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AQUEOUS PHASE KINETIC STUDIES INVOLVING INTERMEDIATES OF ENVIRONMENTAL INTEREST: PHOSPHATE RADICALS AND THEIR REACTIONS WITH SUBSTITUTED BENZENES

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ABSTRACT

This manuscript describes our research work devoted to the understanding of the aqueous phase reactions of phosphate and polyphosphate radicals. Inorganic phosphate and polyphosphate radicals were generated after photolysis of peroxodiphosphate, tripolyphosphate and pyrophosphate ions. The reactions of $SO_4^{\bullet-}$ radicals with $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$ are also discussed.

The logarithm of the bimolecular rate constants for the reactions of the three phosphate radicals ($H_2PO_4^{\bullet}$, $HPO_4^{\bullet-}$, $PO_4^{\bullet 2-}$) with substituted benzenes are discussed in terms of Hammett correlations and a reaction mechanism is proposed. Phenoxyl type radical formation from the reactions of $H_2PO_4^{\bullet}$ and $HPO_4^{\bullet-}$ radicals with phenol, chlorobenzene, and α, α, α-trifluorotoluene (TFT) supports the contribution of an addition pathway yielding a phosphate adduct with the substituted benzene. Additional information on the absorption spectra and decay kinetics of the hydroxycyclohexadienyl radicals of chlorobenzene and TFT is also given.

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INTRODUCTION

Numerous constituents of natural and atmospheric waters contribute to the photochemical and/or thermal production of highly reactive species, such as $HO^{\bullet}$, $HO_2^{\bullet}/\ O_2^{\bullet-}$, $O_2\ (^1\Delta_g)$, $CO_3^{\bullet-}$, $SO_4^{\bullet-}$, organic peroxyl radicals, *etc.* [1,2]. Most of these species are able to initiate chemical (chain) reactions in which undesirable organic components are attacked and ultimately destroyed, thus providing a mechanism for self-cleansing of the water sources. $HO^{\bullet}$ and/or $SO_4^{\bullet-}$radicals are among the most reactive and highly oxidative species, and their photochemical generation is being tested as a promising benign method for detoxification of polluted water streams [3].

The presence of inorganic components in the aqueous matrix is of importance to the chemistry related with these reactive species, *i.e.*, as $HO^{\bullet}$ and/or $SO_4^{\bullet-}$ radicals are able to oxidize most inorganic anions to secondary, less reactive, radicals which might have unexpected consequences in the overall chemical process. In particular, the reaction of $HO^{\bullet}$ and $SO_4^{\bullet-}$ radicals with phosphate ions, reactions R1 and R2, yields phosphate radicals ($H_2PO_4^{\bullet}$, $HPO_4^{\bullet-}$, $PO_4^{\bullet 2-}$) [4,5] and that of $HO^{\bullet}$ with pyrophosphate, reaction R3, yields polyphosphate radicals ($P_2O_7^{\bullet 3-}$) [6].

$$\begin{array}{llllll}
HO^{\bullet} & + & H_3PO_4 & \rightarrow & H_2PO_4^{\bullet} + H_2O & k_{1a} = 2{\cdot}6 \times 10^6\ M^{-1}s^{-1}\quad (R1) \\
 & + & H_2PO_4^{-} & \rightarrow & H_2PO_4^{\bullet}/\ HPO_4^{\bullet-} + HO^{-}/H_2O & k_{1b} = 2{\cdot}2 \times 10^6\ M^{-1}s^{-1} \\
 & + & HPO_4^{2-} & \rightarrow & HPO_4^{\bullet-}/\ PO_4^{\bullet 2-} + HO^{-}/H_2O & k_{1c} = 8 \times 10^5\ M^{-1}s^{-1} \\
SO_4^{\bullet-} & + & HPO_4^{2-} & \rightarrow & HPO_4^{\bullet-} + SO_4^{2-} & k_2 = 1{\cdot}2 \times 10^6\ M^{-1}s^{-1}\quad (R2) \\
HO^{\bullet} & + & P_2O_7^{4-} & \rightarrow & P_2O_7^{\bullet 3-} + HO^{-} & k_3 = 9 \times 10^5\ M^{-1}s^{-1}\quad (R3)
\end{array}$$

Phosphate radicals, which exist in three acid-base forms related by fast equilibria [7], reactions R4, abstract hydrogen from saturated organic compounds, add to olefins and oxidize many organic and inorganic compounds [4,5,8–10], and thus may also initiate chain reactions with organic substrates contained in waste-waters.

$$H_2PO_4^{\bullet} \quad \underset{pK_a\,=\,5{\cdot}7}{\overset{-\,H^+}{\rightleftarrows}} \quad HPO_4^{\bullet-} \quad \underset{pK_a\,=\,8{\cdot}9}{\overset{-\,H^+}{\rightleftarrows}} \quad PO_4^{\bullet 2-} \qquad (R4)$$

As a consequence of the widespread use of phosphates as fertilizers (85–90%) and synthetic detergents, agricultural, domestic and sewage waste-waters usually contain considerable amounts of phosphate ions [11]. The recognized environmental impact of phosphates is caused by the presence of simultaneous unduly high concentrations of nitrates and phosphates, which encourage the excessive growth of algae inducing a severe oxygen depletion in the waters. In addition, anthropogenic and natural generation of sulfate and/ or hydroxyl radicals in phosphate-containing waste-waters may give rise to the formation of phosphate radicals, whose effect and participation in the chemistry of our environment needs being evaluated.

The knowledge of the reaction mechanisms involved in phosphate and polyphosphate radicals – initiated oxidation of organic pollutants is of importance for the understanding of the chemistry of our environment and for the optimization of advanced technologies for waste-waters treatment. Here we report our results on the studies of the chemistry of phosphate and polyphosphate radicals, and on the reactivity of phosphate radicals with substituted benzenes.

REACTIONS OF PHOSPHATE RADICALS IN AQUEOUS SOLUTIONS.

Early studies on the decay kinetics of phosphate radicals [6] used VUV photolysis of HPO_4^{2-} and $H_2PO_4^{-}$ for their generation, as shown in reaction R5. A more efficient procedure for phosphate radical generation involves the UV photolysis of peroxodiphosphate ions, reaction R6 [8–10].

$$HPO_4^{2-} \quad + \quad h\nu\ (\lambda_{exc} < 200\ \text{nm}) \quad \rightarrow \quad HPO_4^{\bullet-} \quad + \quad e_{aq}^{-} \tag{R5}$$

$$P_2O_8^{4-} \quad + \quad h\nu\ (\lambda_{exc} > 200\ \text{nm}) \quad \rightarrow \quad 2\ PO_4^{\bullet 2-} \tag{R6}$$

Photolysis of peroxodiphosphate under controlled pH conditions, *i.e.*, pH = 4, 7 or 10, is a convenient procedure for the study of the reactions of each of the $H_2PO_4^{\bullet}$, $HPO_4^{\bullet-}$ and $PO_4^{\bullet 2-}$ radicals and was used throughout our investigations. All forms of these radicals exhibit moderate absorptions in the 500 nm range, with only slight differences. Figure 1 shows the absorption spectrum of $PO_4^{\bullet 2-}$. The decay kinetics of phosphate radicals are determined in most cases by following the decay of their broad absorptions in the 400–500 nm range.

