = N(CH_3)_2, X = CN \\ \textbf{Sarin: } {R}^1 = \textit{i} Pr, {R}^2 = CH_3, X = F \\ \textbf{Soman: } {R}^1 = CH(CH_3)C(CH_3)_3, {R}^2 = CH_3, X = F \\ \textbf{VX: } {R}^1 = Et, {R}^2 = CH_3, X = S(CH_2)_2N(\textit{i} Pr)_2 \\ \textbf{DMMP: } {R}^1 = CH_3, {R}^2 = OCH_3, X = CH_3 \\ \textbf{DEMP: } {R}^1 = Et, {R}^2 = OEt, X = CH_3 \\ \end{array}$ 



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<sup>\*</sup> To whom correspondence should be addressed. (J.J.K.) Tel: 269-387-5440; Fax: 269-387-2909; E-mail: james.kiddle@wmich.edu. (S.P.M.) Tel: 562-985-4649; Fax: 562-985-8557; E-mail: smezyk@csulb.edu.

<sup>&</sup>lt;sup>†</sup> Western Michigan University.

<sup>\*</sup> California State University at Long Beach.

EtO'' X EtO							
simulant	Х	$pK_a^{\ a}$	$k_{\rm e}^{-} ({\rm M}^{-1} {\rm s}^{-1})$	$k_{OH} (M^{-1} s^{-1})$			
1	Cl	-7	$3.93 \pm 0.24  imes 10^{10}$	$1.37 \pm 0.10  imes 10^{10}$			
2	F	3.2	$1.83 \pm 0.14 \times 10^{9}$	$4.73 \pm 0.35 \times 10^{8}$			
3	OAc	4.8	$1.11 \pm 0.10  imes 10^{10}$	$6.63 \pm 0.82 \times 10^{8}$			
4	CN	9.2	$3.52 \pm 0.32 \times 10^{9}$	$9.04 \pm 0.65 \times 10^{7}$			
5	SCH <sub>2</sub> CH <sub>3</sub>	11	$1.08 \pm 0.06 \times 10^{9}$	$1.40 \pm 0.09 \times 10^{9}$			
6	OCH <sub>2</sub> CF <sub>3</sub>	12	$1.35 \pm 0.09 \times 10^{9}$	$4.13 \pm 0.41 \times 10^{8}$			
7	OH	14	$1.88 \pm 0.13  imes 10^{10}$	$9.88 \pm 0.60 \times 10^{8}$			
8	OCH <sub>2</sub> CH <sub>3</sub>	16	$9.61 \pm 0.05 \times 10^{8}$	$7.19 \pm 0.46 \times 10^{8}$			
9	$OCD_2CD_3$	16		$2.35 \pm 0.17 \times 10^{8}$			
10	CF <sub>3</sub>	$27^{b}$	$5.3 \pm 1.4 \times 10^{8}$	$7.66 \pm 0.56 \times 10^{8}$			
11	$NH_2$	35	$6.38 \pm 0.52 \times 10^{8}$	$6.02 \pm 0.55 \times 10^{8}$			
12	Н	35	$2.21 \pm 0.13 \times 10^{8}$	$7.87 \pm 0.47 \times 10^{8}$			
13	D	35	$7.85 \pm 0.59 \times 10^{7}$	$7.63 \pm 0.44 \times 10^{8}$			
14	$CH_3$	48	$3.36 \pm 0.91 \times 10^{7}$	$6.20 \pm 0.40 \times 10^{8}$			
15	$CD_3$	48	$7.33 \pm 1.16 \times 10^{7}$	$6.34 \pm 0.38 \times 10^{8}$			

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<sup>*a*</sup> March, J.; Smith, M. B. Advanced Organic Chemistry; Wiley: New York, 2001; pp 329–331. pK<sub>a</sub> values represent the ionization of H-X in water. <sup>*b*</sup> Symons, E. A.; Clermont, M. J. J. Am. Chem. Soc. **1981**, 103, 3127.



	$H_{3}C - P C$ $H_{3}C - P C$ <b>16</b> $pK_{a1} = 2.$ $pK_{a2} = 7.$	H H 41 54
species	pH	$k(e^{-}) (M^{-1} s^{-1})$
16	5.08	$1.22 \pm 0.04 \times 10^{10}$
16	10.02	$1.62 \pm 0.12 \times 10^{9}$

SCHEME 1: Synthesis of Fluorine Containing Chemical Warfare Agent Simulants

$$EtO^{\cdot,P}_{I} \leftarrow Cl \xrightarrow{Amberlyst F^{-}}_{100\%} EtO^{\cdot,P}_{I} \leftarrow F \xrightarrow{2 eq. CF_{3}TMS}_{85\%} EtO^{\cdot,P}_{I} \leftarrow F_{3}$$

demonstrated that the reduction process followed a single reaction mechanism, proposed to be initial reduction at the phosphorus atom, followed by elimination of a leaving group. In contrast, the hydroxyl radical oxidation showed two distinct linear regions, indicating more complicated reaction chemistry. The faster reaction rate constants for hydrated electron reduction also indicated that active AO/RP treatments that also produced this radical (e.g., TiO<sub>2</sub>/*hv*, electron beam) would be more efficient options.

