

Reactions of phosphate radicals with substituted benzenes

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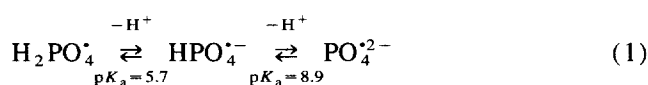
Abstract

Phosphate radicals in the three acid–base forms ($\text{H}_2\text{PO}_4^\cdot$, $\text{HPO}_4^{\cdot-}$ and $\text{PO}_4^{2-\cdot}$) were produced by photolysis of $\text{P}_2\text{O}_8^{4-}$ at different pH. Absolute rate constants for the reactions of the phosphate radicals with substituted benzenes have been determined by flash-photolysis. The results are discussed in terms of Hammett correlations. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Phosphate radicals; Flash-photolysis; Substituted benzenes

1. Introduction

Phosphate radicals exist in three acid–base forms ($\text{H}_2\text{PO}_4^\cdot$, $\text{HPO}_4^{\cdot-}$, $\text{PO}_4^{2-\cdot}$) related by fast equilibria (Eq. (1)). These radicals were reported to react with organic and inorganic substrates either by hydrogen abstraction or by electron transfer with increasing efficiency following the order $\text{H}_2\text{PO}_4^\cdot > \text{HPO}_4^{\cdot-} > \text{PO}_4^{2-\cdot}$ [1].



Huber and Hayon [2] studied the decay kinetics of phosphate radicals generated by VUV photolysis of $\text{HPO}_4^{2-\cdot}$ and $\text{H}_2\text{PO}_4^\cdot$, as shown in reaction (2) for $\text{HPO}_4^{2-\cdot}$.



A second order decay law for $\text{H}_2\text{PO}_4^\cdot$ and $\text{HPO}_4^{\cdot-}$ radicals in Ar-saturated solutions and a first order decay kinetics in the presence of molecular oxygen was reported [2]. The latter results were interpreted in terms of the formation of $\text{H}_2\text{PO}_4^\cdot$ and $\text{HPO}_4^{\cdot-}$ oxygen adducts [2]. No further information on the existence of such adducts is given in the literature, and, in all other reports involving the phosphate radicals, these were generated in the absence of molecular oxygen [3].

A detailed study of the reactions of the phosphate radicals with organic and inorganic substrates is of importance since aqueous phase oxidative procedures based on reactions of

HO^\cdot or $\text{SO}_4^{\cdot-}$ [4] may form phosphate radicals from the reaction of HO^\cdot or $\text{SO}_4^{\cdot-}$ with phosphate ions contained in high concentrations in the water matrix [1,5]. However, the information reported in the literature on the reactivity of the phosphate radicals towards organic and inorganic substrates is scarce [1,6].

We studied here the decay kinetics of $\text{H}_2\text{PO}_4^\cdot$, $\text{HPO}_4^{\cdot-}$, $\text{PO}_4^{2-\cdot}$ generated by photolysis of peroxodiphosphate ions (reaction (3)) in N_2 , air and O_2 -saturated solutions, both in the presence and absence of added substrates.



2. Experimental

Potassium peroxodiphosphate was obtained from the electrolysis of alkaline solutions of KHPO_4 in the presence of KF and K_2CrO_4 , as described in the literature [7] and purified by recrystallization. Distilled water was passed through a Millipore system.

Flash-photolysis experiments were carried out in a conventional apparatus (Xenon model 720C) with modified optics and electronics [8]. The emission of the flash lamps was filtered with saturated aqueous solutions of the substrates in order to avoid photolysis of the aromatic compounds. The analysis source was a high pressure mercury lamp (Osram HBO-100 W). In continuous photolysis experiments, a Philips HPK 125 W lamp was used as irradiation source. In these experiments, oxygen generation was measured in situ

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with a specific oxygen electrode (Orion 97-0899). All experiments were carried out at $25 \pm 1^\circ\text{C}$.