The decay kinetics of the three acid-base forms of the phosphate radicals was observed [8], to be independent on the presence of dissolved molecular oxygen. Bimolecular recombination, with decay rate constants $(2k_{BR}\ /\epsilon_{500\ nm})$ =

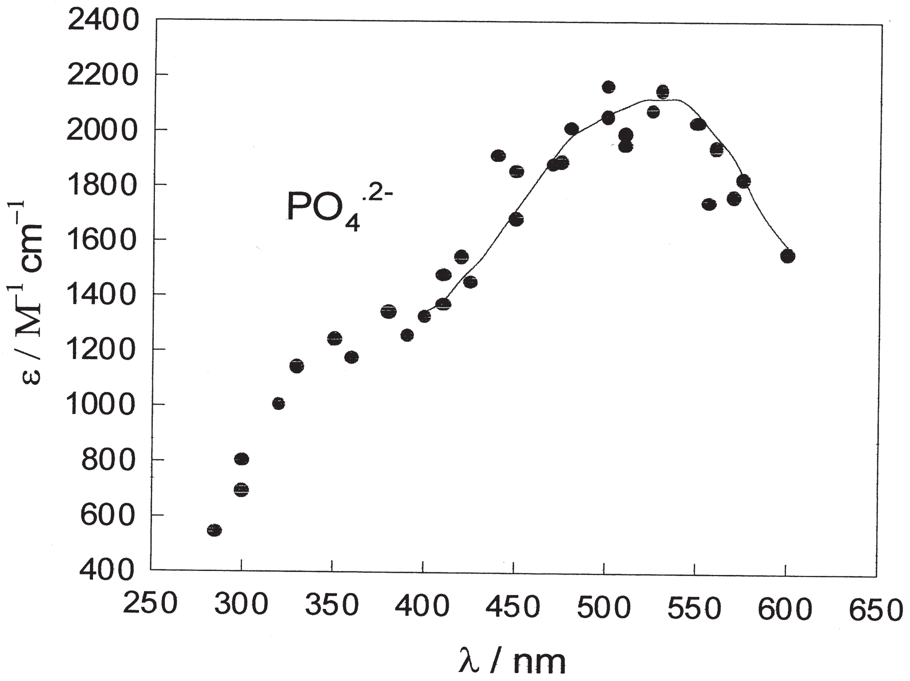


Figure 1 $PO_4^{\bullet 2-}$ absorption spectrum [8] ($\epsilon_{530\ nm}$ = 2150 M^{-1} cm^{-1} [7]). The solid line shows the spectrum reported in [7].

1·3 × 10^5 and 2·8 × 10^5 cm s^{-1} [6,8], is the main process observed for $HPO_4^{\bullet -}$ and $PO_4^{\bullet 2-}$ radical ions, respectively

$H_2PO_4^{\bullet}$ decay kinetics shows the contribution of a mixed second (2 k_{BR}/ $\epsilon_{500\ nm}$ = 1 × 10^6 s^{-1} cm) and first order decay law (k = 5 × 10^3 s^{-1}). The first order decay component was suggested to be due to the reaction of $H_2PO_4^{\bullet}$ with $P_2O_8^{4-}$, similar to that reported for $SO_4^{\bullet -}$ with $S_2O_8^{2-}$ [**12**]. An upper limit of 10^6 $M^{-1}s^{-1}$ is derived for the rate constant of this reaction, though the participation of a reaction between H_2O and $H_2PO_4^{\bullet}$, similar to that reported for sulfate radicals [4,12] should not be neglected [13] (*vide infra*).

Previous literature studies report a first-order decay kinetics for $H_2PO_4^{\bullet}$ and $HPO_4^{\bullet -}$ in the presence of molecular oxygen [6] which was assumed to be due to the formation of $H_2PO_4^{\bullet}$ and $HPO_4^{\bullet -}$ oxygen adducts. Our results, showing oxygen-independent decays either in the presence or absence of organic substrates, do not support the existence of such oxygen adducts. The main difference between the VUV experiments reported in the literature [**6**] and ours, is that in the former case, high concentrations of $HO_2^{\bullet}$/ $O_2^{\bullet -}$ were formed from the reaction of molecular oxygen with hydrated electrons, whereas no detectable amounts of these radicals are generated in our studies. As $HO_2^\bullet/\,O_2^{\bullet-}$ are reported to efficiently reduce $P_2O_8^{4-}$ propagating a chain reaction [7], these radicals can then be expected to affect the overall formation and decay of phosphate radicals in the VUV photolysis experiments.

Continuous photolysis experiments of peroxodiphosphate solutions yield important information on the first order decay processes of phosphate radicals since the very low steady-state concentration of transients achieved in these experiments do not favor radical recombination. In fact, photo-decomposition of peroxodiphosphate under such conditions oxidizes water to molecular oxygen [13], reaction R7. Molecular oxygen can only be formed if phosphate radicals react with water (reaction R8) followed by a complex mechanism involving hydrogen peroxide formation and decomposition (reactions R9 and R10).

$$2\,P_2O_8^{4-} + 2\,H_2O \xrightarrow{h\nu} O_2 + 4\,HPO_4^{-} \qquad (R7)$$

$$PO_4^{\bullet 2-} + H_2O/\,HO^{-} \rightarrow HPO_4^{2-}/\,PO_4^{3-} + HO^{\bullet} \qquad (R8)$$

$$2\,HO^{\bullet} \rightarrow H_2O_2 \qquad (R9)$$

$$2\,H_2O_2 \rightarrow O_2 + 2\,H_2O \qquad (R10)$$

Our continuous irradiation experiments of initially air-saturated $K_4P_2O_8$ solutions show a pH-independent increase in the concentration of dissolved O_2 with the irradiation time, which was about five times lower than the concentration of photo-decomposed $K_4P_2O_8$. Deviations from the 2:1 stoichiometry expected from reaction R7, may be explained by the efficient reactions of hydrogen peroxide with the phosphate radicals [**4**] yielding $HO_2^\bullet/\,O_2^{\bullet-}$ which further react with $P_2O_8^{4-}$ [7]. Moreover, the reaction between phosphate radicals and $P_2O_8^{4-}$ with formation of $P_2O_8^{3\bullet-}$ (*vide supra*) may also contribute to an increased $P_2O_8^{4-}$ depletion.