Whereas specific degradation rate constants for real CWAs was attempted based on this small set of data, there were considerable gaps in the Brönsted plots, resulting in large uncertainty. To establish quantitative estimates for CWA reactivities in water further, we have undertaken a more detailed study here measuring absolute reaction rate constants for both the hydroxyl radical and hydrated electron with a large library of organophosphorus CWA simulants in water.

**Experimental Section.** Eight of the 16 compounds (1, 4, 7, 8, 11, 12, and 14 in Table 1 as well as 16 in Table 2) were commercially available and used as received. The synthesis of simulant 2 can be accomplished from diethyl chlorophosphate (1) in quantitative yield by a solid-phase approach (Scheme 1).<sup>9</sup> Subsequent reaction of diethyl fluorophosphate (2) with 2 equiv of TMSCF<sub>3</sub> and a catalytic amount of CsF provides the trifluoromethylphosphonate analog (10) in pure form after

SCHEME 2: Synthesis of Simulant Compounds 5 and 6



SCHEME 3: Synthesis of Diethyl Phosphonic Acetic Anhydride



## SCHEME 4: Synthesis of Diethyl D-Phosphonate (13)

$$(CH_{3}CH_{2}O)_{3}P \xrightarrow{D_{2}O} CH_{3}CH_{2}O^{\vee,P}_{\Lambda} D CH_{3}CH_{2}O^{\vee,P}_{\Lambda} D CH_{3}CH_{2}O^{\vee,P}_{\Lambda} D CH_{3}CH_{2}O$$
13

chromatography (Scheme 1).<sup>10</sup> Compounds 5 and 6 were both synthesized by substitution reaction using diethyl chlorophosphate as the starting material and the appropriate nucleophile (Scheme 2).<sup>11</sup> The diethyl phosphonic acetic anhydride (3) was synthesized using a modified literature procedure from diethyl phosphonic acid (7) by the formation of an anhydride with acetyl chloride in the presence of triethylamine (Scheme 3).<sup>12</sup> The deuterated analog 13 of simulant 12 was synthesized by refluxing triethylphosphite in D<sub>2</sub>O, followed by distillation to obtain the pure product (Scheme 4).<sup>13</sup> The required deuterated analogs of dimethyl methyl phosphonate were each prepared via a microwave Arbuzov rearrangement of a trialkyl phosphite and iodomethane precursor appropriately deuterated (Scheme 5).<sup>14</sup> All compounds were greater than 98% pure, as characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy as well as GC/MS, and these data were consistent with those previously reported in the literature. Reported rate constant errors are a combination of the measurement precision and compound purity.

## SCHEME 5: Synthesis of Deuterated Analogs of Dimethyl Methyl Phosphonate



**Kinetic Measurements.** The linear accelerator (LINAC) electron pulse radiolysis system at the Radiation Laboratory, University of Notre Dame was used for the hydrated electron and hydroxyl radical reaction rate constant determinations. This irradiation and transient absorption detection system has been described in full detail elsewhere.<sup>15</sup>

CWA simulant solutions were made at this laboratory using water filtered by a Millipore Milli-Q system (>18.2 M $\Omega$ ). All solutions were completely sparged with high purity N<sub>2</sub>O (for hydroxyl radical experiments) or N<sub>2</sub> (for hydrated electron or hydrogen atom) to remove dissolved oxygen. Stability experiments based on <sup>31</sup>P NMR were performed on these solutions to determine the extent of hydrolysis of simulants **1**, **2**, and **4**. These experiments demonstrated that 0.010 M solutions of all three compounds were stable for over 1 week at neutral pH in a 1:1 solution of H<sub>2</sub>O/D<sub>2</sub>O, showing no hydrolysis products. This is in agreement with the literature that indicates that both simulants and CW agents with F, Cl, or CN substituents only show rapid hydrolysis occurs at a slower rate.<sup>16</sup>

During the irradiation process, the solution vessels were bubbled with only the minimum amount of gas necessary to prevent air ingress to prevent loss of chemical. Dosimetry was performed using N<sub>2</sub>O-saturated,  $1.00 \times 10^{-2}$  M SCN<sup>-</sup> solutions at  $\lambda = 475$  nm, ( $G\varepsilon = 5.09 \times 10^4$ ) with average doses of 3–5 Gy per 2 to 3 ns pulse.<sup>17</sup> All kinetic measurements were performed at room temperature, which varied across the range  $18 \pm 2$  °C, although individual measurements were constant to  $\pm 0.3$  °C.