In order to study the reactions of each of the phosphate radicals, photolysis of potassium peroxodiphosphate was performed under controlled pH conditions, i.e., $\text{pH} = 4.0 \pm 0.2$; 7.1 ± 0.1 or 10.1 ± 0.2 , where $\text{H}_2\text{PO}_4^\cdot$, $\text{HPO}_4^{\cdot-}$ or $\text{PO}_4^{2-\cdot}$ are the main radicals formed. The pH was adjusted with mixtures of $\text{H}_3\text{PO}_4/\text{KH}_2\text{PO}_4$, $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ or $\text{K}_2\text{HPO}_4/\text{KOH}$. The ionic strength of the solutions are within the range 0.1–0.2 M.

Solutions of the aromatics were prepared by dilution of saturated aqueous solutions at 25°C . As the solubility of *p*-xylene in aqueous solution had not been reported in the literature, it was determined according to the following procedure: *p*-xylene was extracted from a fixed volume of its saturated aqueous solution with a known amount of benzene or *n*-hexane, until no characteristic UV absorption of the fluoroaromatic was observed in the aqueous phase. The concentration of *p*-xylene in the organic solutions was determined from Lambert–Beer plots at $\lambda_{\text{max}} = 274 \text{ nm}$. A water solubility of $(8.0 \pm 0.3) \times 10^{-4} \text{ M}$ was retrieved at 25°C .

3. Results and discussion

Flash-photolysis of $\text{P}_2\text{O}_8^{4-}$ solutions at $\text{pH} = 4, 7$ and 10 showed the formation of transients absorbing in the range 300–500 nm, which were identified as $\text{H}_2\text{PO}_4^\cdot$, $\text{HPO}_4^{\cdot-}$ and $\text{PO}_4^{2-\cdot}$, since an excellent agreement between the spectrum obtained immediately after the pulse of light and those reported in the literature [1,9] for these radical species is obtained. Fig. 1 shows the absorption spectrum of $\text{PO}_4^{2-\cdot}$ obtained in this work from 300 to 600 nm, together with the reported one for $\lambda > 400 \text{ nm}$, our data representing new spectral information.

The decay kinetics of the three acid–base forms of the phosphate radicals was observed to be independent on the presence of dissolved molecular oxygen. $\text{HPO}_4^{\cdot-}$ and $\text{PO}_4^{2-\cdot}$ radical ions showed second order decay kinetics, both in N_2 - and air-saturated solutions, as shown in Fig. 2 for $\text{PO}_4^{2-\cdot}$ under air-saturation. The bimolecular decay rate constants ($2 k_{\text{BR}}/\epsilon$) obtained at 500 nm for $\text{HPO}_4^{\cdot-}$ and $\text{PO}_4^{2-\cdot}$ were 1.3×10^5 and $2.8 \times 10^5 \text{ cm s}^{-1}$, respectively. Taking the molar absorption coefficients reported in Ref. [1], the following second order rate constants are obtained: ($2 k_{\text{BR}} = 2.0 \pm 0.1$) $\times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{HPO}_4^{\cdot-}$ and $2 k_{\text{BR}} = (6 \pm 2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{PO}_4^{2-\cdot}$, in agreement with the reported values in the absence of molecular oxygen [2,3,10].

$\text{H}_2\text{PO}_4^\cdot$ shows a more complex decay kinetics which could be well fitted by a mixed second ($2 k_{\text{BR}}/\epsilon^{500} = 1 \times 10^6 \text{ cm s}^{-1}$) and first order decay law ($k_f = 5 \times 10^3 \text{ s}^{-1}$). A second order decay was reported for these radicals generated by pulse radiolysis and VUV photolysis of $\text{H}_2\text{PO}_4^\cdot$ in the absence of O_2 with a rate constant ($2 k_{\text{BR}}/\epsilon^{500} = 2 \times 10^6 \text{ cm s}^{-1}$ [2,10]) of the same order of that observed in our experiments. Our flash-photolysis experiments at $\text{pH} = 4.0$ required concentra-