REACTIONS OF POLYPHOSPHATE RADICALS IN AQUEOUS SOLUTIONS

Photolysis of pyrophosphate ions, reaction R11, in aqueous solution yields reactive solvated electrons and phosphorus-containing radicals as the primary photochemical reactions [14]. In air and oxygen-saturated solutions, the detached electrons are efficiently scavenged by molecular oxygen yielding $O_2^{\bullet-}$, reaction R12. Electron detachment after photolysis of $P_2O_7^{4-}$ is supported by the formation of equimolar concentrations of $P_2O_7^{\bullet 3-}$ and $O_2^{\bullet-}$ [14].

$$P_2O_7^{4-} \quad + \quad h\nu \quad \rightarrow \quad P_2O_7^{\bullet 3-} \quad + \quad e^{-}_{aq} \qquad \text{(R11)}$$

$$e^{-}_{aq} \quad + \quad O_2 \quad \rightarrow \quad O_2^{\bullet-} \qquad \text{(R12)}$$

Photoelectron detachment from $P_3O_{10}^{5-}$ (quantum yield lower than 0·1 at 266 nm) yielding a tripolyphosphate radical ion, $P_3O_{10}^{\bullet 4-}$, and hydrated electrons, reaction R13, is supported by the formation of $O_2^{\bullet-}$ in experiments in the presence of dissolved molecular oxygen [**14**]. However, formation of $P_3O_{10}^{\bullet 4-}$ after photolysis of $P_3O_{10}^{5-}$ should involve a complex mechanism, since $P_2O_7^{\bullet 3-}$ is the main phosphorus-containing transient detected. A fast decomposition of $P_3O_{10}^{\bullet 4-}$ to $P_2O_7^{\bullet 3-}$ is proposed to take place within less than 100 μs, reaction R14. $P_3O_{10}^{\bullet 4-}$ recombination and reaction with water or HO^- ions may account for the lower yields of $P_2O_7^{\bullet 3-}$ radicals formed with respect to those of $O_2^{\bullet-}$.

$$P_3O_{10}^{5-} \quad + \quad h\nu \quad \rightarrow \quad P_3O_{10}^{\bullet 4-} \quad + \quad e^{-}_{aq} \qquad \text{(R13)}$$

$$P_3O_{10}^{\bullet 4-} \quad \xrightarrow{\text{fast}} \quad P_2O_7^{\bullet 3-} \quad + \quad PO_3^{-} \qquad \text{(R14)}$$

The oxygen-independent decay of $P_2O_7^{\bullet 3-}$,observed after photolysis of both $P_3O_{10}^{5-}$ and $P_2O_7^{4-}$ ions, followed a mixed first and second order kinetics ($2k/\epsilon_{580nm} = (2.8 \pm 0.5) \times 10^5$ cm s^{-1}). The first order decay component is independent of the concentration of $P_3O_{10}^{5-}$ or $P_2O_7^{4-}$ and increases with increasing concentration of HO^- ions in the solution [**14**], thus indicating the occurrence of a reaction between $P_2O_7^{\bullet 3-}$ radicals and HO^- ions, reaction R15 with $k_{15} = (1.4 \pm 0.3) \times 10^6$ M^{-1}s^{-1}. No contribution of a reaction of $P_2O_7^{\bullet 3-}$ radicals with H_2O was observed.

$$P_2O_7^{\bullet 3-} \quad + \quad HO^- \quad \rightarrow \quad P_2O_7^{4-} \quad + \quad HO^{\bullet} \qquad \text{(R15)}$$

Formation of hydroxyl ions from reaction R15 was verified by experiments with air-saturated $P_3O_{10}^{5-}$ and $P_2O_7^{4-}$ solutions of pH > 12·5, which showed absorption of $O_3^{\bullet-}$ from the reversible reaction of the conjugate base of $HO^{\bullet}$, $O^{\bullet-}$, with molecular oxygen. In alkaline solutions of pH ≅ 10, $HO^{\bullet}$ radicals may decay by reaction with $P_2O_7^{4-}$ or $P_3O_{10}^{5-}$, reaction R16 [**5**], with $O_2^{\bullet-}$ and by bimolecular recombination [**15**].

$$P_2O_7^{4-} / P_3O_{10}^{5-} \quad + \quad OH^{\bullet} \quad \rightarrow \quad P_2O_7^{\bullet 3-} / P_3O_{10}^{\bullet 4-} \quad + \quad HO^{-} \qquad (R16)$$

A fast-decay component of $O_2^{\bullet-}$ is assigned to its reaction with $P_2O_7^{\bullet 3-}$, reaction R17, and / or with $HO^{\bullet}$ radicals [**5**].

$$P_2O_7^{\bullet 3-} \quad + \quad O_2^{\bullet-} \quad \rightarrow \quad P_2O_7^{4-} \quad + \quad O_2 \qquad (R17)$$

Reaction R17 and the recombination of $O_2^{\bullet-}$/ $HO_2^{\bullet}$ radicals are the main reaction channels leading to the formation of molecular oxygen in steady-state photolysis experiments with $P_3O_{10}^{5-}$ solutions of pH ≅ 10.

Reaction of $P_3O_{10}^{5-}$ and $P_2O_7^{4-}$ with sulfate radicals

The bimolecular rate constants for the reaction of $SO_4^{\bullet-}$ radicals with $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$ obtained from photolysis experiments of alkaline (pH = 10) air-saturated $S_2O_8^{=}$ solutions in the presence $P_3O_{10}^{5-}$ or $P_2O_7^{4-}$ are $(1{\cdot}4 \pm 0{\cdot}2) \times 10^5\ M^{-1}s^{-1}$ and $(3{\cdot}4 \pm 0{\cdot}5) \times 10^6\ M^{-1}s^{-1}$, respectively. Formation of $P_2O_7^{\bullet 3-}$ radicals after reaction of sulfate radicals with $P_2O_7^{4-}$ anions suggests that the reaction takes place by a one-electron charge transfer process, reaction R18, as reported for the reactions of $SO_4^{\bullet-}$ radicals with inorganic ions [4]. A similar process may be expected for the reaction of $SO_4^{\bullet-}$ with $P_3O_{10}^{5-}$ ions, reaction R19. However, $P_2O_7^{\bullet 3-}$ radicals are the only radicals detected following reaction R19. A charge transfer reaction yielding $P_3O_{10}^{\bullet 4-}$ radicals followed by their fast decomposition to $P_2O_7^{\bullet 3-}$ and phosphate ions, reaction R14, as also proposed for the photolysis of $P_3O_{10}^{5-}$ (*vide supra*), may account for the formation of $P_2O_7^{\bullet 3-}$.

$$SO_4^{\bullet-} \quad + \quad P_2O_7^{4-} \quad \rightarrow \quad SO_4^{2-} \quad + \quad P_2O_7^{\bullet 3-} \qquad (R18)$$

$$SO_4^{\bullet-} \quad + \quad P_3O_{10}^{5-} \quad \rightarrow \quad SO_4^{2-} \quad + \quad P_3O_{10}^{\bullet 4-} \qquad (R19)$$