Upon completion of experiments, waste samples were mixed with bleach solution to neutralize the residual CWA simulants.<sup>18</sup>

## **Results and Discussion**

The electron pulse radiolysis of water produces hydroxyl radicals, hydrated electrons, hydrogen atoms, and other species according to the stoichiometry<sup>19</sup>

H<sub>2</sub>O -/////// → 0.28<sup>•</sup>OH + 0.27 
$$e_{aq}^-$$
 + 0.06<sup>•</sup>H +  
0.05 H<sub>2</sub> + 0.07 H<sub>2</sub>O<sub>2</sub> + 0.27 H<sup>+</sup> (1)

where the numbers in this equation are the *G* values (yields) of production for each species in units of  $\mu$ mol Gy<sup>1–</sup>. Typical total radical concentrations generated were  $\sim 3-5 \,\mu$ M, thus ensuring that pseudo-first-order kinetics were always maintained.

The study of only hydroxyl radical reactions was achieved by presaturating the simulant solutions with  $N_2O$ , which quantitatively converts the produced hydrated electrons and some hydrogen atoms to hydroxyl radicals

$$e_{aq}^{-} + N_2O + (H_2O) \rightarrow N_2 + OH^{-} + {}^{\bullet}OH$$
  
 $k_2 = 9.1 \times 10^9 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$  (2)

$$H^{\bullet} + N_2 O \rightarrow N_2 + {}^{\bullet}OH \quad k_3 = 2.1 \times 10^6 M^{-1} s^{-1}$$
(3)

However, the reaction of hydroxyl radicals with our CWA simulants did not generate any significant intermediate species absorption in the range of 250-800 nm. Therefore, the hydroxyl radical reaction rate constant for all species of this study was determined using SCN<sup>-</sup> competition kinetics, based on the competing reactions

$$^{\circ}OH + (EtO)_{2}P(O) - X \rightarrow products$$
 (4)

$$OH + SCN^{-}(+SCN^{-}) \rightarrow OH^{-} + (SCN)_{2}^{\bullet-}$$
(5)

and monitoring the  $(SCN)_2^{\bullet-}$  absorption at 475 nm. This hydroxyl radical competition can be analyzed to give the following analytical expression

$$\frac{\text{Abs(SCN)}_{2}^{\bullet-\circ}}{\text{Abs(SCN)}_{2}^{\bullet-}} = 1 + \frac{k_4[(\text{EtO})_2 \text{P(O)-X}]}{k_5[\text{SCN}^-]}$$
(6)

where  $Abs(SCN)_2^{\bullet-o}$  is the maximum absorbance of the  $(SCN)_2^{-}$  transient measured for only the blank  $SCN^{-}$  solution, and  $Abs(SCN)_2^{-}$  is the reduced yield of this transient when  $(EtO)_2P(O)$ -X was added. Typical data are shown in Figure 2a. A plot of  $Abs(SCN)_2^{\bullet-o}/Abs(SCN)_2^{\bullet-}$  against the ratio [ $(EtO)_2P(O)$ -X]/[ $SCN^{-}$ ] gives a straight line of slope  $k_4/k_5$  and based on the established rate constant for hydroxyl radical reaction with  $SCN^{-}$ ,  $k_5 = 1.05 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>19</sup> the  $k_4$  rate constant can then readily be calculated. (See Figure 2b.) The simulant oxidation rate constants obtained are summarized in Table 1 and shown in a Brönsted plot in Figure 3a.

The Brönsted plot shows a distinct break in the leaving group dependence, clearly indicating a change in mechanism between the simulants with good and poor leaving groups. These new data show excellent consistency with previous measurements.<sup>8</sup> In addition, the new data for simulants with leaving group  $pK_a$ values in the range of 12-16 show no rate constant variation and are in very good agreement with the higher  $pK_a$  values previously measured. This is not a surprise because the net atomic charge on phosphorus will be greater in those compounds with deactivating groups (1-4), which will favor the initial reaction of the hydroxyl radical directly at the phosphorus atom. Alternatively, simulants 5-8, 10-12, and 14 have less atomic charge on the P atom, which would promote the initial oxidation to be a hydrogen atom abstraction from the methylene carbon to produce a carbon-centered radical. Verification of this mechanism has been established by study of the deuterated analog 9, of triethylphosphate (8) that resulted in a primary kinetic isotope effect of  $k_{\rm H}/k_{\rm D} = 3.06$ . These data confirmed the hydrogen-atom abstraction by the hydroxyl radical at the methylene carbon consistent with the proposed change in mechanism.