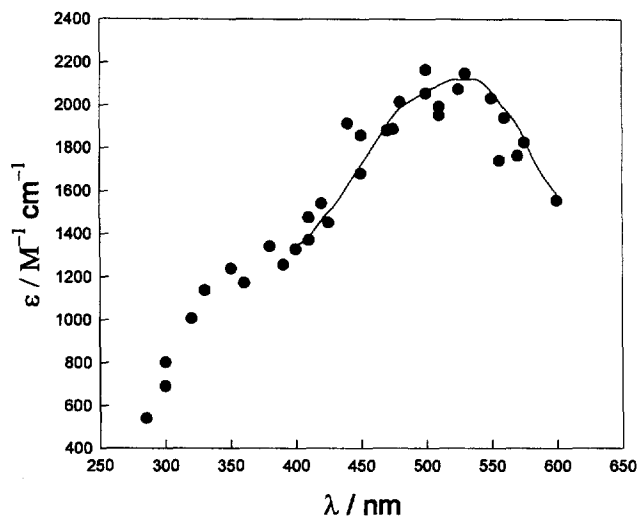


Fig. 1. Normalized $\text{PO}_4^{2-\cdot}$ absorption spectrum ($\epsilon^{500} = 2150 \text{ M}^{-1} \text{ cm}^{-1}$ [1]) obtained from an air-saturated $2.74 \times 10^{-4} \text{ M}$ $\text{K}_4\text{P}_2\text{O}_8$ solution at $\text{pH} = 10.3$. The solid line shows the spectrum reported in Ref. [1].

tions of $\text{P}_2\text{O}_8^{4-}$ of the order of $3 \times 10^{-3} \text{ M}$, while no $\text{P}_2\text{O}_8^{4-}$ is present in the reported VUV photolysis and radiolysis experiments [2,10]. Consequently, the first order decay component observed under our experimental conditions could arise from a reaction of $\text{H}_2\text{PO}_4^\cdot$ with $\text{P}_2\text{O}_8^{4-}$, similar to that reported for $\text{SO}_4^{\cdot-}$ with $\text{S}_2\text{O}_8^{2-}$ [11,12]. From experiments performed at $\text{pH} = 4.0$ with different $\text{P}_2\text{O}_8^{4-}$ concentrations in the range $(1\text{--}6) \times 10^{-3} \text{ M}$, an upper limit of $10^6 \text{ M}^{-1} \text{ s}^{-1}$ is derived for the rate constant of this reaction. However, the participation of a reaction between H_2O and $\text{H}_2\text{PO}_4^\cdot$, similar to that reported for sulphate radicals [3], should not be discarded [13].

Our results do not support the proposed formation of molecular oxygen adducts of these radicals [2], since molecular oxygen has no detectable effect on the decay kinetics of the phosphate radicals. Moreover, in order to further check our observations, we have studied the decay of $\text{HPO}_4^{\cdot-}$ in

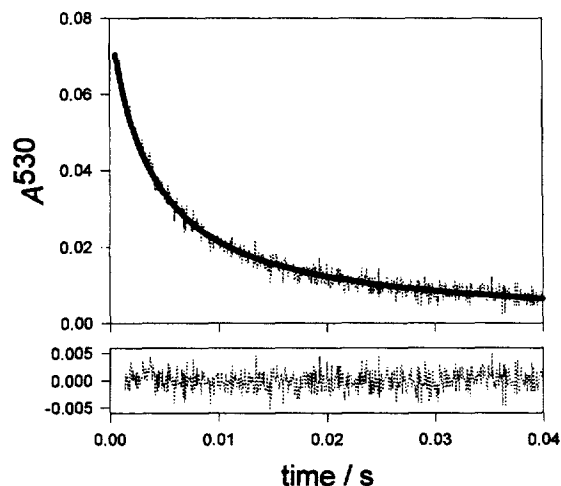


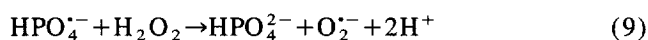
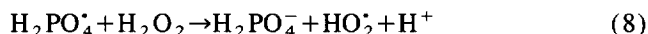
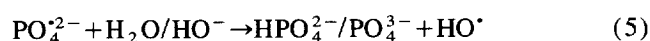
Fig. 2. Experimental $\text{PO}_4^{2-\cdot}$ decay (dotted lines) obtained at $\lambda = 530 \text{ nm}$ from an air-saturated $2.74 \times 10^{-4} \text{ M}$ $\text{K}_4\text{P}_2\text{O}_8$ solution at $\text{pH} = 10.3$. The solid line shows the second order fitting. The lower plot shows the residuals.