For pyrophosphate ions, reaction R15 is the reverse of reaction R16. If both reactions take place by a charge transfer process, the equilibrium constant for reaction R20, $K_{20} = k_{16} / k_{15} = 0{\cdot}16\text{–} 0{\cdot}64$ is estimated taking $k_{16} = (2{\cdot}2\text{–}9) \times 10^5\ M^{-1}s^{-1}$ [**5**]. As the calculated ΔG for equilibrium R20 is very small, the one electron redox potential of $HO^{\bullet}$ and $P_2O_7^{\bullet 3-}$ should be very similar, *i.e.*, of the order of 1·9V vs. standard hydrogen electrode [16]. However, hydroxyl radicals are known to efficiently react with inorganic ions by an addition and fast elimination of HO^- ions mechanism, as with chloride ions [17]. If this were also the case for the reaction with $P_2O_7^{4-}$ ions, the estimation of K_{20} is not valid.

$$P_2O_7^{4-} \quad + \quad HO^{\bullet} \quad \rightleftarrows \quad P_2O_7^{\bullet 3-} \quad + \quad HO^- \qquad \text{(R20)}$$

On the other hand, the low rate constants obtained for the charge transfer reactions R18 and R19, could indicate that the one-electron reduction potential for the $P_2O_7^{\bullet 3-}/ P_2O_7^{4-}$ and $P_3O_{10}^{\bullet 4-}/ P_3O_{10}^{5-}$ couples should be higher than that of the $SO_4^{\bullet -}/SO_4^{2-}$ couple (2·43 V [16]). These observations support an addition mechanism for the reaction of $HO^{\bullet}$ radicals with $P_2O_7^{4-}$.

REACTIVITY OF PHOSPHATE RADICALS WITH SUBSTITUTED BENZENES

The reactions of phosphate radicals with substituted benzenes, reactions R21, are conveniently studied following the phosphate radical decay rate as a function of added solute concentration. Photolysis experiments of $P_2O_8^{4-}$ solutions of pH = 4·0, 7·1 and 10·0, in the presence of low concentrations of substrates ([PhX] < 10^{-4} M) showed absorption traces at λ > 400 nm, whose spectrum immediately after the flash of light agreed with those of the phosphate radicals. The absorption traces showed faster decay kinetics with increasing concentrations of the organic substrates and could be well fitted to a first order law with an apparent rate constant, k_{app}. The slopes of the linear plots of k_{app} *vs* solute concentration yield the bimolecular rate constants k_{21} [8–10]. The values of k_{21} obtained for the different aromatics and phosphate radicals are shown in Table 1. For comparison, bimolecular rate constants for the reactions of $SO_4^{\bullet -}$ and $HO^{\bullet}$ radicals are also included.

$$\begin{pmatrix} H_2PO_4^{\bullet} \\ HPO_4^{-} \\ PO_4^{\bullet 2-} \end{pmatrix} \quad + \quad PhX \quad \rightarrow \quad \begin{pmatrix} H_2PO_4^{-} \\ HPO_4^{2-} \\ PO_4^{3-} \end{pmatrix} \quad + \quad \text{organic radicals} \qquad \text{R21}$$

Table 1 Bimolecular rate constants ($M^{-1}\ s^{-1}$) for the reaction of several radicals with aromatic substrates

	$HO^{\bullet}$ (*a*)	**$SO_4^{\bullet-}$** (*b*)	**$H_2PO_4^{\bullet}$** (*c*)	**$HPO_4^{\bullet-}$** (*d*)	**$PO_4^{\bullet 2-}$** (*c*)
Aniline	1.5×10^{10}		1.0×10^{10} (*e*)	1.5×10^{9} (*e*)	7.1×10^{8} (*e*)
Phenol	1.4×10^{10}	2.2×10^{9} (*f*)		5.3×10^{8}	
Anisole	5.4×10^{9}	4.9×10^{9}		4.6×10^{7}	
Benzyl alcohol	8.4×10^{9}		1.0×10^{9}	1.3×10^{8}	8.3×10^{7}
tert-Butylbenzene				1×10^{8}	
Toluene	2.1×10^{9}	1.3×10^{9}	5.2×10^{8}	1.4×10^{7}	1.4×10^{7}
Fluorobenzene	5.7×10^{9}	9.8×10^{8}		7×10^{6}	
Benzene	7.8×10^{9}	3.0×10^{9}	8.9×10^{7}	1.7×10^{7}	4.3×10^{6}
Chlorobenzene	5.6×10^{9}	1.5×10^{9}		6.9×10^{6}	
Iodobenzene	5.6×10^{9}	9×10^{8} (*f*)		1.2×10^{7}	
Bromobenzene	7.4×10^{9}	1.8×10^{9}		4×10^{6}	
Benzoic acid	1.8×10^{9}	5.4×10^{8} (*f*)	2.4×10^{8}		
Benzonitrile	3.9×10^{9}	1.2×10^{8}		6.5×10^{6}	
α, α, α-Trifluorotoluene	1.1×10^{9} (*g*)	2.0×10^{7} (*h*)	3.4×10^{7} (*h*)	2.7×10^{6} (*h*)	9×10^{5} (*h*)
p-xylene	1.8×10^{9}	2.7×10^{9}	8.8×10^{8}	3.8×10^{7}	4.6×10^{7}

(*a*) Ref. **5** and **38**. (*b*) Ref. **4** and **38**, otherwise indicated. (*c*) Ref. **8**, otherwise indicated. (*d*) Ref. **8** and **9**, otherwise indicated. (*e*) Ref. **38**. (*f*) Ref. **20**. (*g*) Ref. **39**. (*h*) Ref. **10**.

For all the substrates, phosphate radicals are much less reactive than $HO^{\bullet}$ radicals though they show much higher selectivity. $H_2PO_4^{\bullet}$ is slightly less reactive than $SO_4^{\bullet-}$ radical ions but the other phosphate radical species are much less reactive. The general tendency in reactivity observed is $HO^{\bullet} > SO_4^{\bullet-} \geq H_2PO_4^{\bullet} > HPO_4^{\bullet-} > PO_4^{\bullet 2-}$. The latter trend is not, necessarily, that of their one electron oxidizing capabilities, as is the case of the $HO^{\bullet}$ radical (2·3 V *vs* NHE in neutral solutions), which is a weaker oxidant than $SO_4^{\bullet-}$ radical (2·5 to 3·1 V *vs* NHE), but much more reactive in addition and hydrogen abstraction reactions. Consequently, reported reduction potential tendencies $E(SO_4^{\bullet-}) > E(H_2PO_4^{\bullet}) > E(HPO_4^{\bullet-}) > E(PO_4^{\bullet 2-})$, based on the relative reactivity of the radicals towards inorganic and organic substrates [**7**] should be reviewed considering the possibility that phosphate radicals may undergo addition reactions followed by fast elimination of phosphate (*vide infra*).