**Hydrated Electron Reaction.** The hydrated electron rate constant with these simulants was determined by directly following its near-infrared absorption at 700 nm.<sup>20</sup> These values



**Figure 2.** (a) Measured  $(SCN)_2^{-1}$  absorbance at 475 nm in N<sub>2</sub>Osaturated 136.1  $\mu$ M KSCN with 0 ( $\Box$ ), 264 ( $\bigcirc$ ), and 728 ( $\triangle$ )  $\mu$ M (EtO)<sub>3</sub>P=O at 19 °C and natural pH. (b) Transformed competition kinetics plot for this compound using maximum absorbance intensities of part a. Line corresponds to weighted linear fit, with: slope = 0.0686  $\pm$  0.0035, intercept = 1.001  $\pm$  0.014,  $R^2$  = 1.000, corresponding to reaction rate constant of 7.19 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>.



**Figure 3.** Brönsted plot for reaction of CWA simulants with (a) hydroxyl radical and (b) hydrated electron from values given in Table 1. Also shown are predicted rate constants for GA ( $\bigcirc$ ), GB ( $\bigtriangledown$ ), GD ( $\diamondsuit$ ), and VX ( $\triangle$ ) reaction with both radicals.

were determined by fitting exponential decays to the pseudofirst-order kinetics of this species in pulse-electron irradiated, nitrogen-saturated, solutions at natural pH. (See Figure 4a.) These solutions also contained 0.10 M methanol to scavenge the hydroxyl radicals and hydrogen atoms, converting them into relatively inert methanol radicals.<sup>19</sup> The pseudo-first-order rate constants were plotted against the simulant concentrations (Figure 4b), and from these kinetic data (Table 1), it is evident that simulants that more precisely resemble CW agents in their structure have reduction rate constants 20–40 times faster than those for their oxidation. This suggests that treatments that generate both oxidizing and reducing species in water, for example, heterogeneous catalysis by TiO<sub>2</sub>, sonolysis, or the electron beam irradiation processes, would be the most efficient approach for the destruction of these types of agents.<sup>21</sup>



**Figure 4.** (a) Pseudo-first-order decay kinetics of hydrated electron at 700 nm and natural pH in the presence of 25.0 ( $\Box$ ), 51.6 ( $\bigcirc$ ), 80.2 ( $\triangle$ ), and 144.7 ( $\nabla$ )  $\mu$ M (EtO)<sub>2</sub>P(O)OAc. Solid lines correspond to fitted exponential decays. (b) Second-order rate constant determination for (EtO)<sub>2</sub>P(O)OAc. Solid line corresponds to rate constant of  $k = 1.10 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .

The Brönsted plot for the series of CW simulants reacting with the hydrated electron is presented in Figure 3b. This plot highlights the previous excellent linearity for the majority of our simulants over the entire range of leaving group  $pK_a$  values. The linearity suggests a single mechanism for reaction of the hydrated electron with all simulant compounds. This mechanism appears to be consistent with initial electron capture at phosphorus, followed by loss of a leaving group. The measured rate constants are faster for compounds 1-4, which have good leaving groups in water, where it is reasonable that the reduced X<sup>-</sup> is released into solution. However, compounds with poor leaving groups (5-8, 10-12, and 14) undergo much slower reduction, and by analogy to the loss of hydrogen atoms from the reaction of hydrated electrons with phosphate ( $H_2PO_4^-$ , k =  $1.5 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup>) may instead be eliminating radical fragments (X<sup> $\cdot$ </sup>, C<sub>2</sub>H<sub>5</sub><sup> $\cdot$ </sup>).<sup>22</sup> Again, the mechanism is consistent with data from primary kinetic isotope effect measurements between the non deuterated species 12 and its deuterated analogue 13  $(k_{\rm H}/k_{\rm D} = 3.17)$ . In addition, compounds 14 and 15 show a secondary isotope effect  $(k_{\rm H}/k_{\rm D} \approx 2.2)$  again confirming the capture of the electron at the phosphorus atom.