the presence of increasing concentrations of methanol in air-saturated solutions. The absolute second order rate constant determined from these experiments ($1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) is in complete agreement with that reported in the absence of oxygen [14], further indicating that the oxygen adducts of $\text{HPO}_4^{\cdot-}$ are not formed under our experimental conditions. The main difference between the experiments of Huber and Hayon [2] in air-saturated solutions and ours, is that in the former case, high concentrations of $\text{HO}_2^{\cdot}/\text{O}_2^{\cdot-}$ were formed, whereas no detectable amounts of these radicals were observed in our flash-photolysis experiments. As $\text{HO}_2^{\cdot}/\text{O}_2^{\cdot-}$ are reported to efficiently reduce $\text{P}_2\text{O}_8^{4-}$, propagating a chain reaction [1], these radicals can then be expected to affect the overall formation and decay of phosphate radicals in the VUV photolysis experiments of Huber and Hayon.

Photodecomposition of peroxodiphosphate to phosphate has been reported to oxidise water to molecular oxygen [13] (reaction (4)). In the present work, we followed the simultaneous evolution of the concentration of molecular oxygen and depletion of peroxodiphosphate during continuous irradiation of initially air-saturated $\text{K}_4\text{P}_2\text{O}_8$ solutions of pH = 4.0, 7.1 and 10.1, contained in closed vessels without dead volume. In all cases, an increase in the dissolved O_2 concentration with the irradiation time was observed. The rates of oxygen formation and the photodecomposition of peroxodiphosphate were observed to be pH-independent in the range 4–10, in agreement with the literature reports [13].

The concentration of photodecomposed $\text{K}_4\text{P}_2\text{O}_8$ (determined from the change of absorption at $\lambda = 240 \text{ nm}$ taking $\epsilon^{240} = 39 \text{ M}^{-1} \text{ cm}^{-1}$) at different irradiation times, was about 5 times higher than the concentration of evolved oxygen.² The reported overall reaction for peroxodiphosphate decomposition (reaction (4)) indicates a 2:1 molar ratio for $\text{P}_2\text{O}_8^{4-}$ to O_2 [13]. Molecular oxygen was reported to be formed through a complex mechanism involving hydrogen peroxide (reactions (5)–(7)). Due to the very low steady-state concentrations of transients achieved in the continuous photolysis experiments, the second order decay processes of the phosphate radicals observed in the flash-photolysis experiments do not appreciably contribute, and thus, first order reactions in phosphate radicals, such as reaction (5), leading ultimately to oxygen formation are favoured.

However, since hydrogen peroxide efficiently reacts with the phosphate radicals [3] (reactions (8) and (9)) and $\text{HO}_2^{\cdot}/\text{O}_2^{\cdot-}$ are able to reduce $\text{P}_2\text{O}_8^{4-}$ [1], deviations from the 2:1 stoichiometry should be expected. Moreover, a reaction between phosphate radicals and $\text{P}_2\text{O}_8^{4-}$ with formation of $\text{P}_2\text{O}_8^{3-}$ (vide supra) [11,12] may also contribute to an increased $\text{P}_2\text{O}_8^{4-}$ depletion.



Flash-photolysis experiments with air-saturated peroxodiphosphate solutions (pH = 4.0, 7.1 or 10.1) containing variable amounts of added substrates showed absorption traces at $\lambda > 400 \text{ nm}$, whose spectra immediately after the flash of light agreed with those of the corresponding phosphate radicals. The experimental traces could be well fitted according to Eq. (10). The calculated wavelength independent constant b linearly increases with the substrate concentration, as shown in Fig. 3 for several substrates. The very small constant term c can be associated to the absorption of a longer lived species, mainly organic radicals, formed following phosphate radicals depletion [15].