The effect of the substituents can be quantitatively represented in a Hammett type plot [8,18,19] of log k_{21} *vs* σ or σ^+. The Hammett treatment using σ values is reasonably successful whether the substrates are attacked by electrophilic, nucleophilic, or free radical reagents, the important thing being that the mechanism remains the same within a given reaction series. However, in reactions in which an electron donating substituent interacts with a developing positive charge in the transition state, as may be the case for the reactions under study, σ^+ values may be a better option. As our set of substituents present considerably different electron withdrawing or donating abilities and, σ and σ^+ are not colinear [19], the better correlation found with σ^+ implies that the transition state of the radical reaction must have, either significant polar character or important resonance interaction with the substituents. Figure 2 shows the Hammett correlation of log k_{21} vs σ^+ for the three forms of phosphate radicals.

Negative values of the slopes ρ imply a reaction favored by high electron density at the reaction site [18,20], as expected from the electrophilicity of the phosphate radicals [21]. The value of $\rho^+ = -1{\cdot}7 \pm 0{\cdot}3$ for $PO_4^{\bullet 2-}$ compares well with that found for the reactions between sulfate radicals and substituted benzenes ($\rho^+ = -1{\cdot}5 \pm 0{\cdot}3$ [20] and $\rho = -2{\cdot}4$ [21]). Such values of ρ indicate that these radicals react with high selectivity with the substrates, where an important reaction channel is the electron transfer from the aromatic ring to $SO_4^{\bullet -}$, initially yielding an organic radical cation [21]. The ρ^+ values for $H_2PO_4^{\bullet}$ and $HPO_4^{\bullet -}$ radicals ($-1{\cdot}2 \pm 0{\cdot}3$ and $-1{\cdot}3 \pm 0{\cdot}3$, respectively) are between those found for the reactions involving similar aromatic substrates and $SO_4^{\bullet -}$ radicals [20,21], and those observed for additions of $HO^{\bullet}$ radicals to aromatic compounds ($\rho = -0{\cdot}5$ to $-0{\cdot}4$) [22]). Consequently, the participation of, both, electron transfer and addition mechanisms, as shown in Scheme 1 for $HPO_4^{\bullet -}$, should be expected to take place during the electrophilic attack of phosphate radicals towards monosubstituted benzenes. The participation of an addition pathway is in agreement with the reported fact that direct electron transfer is not the predominant process in the reaction of $H_2PO_4^{\bullet}$ and $HPO_4^{\bullet -}$ radicals with aromatic and aliphatic carboxylic acids [23], as no decarboxylation is observed.

Electron transfer from the aromatic ring to $PO_4^{\bullet 2-}$, $HPO_4^{\bullet -}$ or $H_2PO_4^{\bullet}$, reaction channel ***a***, yields aromatic radical cations. The latter radical ions are stabilized in acid medium, otherwise they decay to a more stable radical. Reversible hydration to hydroxycyclohexadienyl radicals (XHCHD), reaction channel ***c***, takes place when no other reaction pathway is available [7,24,25].

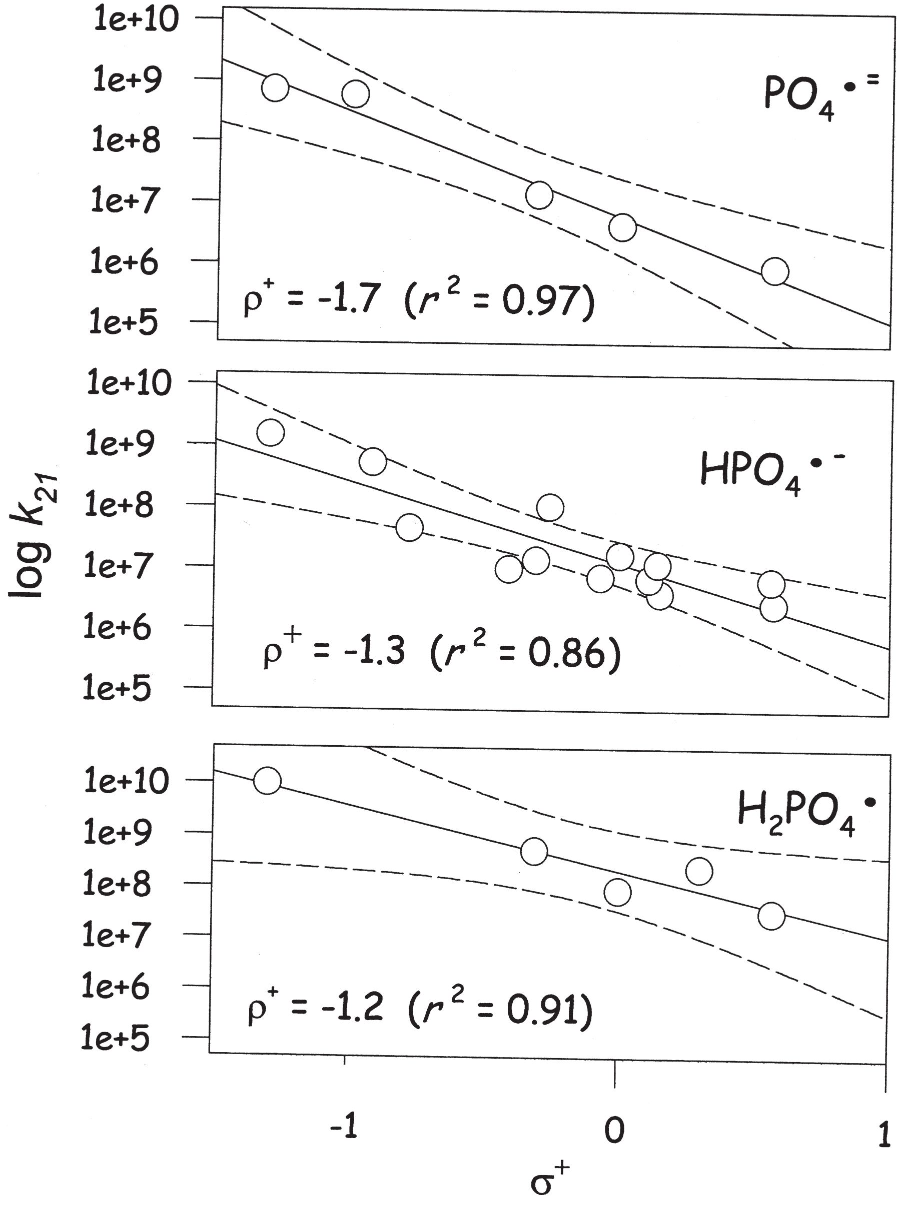
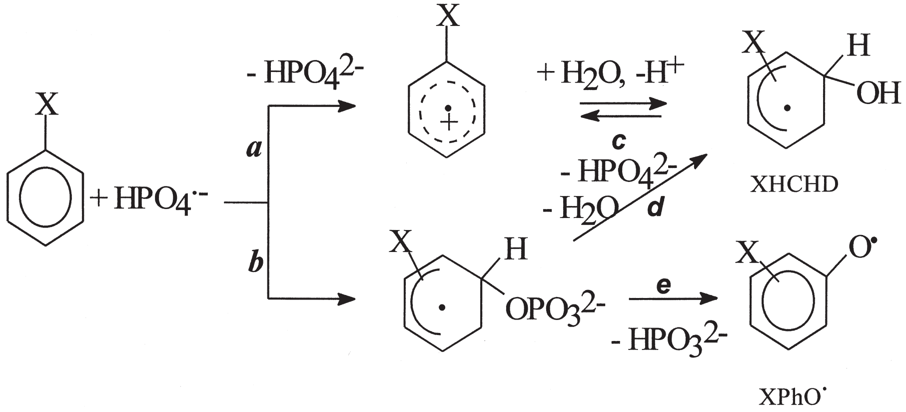


