

Experimental upper bound on phosphate radical production in TiO₂ photocatalytic transformations in the presence of phosphate ions

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The spin trapping technique using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was used to investigate the involvement of phosphate radicals in TiO₂-photocatalyzed systems. A persistent (HO)₂PO₂-DMPO[•] adduct ($a^N = 14.6$ G, $a^H_\beta = 12.4$ G, $a^H_\gamma = 1.1$ G and $a^P = 0.5$ G) was first synthesized by UV photolysis of aqueous peroxodiphosphate solutions, at pH 4.0, in the presence of DMPO. The trapping efficiency of the phosphate radicals, η , determined at [DMPO] = 0.3 mM was $\eta = 35\%$. In the heterogeneous system, the rate of HO-DMPO[•] aminoxyl radical generation under continuous UV irradiation of TiO₂ sols, at [DMPO] = 0.3 mM and pH = 4.0, becomes gradually inhibited increasing [(HO)₂PO₂⁻] above 0.1 mM. However, no evidence of (HO)₂PO₂-DMPO[•] could be obtained in the whole range of conditions explored in this work ($0.1 \leq [\text{DMPO}]/\text{mM} \leq 1$ mM, $0.1 \leq [(\text{HO})_2\text{PO}_2^-]/\text{mM} \leq 100$ mM). Based on the above experiments, we estimated a conservative upper limit for the quantum yield of (HO)₂PO₂[•] production, $\Phi = 2.0 \times 10^{-4}$, in phosphate loaded TiO₂ particles. The analysis of this result and its implications for the mechanism of the TiO₂ photocatalytic oxidations of organic compounds in the presence of phosphate are discussed.

Introduction

Common inorganic ions frequently present in wastewater influence the TiO₂ photocatalytic degradation processes of organic compounds.¹ The effect is known to be more pronounced for specifically adsorbed anions.^{2,3} Both phosphate and fluoride belong to this group, however, the estimated redox potential of fluoride ($E^\theta(\text{F}^\bullet/\text{F}^-) = 3.6$ V vs. NHE)⁴ makes it stable against oxidation, at variance with phosphate anion ($E^\theta((\text{HO})_2\text{PO}_2^\bullet, \text{H}^+/\text{H}_3\text{PO}_4) = 2.65$ V vs. NHE).⁵ A recent study on the effect of fluoride on phenol photocatalytic degradation revealed the somewhat unexpected result that the rate of phenol degradation at 10 mM NaF is three times that in the absence of fluoride anion. On the other hand, Abdullah and coworkers showed that phosphate at millimolar concentration and pH 4 reduces the rates of mineralization of model organic compounds, salicylic acid, aniline and ethanol, by ~70%.

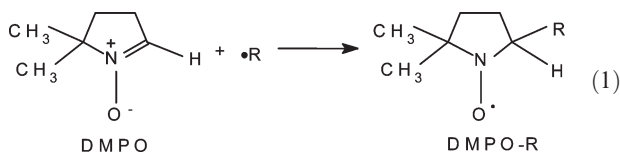
The strong interaction of phosphate with TiO₂ surface was established using X-ray photoelectron spectroscopy⁶ and *in situ* internal reflection infrared spectroscopy,⁷ besides, electrophoretic mobility measurements proved that the adsorption of phosphate affects the surface ζ -potential shifting the isoelectric point from pH ~5 to pH ~2.³ As pointed out by Anderson *et al.*, this results highlights the possibility of exploiting the change in surface charge-induced by specifically adsorbed anions-to control the adsorption of other charged molecules.³

In a recent report we showed that phosphate significantly modifies phthalate dark-adsorption isotherms on TiO₂ nanoparticles, however, the initial quantum yields for phthalate degradation-at variance with the trapping of reactive OH radicals by DMPO-were found to be independent of the presence of phosphate.⁸

It has been suggested that advanced oxidation processes (AOP), based on the generation of hydroxyl radicals to

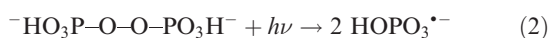
induce pollutants oxidation, may originate phosphate radicals by reaction of OH with phosphate ions, contained in high concentrations in the water matrix. Homogeneous specific rate constants between phosphate and hydroxyl radicals are known to be low,⁹ however, in photocatalytic TiO₂ systems: the trapping of the primary oxidant species, h^+ , by phosphate anions adsorbed on the semiconductor surface may be envisaged as an adequate route to (HO)₂PO₂[•].^{10,11} If formed, phosphate radicals are expected to participate in the degradation process, since they are known to readily oxidize many organic and inorganic compounds, abstract H from saturated organic radicals and add to olefins at significant rates.^{12,13}