Also, transient spectral data obtained for the reduction of simulant **1** showed the loss of the absorption for the hydrated electron (700 nm) directly correlated with the growth of a new transient at 340 nm. This new transient is attributed to the phosphinoyl radical, formed by the loss of chloride; however, it is not clear which of the two tautomeric structures is responsible for the absorption.<sup>23</sup>

Three simulant reduction measurements were found to deviate from the overall linearity shown in Figure 3b. The fluoridesubstituted simulant reaction rate constant was slower than expected; however, our measured value can only be considered a lower limit because of the slight material loss observed as vapor upon the injection of this simulant. However, compound 7, the diethyl phosphonic acid, showed a significantly higher than expected rate constant, on the same order of magnitude as the diethyl chlorophosphate (1). At neutral pH, the phosphonic acid will be ionized ( $pK_a = 1.42$ ), and it is unlikely that a charged oxygen atom ( $O^{2-*}$ ) would act as a leaving group in

**TABLE 3: Estimated Rate Constants for the Reaction of** CWAs in Water Based on Brönsted Plot values of this Study (See Figure 3)

CW agent <sup>a</sup>	leaving group	$\sim pK_a^{\ b}$	$k(e^{-}) M^{-1} s^{-1}$	$k(\text{HO}\bullet) \text{ M}^{-1} \text{ s}^{-1}$
Tabun, GA	CN	9.2	$3.6 \times 10^{9}$	$8.0 \times 10^{7}$
Sarin, GB	F	3.2	$6.8 \times 10^{9}$	$8.8 \times 10^{8}$
Soman, GD	F	3.2	$6.8 \times 10^{9}$	$8.8 \times 10^{8}$
VX	$S(CH_2)_2N(iPr)_2$	10.6 <sup>c</sup>	$3.2 \times 10^{9}$	$8.8 \times 10^{8}$

<sup>a</sup> Complete structures shown in Figure 1. <sup>b</sup> March, J.; Smith, M. B. Advanced Organic Chemistry; Wiley: New York, 2001; pp 329-331. pK<sub>a</sub> values represent the ionization of H-X in water. <sup>c</sup> Value for CH<sub>3</sub>CH<sub>2</sub>SH. Silva, C. O.; da Silva, E. C.; Nascimento, M. A. C. J. Phys. Chem. A 2000, 104, 2402.

water. Therefore, we believe that the dominant operating mechanism for this compound is direct electron capture to form a phosphoranyl radical. We posit that this fast rate constant is due to enhanced resonance stabilization available within the delocalized  $\pi$ -system of the phosphoryl anion, which assists the radical formation occurring at the phosphorus atom. The direct electron capture at phosphorus has been shown by electron spin resonance to produce these phosphoranyl radicals.<sup>24</sup>

However, because of its low  $pK_a$  values, we could not directly determine the rate constant for the nonionized form of the diethyl phosphonic acid (7) with the hydrated electron. Therefore, to gain further insight into this particular reduction process, reaction rate constants for the analogous species methylphosphonic acid (16) were determined with the hydrated electron at pH 5.08 and 10.02 (Table 2). The rate constant of  $k = (1.22 \pm 0.04) \times$  $10^{10}\ M^{-1}\ s^{-1}$  determined at pH 5.08 for the monoionized form of 16 is similar to the value obtained for the diethyl phosphonic acid of  $k = (1.88 \pm 0.04) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , indicating a consistent reaction mechanism. Moreover, at pH 10.02, the reaction rate constant for the doubly ionized methylphosphonic acid with the hydrated electron is only an order of magnitude slower (k = $(1.62 \pm 0.12) \times 10^9 \,\mathrm{M^{-1} \, s^{-1}})$ , a difference that can be attributed to ionic strength effects. These rate constants are all significantly faster than that reported for the dissociative reduction occurring for HPO<sub>4</sub><sup>2-</sup> over the pH range of 9–12.3 ( $k = 1.4 \times 10^5 \text{ M}^{-1}$  $s^{-1}$ ).<sup>19</sup> This indicates that the same reaction mechanism is occurring for both the mono- and di-ionized species.

On the basis of our data in our Brönsted plots, we can readily extrapolate hydrated electron and hydroxyl radical rate constants for actual CW agents in water based on the  $pK_a$  values for their leaving groups. These rate constant values are given in Table 3 and are also indicated in Figure 3a,b.

## Conclusions

The reaction of chemical simulants containing leaving groups that mimic those in actual agents are better representatives for the development of methods for the detection, decontamination, and destruction of CW agents. The predicted rate constants for the true CW agents demonstrate that reductive-based radical destruction would be more efficient than oxidative species. The kinetic evidence also suggests that alkyl phosphonates such as diethyl methylphosphonate, although easy to handle, may undergo different oxidation and reduction chemistry. Therefore, caution should be exercised when suggesting that these latter, nontoxic, compounds are automatically reasonable models for chemical warfare agents.

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