Figure 2 Plots of the logarithm of the bimolecular rate constants for the reactions of $H_2PO_4^{\bullet}$, $HPO_4^{\bullet -}$ and $PO_4^{\bullet 2-}$ radicals vs. the substituent Hammett parameter σ^+. The linear regressions and the 99% confidence intervals are also shown.



Scheme 1

An addition pathway, reaction channel ***b***, would yield a phosphate radical adduct of the aromatic substrate. Such radical adducts are expected to be unstable (as is the case of the corresponding sulfate radical adducts [26], *vide infra*) and rapidly eliminate, either phosphate ions, reaction channel ***d***, or phosphite ions, reaction channel ***e***, yielding XHCHD or phenoxyl radicals (XPhO·) , respectively.

Phosphate radicals are known to abstract H atoms from aliphatic hydrocarbons [27], thus H abstraction from side chains in the substituents may also contribute to the reaction mechanism. The observed rate constant for *tert*-butyl benzene (Table 1) is higher than that expected from the Hammett correlation, even when a 99% confidence level is considered. The contribution of an H abstraction reaction channel from the CH_3 groups in the substituent might explain the observed higher values.

Detection of the organic radicals

The proposed reaction channels may be further verified if the organic radicals formed after reaction R21 are detected and identified.

Photolysis experiments of peroxodiphosphate solutions containing almost saturated concentrations of the organic substrates, show depletion of $H_2PO_4^{\bullet}$ and $HPO_4^{\bullet -}$ radicals within less than 100 μs and the formation of transient species absorbing in the wavelength region from 250 to 450 nm due to the organic radicals formed after reaction R21. As the reactions of $PO_4^{\bullet 2-}$ radicals with the aromatics are not very efficient, the traces obtained from solutions at pH 10 show important absorbance contributions due to $PO_4^{\bullet 2-}$ radicals, thus hindering the identification of the organic radicals formed at this pH.

For comparison, XHCHD radicals of some of the substrates were generated from photolysis of hydrogen peroxide solutions containing the aromatics, as reaction between HO· radicals and most aromatic substrates yields XHCHD radicals [22,28].

The absorption maxima, the second order decay rate constants ($2k/\epsilon$) and the assignment of the organic radicals generated after reaction of $H_2PO_4^{\bullet}$, $HPO_4^{\bullet -}$ and $HO^{\bullet}$ radicals with some substituted benzenes are depicted in Table 2.

XHCHD radicals of chlorobenzene show an intense absorption maximum at 320 nm **[30]** and a second order decay kinetics, reaction R22, of the order of those reported for most XHCHD radicals [22,24,25,31–33]. In the presence of molecular oxygen but otherwise identical experimental conditions, the same transient spectrum is observed although with lower absorbance and faster decay kinetics. The latter behavior can be rationalized by a reversible reaction of ClHCHD with molecular oxygen, reaction R23, yielding hydroxyciclohexadienyl peroxyl radicals (ClPR) not absorbing at 320 nm. A careful kinetic analysis with the aid of computer simulations show that the decay of ClHCHD radicals in air and oxygen – saturated solutions is controlled by the first order decomposition of ClPR, reaction R24, with $k_{24} = 750\ \mathrm{s^{-1}}$ in agreement with the rate constants reported for many alkyl peroxyl radicals [29] and with the first order $HO_2^{\bullet}$ elimination rate from the hydroxycyclohexadienyl/ O_2 system [28].

$$\mathrm{ClHCHD} + \mathrm{ClHCHD} \xrightarrow{k_{22}} \qquad k_{22} = 2{\cdot}2 \times 10^{8}\ \mathrm{M^{-1}\,s^{-1}}\ [9,30] \quad \mathrm{(R22)}$$

$$\mathrm{ClHCHD} + \mathrm{O_2} \underset{k_{-23}}{\overset{k_{23}}{\rightleftarrows}} \mathrm{ClPR} \qquad k_{23} = 2{\cdot}6 \times 10^{8}\ \mathrm{M^{-1}\,s^{-1}},\quad k_{-23} = 5{\cdot}5 \times 10^{4}\ \mathrm{s^{-1}}\ [30] \quad \mathrm{(R23)}$$

$$\mathrm{ClPR} \xrightarrow{k_{24}} \qquad k_{24} = 750\ \mathrm{s^{-1}} \quad \mathrm{R(24)}$$

The organic transient observed after reaction of $HPO_4^{\bullet -}$ radicals with chlorobenzene shows absorption bands at 290–300nm and a less intense one at 390 nm with a ratio of the absorbance at 300 and 390 nm coincident with the ratio of $2k/\epsilon$ values at these wavelengths, thus indicating that both absorption bands

Table 2 Characterization of the organic radicals formed after reaction of phosphate and hydroxyl radicals with substituted benzenes.

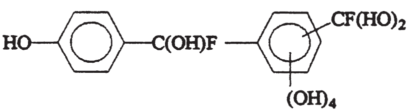
Inorganic radical	**Substrate**	**Organic radical** λ_{max}/ **nm**	**(2k/ϵ) × (cm s^{-1})**	**Assignment**	**Ref**
$HPO_4^{\bullet-}$	Chlorobenzene	290– 300 (ϵ_{300} = (5300 ± 900) M^{-1} s^{-1}) 390– 400 (ϵ_{400} = (1600 ± 200) M^{-1} s^{-1})	(4.0 ± 0.8) × 10^5 at 300 nm (1.2 ± 0.4) × 10^6 at 390 nm	$ClPhO^{\bullet}$	9
$HO^{\bullet}$	Chlorobenzene	320 ($\epsilon \approx$ 4600 M^{-1} s^{-1} (a))	(9.3 ± 1.1) × 10^5	ClHCHD (b)	9
$HPO_4^{\bullet-}$	Phenol	300 ($\epsilon \approx$ (4000 M^{-1} s^{-1}) 400 ($\epsilon \approx$ 2000 M^{-1} s^{-1})	(8.5 ± 2.0) × 10^5 (4.2 ± 1.0) × 10^5	$HPhO^{\bullet}$	9
$H_2PO_4^{\bullet}$	TFT	290–300 (intense) 400 (less intense)	(3.0 ± 1.5) × 10^5 at 300 nm (7 ± 3) × 10^4	$CF_3PhO^{\bullet}$ (c)	10
$HPO_4^{\bullet-}$	TFT	290–300 (intense) 400 (less intense)	(3.0 ± 1.5) × 10^5 at 300 nm (7 ± 3) × 10^4	$CF_3PhO^{\bullet}$ (c)	10
$HO^{\bullet}$	TFT	280–290	(6 ± 4) × 10^5 at 290 nm	$CF_3HCHD^{\bullet}$ (d)	10