$$\Delta A = a \exp(-bxt) + c \quad (10)$$

The slopes of the plots similar to those shown in Fig. 3 yield the bimolecular rate constants for the reaction of $\text{H}_2\text{PO}_4^{\cdot}$, $\text{HPO}_4^{\cdot-}$ or $\text{PO}_4^{\cdot 2-}$ radicals with the substituted benzenes, shown in Table 1. For comparison, the corresponding bimolecular rate constants for the reactions of $\text{SO}_4^{\cdot-}$ radical

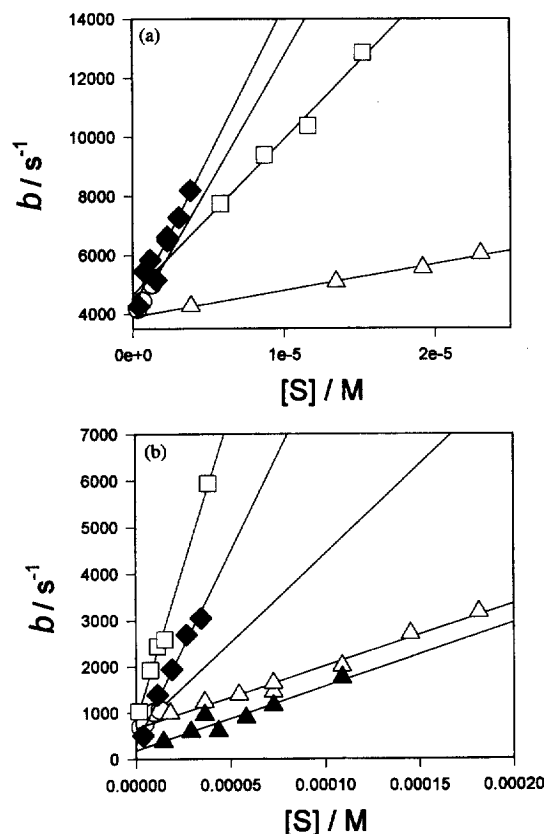


Fig. 3. Dependence of b on substrate concentration: (a) for $\text{H}_2\text{PO}_4^{\cdot}$ with added: *p*-xylene (\circ); benzene (Δ); toluene (\square) and benzyl alcohol (\blacklozenge); (b) for $\text{HPO}_4^{\cdot-}$ with added: *p*-xylene (\circ); toluene (Δ) and benzyl alcohol (\square) and for $\text{PO}_4^{\cdot 2-}$ with added: benzyl alcohol (\blacklozenge) and toluene (\blacktriangle).

² The molar absorption coefficients of $\text{H}_n\text{P}_2\text{O}_8^{n-4}$ ($n=0, 1, 2, 3$) are reported to be identical [13].

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

	$SO_4^{\cdot-}$	$H_2PO_4^{\cdot+}$	$HPO_4^{\cdot-}$	$PO_4^{\cdot2-}$
Benzene	3.0×10^{9c}	$(8.9 \pm 0.5) \times 10^7$	$(1.7 \pm 0.2) \times 10^7$	$(4.3 \pm 0.3) \times 10^6$
TFT ^d	2.0×10^{7c}	3.4×10^7	2.7×10^6	9×10^5
Toluene	1.3×10^{9c}	$(5.2 \pm 0.5) \times 10^8$	$(1.4 \pm 0.1) \times 10^7$	$(1.4 \pm 0.1) \times 10^7$
Benzyl alcohol	—	$(1.0 \pm 0.1) \times 10^9$	$(1.3 \pm 0.1) \times 10^8$	$(8.3 \pm 0.6) \times 10^7$
<i>p</i> -xylene	2.7×10^{9b}	$(8.8 \pm 0.7) \times 10^8$	$(3.8 \pm 0.5) \times 10^7$	$(4.6 \pm 0.5) \times 10^7$

^aThe error bars designate standard deviations.

^bThis work.

^cRef. [3].

^d α,α,α -trifluorotoluene.

^eRef. [15].

ions are also included in Table 1. For all the substrates, the observed tendency in the rate constants is: $SO_4^{\cdot-} > H_2PO_4^{\cdot+} > HPO_4^{\cdot-} > PO_4^{\cdot2-}$, in agreement with previously reported data [1].