(a) [30]. (b) Oxygen-dependent decay kinetics (see text). (c) The contribution of CF_3HCHD radicals cannot be neglected. (see text). (d) Oxygen-independent decay kinetics.

corresponds to the same transient species. A recombination rate constant $2k = 2 \times 10^9$ M^{-1} s^{-1} is obtained in air saturated solutions. The absorption and kinetic properties of the observed transient are very similar to those reported for phenoxyl-type radicals [31] and may thus be assigned to a phenoxyl radical of chlorobenzene.

XHCHD radicals of α,α,α -trifluorotoluene (TFT) show a band with maximum around 290–300 nm with oxygen independent decay kinetics. The oxygen-independent decay of the hydroxycyclohexadienyl radicals of TFT (CF_3HCHD) is explained by the requirement of a considerable electron-density at the carbon atom for the formation of $C{-}OO^\bullet$ bonds of peroxyl radicals. Thus, XHCHD radicals containing strong electron-attracting groups, as CN [28] or CF_3 [10] do not show formation of peroxyl radicals. A blue shift in λ_{max} with respect to other XHCHD radicals [30] is also expected for the electron withdrawing substituent CF_3.

The absorption spectrum and the oxygen independent decay kinetics of the organic transients formed after reaction of $H_2PO_4^\bullet$ and $HPO_4^{\bullet-}$ radicals with TFT (depicted in Table 2) are very similar to those reported for phenoxyl-type radicals [31] and may thus be assigned to a phenoxyl radical of TFT. However, the contribution of CF_3HCHD radicals to the band at 290 nm cannot be neglected. CF_3HCHD radical participation is further supported by the formation of the polymeric



phenolic structure as a reaction product, both, in experiments with $HO^\bullet$ and phosphate radicals. Formation of such polymeric structure may only be explained if the primary products of oxidation contain HO groups para-and/or ortho to CF_3 in the aromatic ring [10], as expected for the phenol type products formed after the bimolecular disproportionation of XHCHD radicals [34,35]. Otherwise, formation of hydroxylated open chain products of 5 or 7 C atoms, not containing fluorine in their structure, are observed as reaction products [10].

The absorption spectrum, with absorption maxima at 300 and 400 nm, and the second order decay rate $2k = (1{\cdot}7 \pm 0{\cdot}3) \times 10^9$ s^{-1} M^{-1} observed for the organic transients formed after the reaction of $HPO_4^{\bullet-}$ radicals with phenol agree with reported data for unsubstituted phenoxyl radicals [31]. Water elimination from XHCHD radicals of phenol, HOHCHD, yielding phenoxyl radicals has been reported to take place within less than 400 μs and to be catalysed by phosphate radicals [31,32]. Consequently, formation of HOHCHD radicals is a possible reaction pathway leading to phenoxyl radicals.

Formation of XHCHD (inferred, though not observed) and phenoxyl radicals further supports the reaction paths proposed in Scheme 1 for the reactions of $H_2PO_4^{\bullet}$ and $HPO_4^{\bullet-}$ radicals with substituted benzenes. Either, an electron transfer mechanism (reaction paths ***a*** and ***c***) or an addition pathway (reaction channel ***b***) followed by elimination of HPO_4^{2-} (reaction channel ***d***), can account for XHCHD generation. However, phenoxyl radical generation further stress the contribution of the addition mechanism followed by elimination of HPO_3^- from the phosphate radical adduct of the aromatic (reaction channels ***b*** and ***e***).

Elimination of HPO_4^{2-} from the phosphate radical adduct (reaction channel ***d***) is an heterolysis reaction to which the classical mechanistic solvolysis concepts may be applied [36,37]. The heterolysis of sulfate and phosphate adducts of the same aromatic substrate differ with respect to their leaving groups. If the Brønsted catalysis law is applicable and α is assumed to be 0·5, the difference between the pK_a values of the conjugate acids, HSO_4^- ($pK_a = 1{\cdot}9$) and $H_2PO_4^-$ ($pK_a = 7{\cdot}2$) translates into an heterolysis rate ratio of $10^{2{\cdot}65}$ in favor of sulfate elimination. As the lifetime of $HSO_4^{\bullet-}$ adducts is reported to be shorter than 10 ns [26,30], a lifetime shorter than 10 μs may then be expected for $HPO_4^{\bullet-}$ adducts, in agreement with the fact that mainly organic radicals are detected 100 μs after the pulse of light.

CONCLUSIONS

Phosphate radicals are able to initiate oxidation of many aromatic compounds, either by an electron transfer mechanism or an addition pathway, and they are in general less selective and reactive than $SO_4^{\bullet-}$. For TFT as a substrate, efficient subsequent thermal reactions lead to the formation of less harmful, highly oxidised derivatives, as complete defluorination and rupture of the aromaticity is observed. Consequently, phosphate radical generation should contribute to the cleaning efficiency towards organic contaminants in the water streams.

Photolysis of $P_2O_8^{4-}$ aqueous solutions is a potential environmentally benign method for treating polluted water streams which deserves been evaluated.

REFERENCES

[1] Helz G.R., Zepp R.G. and Crosby D.G. (eds), *Aquatic and Surface Photochemistry*, Lewis Publishers, London, 1994.

[2] Faust B.C. Photochemistry of clouds, fogs and aerosols. *Environ. Sci. Technol.* , 1994, 28, 217–222A.

[3] Legrini O., Oliveros E. and Braun A.M., Photochemical Processes for water treatment, *Chem. Rev.* 1993, **93**, 671–698.

[4] Neta P.; Huie R.E. and Ross A.B. Rate constants for reactions of inorganic radicals in aqueous solution. *J. Phys. Chem. Ref. Data*, 1988, **17***,* 1027–1284. And references therein.

[5] Buxton G.V., Greenstock C.L., Helman W.P. and Ross A.B. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution. *J.Phys. Chem. Ref. Data*, 1988, **17**, 513–816. And references therein.

[6] Huber J.R. and Hayon E. Flash-photolysis in the vacuum ultraviolet region of the phosphate anions, $H_2PO_4^-$, HPO_4^{2-}, and $P_2O_7^{4-}$ in aqueous solutions. *J. Phys. Chem.* 1968, **72**, 3820–3827.

[7] Maruthamuthu P.and Neta P., Phosphate radicals. Spectra, acid – base equilibria, and reactions with inorganic compounds. *J. Phys. Chem.* 1978, **82**, 710–713.