For each one of the phosphate radicals, the absolute second order rate constants for the reactions with aromatic substrates decrease with the electron withdrawing ability of the substituent, as expected from the electrophilicity of these radicals. The effect of the substituents can be quantitatively represented in a Hammett type plot of the logarithm of the rate constant vs. the substituent constant, σ , for each radical [16–18] as shown in Fig. 4 for $HPO_4^{\cdot-}$ and $PO_4^{\cdot2-}$. All data

shown in Table 1 along with the available data for benzoate anion, benzoic acid [14] and phenoxide ion [3] are shown in Fig. 4. Benzyl alcohol was not included in the Hammett correlation since no literature σ value is available for the CH_2OH substituent. In all cases, the most probable site of attack, taken as the minimum σ value, was considered. For the monosubstituted benzenes, the minimum of σ_{ortho} [18], σ_{meta} and σ_{para} [17] was used. For *p*-xylene the attack at the *ipso* position [19] with respect to one of the methyl groups yields the minimum of the algebraic sum of σ for each substituent, but this substrate was not considered in the regressions for being a disubstituted benzene. The slopes (ρ) of the correlations were -1.3 ± 0.3 and -2.3 ± 0.2 for $HPO_4^{\cdot-}$ and $PO_4^{\cdot2-}$ radicals, respectively. For $H_2PO_4^{\cdot+}$, a linear dependence of $\log k$ vs. σ was found with $\rho = -1.2 \pm 1.0$. However, since the correlation was poor, these data are not shown in Fig. 4.

Negative values of ρ imply a reaction favoured by high electron density at the reaction site, i.e., an electrophilic attack [16–18,20]. The value of $\rho = -2.3$ for $PO_4^{\cdot2-}$ compares well with that found for the reactions between sulphate radicals and substituted benzenes ($\rho = -2.4$ [20]). Such values of ρ indicate that these radicals react with high selectivity with the substrates, most likely by an electron transfer mechanism, initially yielding an organic radical cation. The ρ value found for $HPO_4^{\cdot-}$ radicals are between those found for reactions involving $SO_4^{\cdot-}$ radicals with similar substrates and those observed for additions of HO^{\cdot} radicals to aromatic compounds (ρ from -0.5 to -0.4 [20–22]). Consequently, the participation of both types of mechanisms should be expected, as also proposed for the reaction of sulphate radicals with substituted toluenes showing ρ values of the order of -1.2 [23]. Moreover, these observations are in agreement with the reported fact that direct electron transfer is not the predominant process in the reaction of $HPO_4^{\cdot-}$ with aromatic and aliphatic carboxylic acids [6].

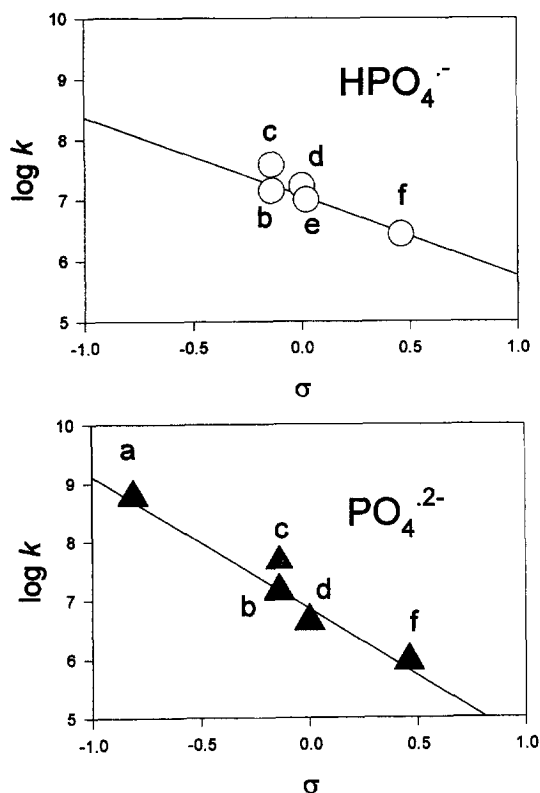


Fig. 4. Logarithmic plots of the rate constants for the reactions of $HPO_4^{\cdot-}$ (○); and $PO_4^{\cdot2-}$ (▲) vs. the Hammett parameter σ [17] for: phenoxide ion (a); toluene (b); *p*-xylene (c); benzene (d); benzoate ion (e) and α,α,α -trifluorotoluene (f).