[8] Rosso J.A., Rodríguez Nieto F.J., Gonzalez M.C. and Mártire D.O., Reactions of phosphate radicals with substituted benzenes. *J. Photochem. Photobiol. A: Chemistry* 1998, **116**, 21–25.

[9] Cencione S.S., Gonzalez M.C. and Mártire D.O. Reactions of phosphate radicals with substituted benzenes. A structure – reactivity correlation study. *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2933–2937.

[10] Rosso J. A., Alegretti P.E., Mártire D.O. and Gonzalez M.C. Reaction of sulfate and phophate radicals with α, α, α – trifluorotoluene. *J. Chem. Soc., Perkin Transactions* **2**, 1999, 205–210.

[11] Corbridge D.E.C. in Phosphorus. An outline of its chemistry, biochemistry and technology. *Studies in Inorganic Chemistry* **20**, 5th edn; Elsevier, New York, 1995.

[12] Bao Z.-C. and Barker J.R. Temperature and ionic strength effects on some reactions involving sulfate radical. *J. Phys. Chem.* 1996, **100**, 9780–9787.

[13] Lussier R.L., Risen W.M., and Edwards J.O. The photochemistry of peroxodiphosphates. The oxidation of water and two alcohols. *J.Phys.Chem.* 1970, **74**, 4039– 4046.

[14] Rosso J. A., Gonzalez M.C. and Mártire D.O. Photolysis of polyphosphate ions in alkaline aqueous solution. *Int. J. Chem. Kinet.*, in press.

[15] Gonzalez M.C., Mártire D.O. and Braun A.M. Aqueous phase kinetic studies involving highly reactive species of environmental interest. *Rec. Res. Devel. Photochem. Photobiol.*, **2**, 1998, 25–45 and references therein.

[16] Wardman P. Reduction potentials of one – electron couples. *J. Phys. Chem. Ref. Data* 1989, **18**, 1637–1716.

[17] G.G. Jayson, B.J. Parsons, and A.J. Swallow. Some simple, highly reactive, inorganic chlorine derivatives in aqueous solution. *J. Chem. Soc.*, *Faraday Trans. 1*, 1973, **69**, 1597–1607.

[18] J. March. Reactions, mechanisms, and structure. In *Advanced Organic Chemistry*, pp. 258–259, 4th edn, Wiley-Interscience, New York, 1991, and references therein.

[19] Hansch C. and Gao H. Comparative QSAR: Radical reactions of benzene derivatives in chemistry and biology. *Chem. Rev.*, 1997, **97** , 2995–3059.

[20] Gonzalez M.C. and Mártire D.O. Reactions of sulfate radicals with substituted benzenes studied by time-resolved spectroscopy. A structure-reactivity correlation analysis. *Asi. J. Spectrosc.*, 1999, **3**, 125–128.

[21] Neta P., Madhavan V., Zemel H. and Fessenden R.W. Rate constants and mechanism

of reaction of $SO_4^{\cdot -}$ with aromatic compounds. *J. Am. Chem. Soc.* 1977*,* **99**, 163–164.

[22] Mohan H., Mohan Mudaliar, Aravindakumar C.T., Rao B.S. and Mittal J.P. Studies on structure-reactivity in the reaction of HO radicals with substituted halobenzenes in aqueous solutions. *J. Chem. Soc. Perkin Trans.* **2** 1991, 1387–1392.

[23] Maruthamuthu P. and Taniguchi H. An in-situ photolysis-electron spin resonance study of some reactions of phosphate radicals. *J. Phys. Chem.*, 1977, **81**, 1944– 1948.

[24] Mohan H. and Mittal J.P. . Formation and Reactivity of the radical cation of bromobenzene in aqueous solutions: A pulse radiolysis study. *J. Phys. Chem.,* 1995, **99**, 6519–6524.

[25] H. Mohan and J.P. Mittal. Direct evidence for H^+-catalysed dehydration of fluorohydroxycyclohexadienyl radical: A pulse radiolysis study. *J. Chem. Soc. Faraday Trans.,* 1995, **91**, 2121–2126.

[26] S. Steenken, in *Free Radicals in Synthesis and Biology*. NATO ASI Series C -260, 1989, 220. F. Minisci *Ed.*, Kluwer Academic Publishers, Dordrecht, The Netherlands.

[27] Maruthamuthu P.and Neta P., Reactions of phosphate radicals with organic compounds. *J. Phys. Chem.* 1977, **81**, 1622–1625.

[28] von Sonntag C. and Schuchmann H.-P. The elucidation of peroxyl radical reactions in aqueous solution with the help of radiation-chemical methods. *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 1229–1253.

[29] Neta P., Huie R.E. and Ross A.B. Rate constants for reactions of peroxyl radicals in fluid solutions. *J. Phys. Chem. Ref. Data*, 1990, **19**, 413–513.

[30] Merga G., Rao B.S.M., Mohan H. and Mittal J.P. Reactions of OH and $SO_4^{\cdot -}$ with some halobenzenes and halotoluenes: A radiation chemical study. *J. Phys. Chem.,* 1994, **98**, 9158–9164.

[31] Draper P.B., Fox M.A., Pelizetti E., Serpone N. Pulse radiolysis of 2,4,5 trichlorophenol: formation, kinetics and properties of hydrotrichlorocyclohexadyene, trichlorophenoxyl, and dihydroxytrichlorociclohexadienyl radicals. *J. Phys. Chem.*, 1989, **93**, 1938–1943 and references therein.

[32] Adams G.E., Mitchel B.D. and Land E.J. Pulse radiolysis investigations of unimolecular elimination reactions in free radicals produced by OH addition to hydroxy benzenes. *Nature,* 1966, **211**, 293–294.

[33] A.J. Swallow in *Progress in Reaction Kinetics,* 1979, **9**, 195–365.

[34] J.K. Kochi in Free Radicals, vol.1, J.K. Kochi ed. John Wiley & Sons, New York, 1973.

[35] Karpel Vel Leitner N., Gombert B., Ben Abdessalem R. and Doré M. Kinetics and mechanism of the photolytic and $OH_{\cdot}$ radical induced oxidation of fluorinated aromatic compounds in aqueous solutions. *Chemosphere*, 1996, **32**, 893–906.

[36] S.Steenken, *Topics in Current Chemistry*, Vol. 177, Springer-Verlag, Berlin, 1996.

[37] E.S. Gould, *Mechanism and Structure in Organic Chemistry*. Holt, Rinehart and Winston, New York, 1959.

[38] NDRL Radiation Chemistry Data Center, INTERNET compilations, University of Notre Dame, USA. Address:

[39] Villata L.S., Rosso J. A., Gonzalez M.C. and Mártire D.O. Kinetics of the reactions of $O^{\bullet -}$ and $HO_{\cdot}$ with α, α, α -trifluorotoluene and 4-fluorotoluene. *J. Chem. Res.*, 1997, 172–173.