4. Conclusions

The evidences found in this work against the formation of molecular oxygen adducts of $HPO_4^{\cdot-}$ or $H_2PO_4^{\cdot+}$ validates the

determination of bimolecular rate constants for the interaction of these radicals with organic substrates by monitoring the increase of the apparent decay rate constant as a function of the substrate concentration in solutions containing dissolved molecular oxygen. Following this methodology, the reactions of several aromatic substrates with $\text{H}_2\text{PO}_4^\cdot$, $\text{HPO}_4^{\cdot-}$ or $\text{PO}_4^{\cdot 2-}$ radicals were determined. The obtained bimolecular rate constants for these reactions correlate with the electron withdrawing ability of the substituent, as expected from the electrophilicity of the phosphate radicals.

Acknowledgements

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References

- [1] P. Maruthamuthu, P. Neta, J. Phys. Chem. 82 (1978) 710.
- [2] J.R. Huber, E. Hayon, J. Phys. Chem. 72 (1968) 3820.
- [3] P. Neta, R.E. Huie, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 1027.
- [4] M.C. Gonzalez, D.O. Mártire, A.M. Braun, Aqueous phase kinetic studies involving highly reactive species of environmental interest, in: S.G. Pandalai (Ed.), Recent Research Developments in Photochemistry and Photobiology, 1998, in press, and references therein.
- [5] P. Haygarth, Scope Newsletter in Europe 21 (1997) 1.
- [6] P. Maruthamuthu, H. Taniguchi, J. Phys. Chem. 81 (1977) 1944.
- [7] I.I. Creaser, J.O. Edwards, Top. Phosphorus Chem. 7 (1972) 379.
- [8] M.C. Gonzalez, D.O. Mártire, Int. J. Chem. Kin. 29 (1997) 589.
- [9] G.L. Hug, Nat. Stand. Ref. Data Ser., U.S. Nat. Bur. Stand., No. 69, 1981.
- [10] E.D. Black, E. Hayon, J. Phys. Chem. 74 (1970) 3199.
- [11] W.J. McElroy, S.J. Waygood, J. Chem. Soc., Faraday Trans. 86 (1990) 2557.
- [12] Z.-C. Bao, J.R. Barker, J. Phys. Chem. 100 (1996) 9780.
- [13] R.L. Lussier, W.M. Risen, J.O. Edwards, J. Phys. Chem. 74 (1970) 4039.
- [14] P. Maruthamuthu, P. Neta, J. Phys. Chem. 81 (1977) 1622 and references cited therein.
- [15] J.A. Rosso, D.O. Mártire, M.C. Gonzalez, submitted for publication.
- [16] E.S. Gould, Mechanism and Structure in Organic Chemistry, Holt, Rinehart and Winston, New York, 1959.
- [17] J. March, Advanced Organic Chemistry, 4th edn., Wiley-Interscience, New York, 1991, and references therein.
- [18] P. Segura, J. Org. Chem. 50 (1985) 1045.
- [19] G. Merga, C.T. Aravindakumar, B.S.M. Rao, H. Mohan, J.P. Mittal, J. Chem. Soc., Faraday Trans. 90 (1994) 597.
- [20] P. Neta, V. Madhavan, H. Zemel, R.W. Fessenden, J. Am. Chem. Soc. 99 (1977) 163.
- [21] H. Mohan, M. Mudaliar, C.T. Aravindakumar, B.S. Rao, J.P. Mittal, J. Chem. Soc., Perkin Trans. 2 (1991) 1387.
- [22] P. Neta, L.M. Dorfman, Adv. Chem. Ser. 81 (1968) 222.
- [23] G. Merga, B.S.M. Rao, H. Mohan, J.P. Mittal, J. Phys. Chem. 98 (1994) 9158.