Here, we reported a detailed study on the possible involvement of phosphate radicals in the heterogeneous photocatalyzed degradation of aqueous TiO₂ sols by EPR spectroscopy. Direct EPR detection of inorganic radicals in fluid solutions is often complicated due to their high reactivity, and their usually short spin-lattice relaxation times which causes intense line-broadening.¹⁴⁻¹⁷ Therefore, the spin trapping technique is a suitable strategy to overcome these problems, allowing the quantitative determination of the radical species through their derivatization in persistent paramagnetic adducts.¹⁸ Previous reports of phosphate trapping involve the addition of this radical to fumarate or the nitromethane anion, (CH₂=NO₂⁻), however, the resulting paramagnetic species are very short lived, so that their concentration does not build up to detectable values unless a flow method is used.^{13,19,20} Since this last option cannot be developed for TiO₂ suspensions, we become interested in the trapping of phosphate radicals leading to a more stable complex. Nitrones such as DMPO are known to originate persistent nitroxides (DMPO-R) upon reaction with paramagnetic species R (reaction (1)).²¹



Despite no references existing in the literature for the $(\text{HO})_2\text{PO}_2\text{-DMPO}^\bullet$ radical adduct, we were led by the fact that $\text{SO}_4^{\bullet-}$ radicals, which may be expected to behave in a similar fashion than phosphate, are known to be effectively trapped by DMPO.^{22,23}

Phosphate radicals can be produced from peroxodiphosphate ions by reaction with hydrated electrons or by direct UV photolysis of this ion:^{13,24–26}



The quantum yield for peroxide photodissociation has been thoroughly investigated,^{24,27} thus, we used this technique to generate the radicals and we carefully design homogeneous experiments in order to establish the conditions under which we could be able to detect and quantify the involvement of phosphate radical in the heterogeneous TiO_2 system.

Experimental section

Chemicals

All chemicals used in the experiments were of analytical reagent grade. 5,5-Dimethyl-1-pyrroline *N*-oxide, (DMPO, Aldrich), 2,2,6,6-tetramethylpiperidine-1-oxyl, (TEMPO, Aldrich), potassium phosphate monobasic (KH_2PO_4 , Mallinckrodt) and potassium peroxodiphosphate, (Aldrich) were used as received. Stock solutions of DMPO were prepared under nitrogen and stored in dark-sealed bottles at 268 K. Phenylglyoxylic acid (Sigma) was recrystallized from carbon tetrachloride (Merck) prior to use. All solutions were daily made using redistilled water. Solution pH was adjusted using HClO_4 (Carlo Erba) and measured using a HI 9321 Hanna pH meter. When necessary the solutions were deaerated by bubbling nitrogen (ultrahigh purity, AGA).

Titanium dioxide suspensions were prepared by repeated ultracentrifugation of Degussa P-25 TiO_2 slurries in doubly-distilled water. Slurries (2 g L^{-1}) were magnetically stirred for 60 min, then sonicated for 15 min, and finally subjected to three 5 min centrifugation cycles at 9000 g in a PK 121 (ALC International) ultracentrifuge.

Photolysis

Steady-state photolysis were carried out in a 2.5 mL solution placed in a 1 cm optical cell at the selected wavelength using a 1000 W Hg-Xe lamp coupled to a Kratos-Schoeffel monochromator. Light intensity measurements were performed by chemical actinometry using phenylglyoxylic acid, as described elsewhere.²⁸ Incident photon fluxes, I_0 , were: 8.9×10^{-7} and $4.0 \times 10^{-6} \text{ Einstein L}^{-1} \text{ s}^{-1}$ at 275 ± 10 and 303 ± 10 nm, respectively. Well-determined volumes of the irradiated sample were withdrawn at the early times of the photolysis and immediately analyzed by EPR or HPLC.

Alternatively, a set of heterogeneous spin trapping experiments were performed by irradiating air-saturated TiO_2 suspensions containing DMPO and variable amount of phosphate within a 50 μL , silica cell located in the optical cavity of the EPR spectrometer, to allow continuous monitoring of the paramagnetic signals and the determination of radical generation rates, as described elsewhere.⁸ In this case, the samples were irradiated with a 400 W, medium-pressure metal halide lamp (Phillips, HPA 400), emitting predominantly light between 300 and 450 nm. The output passed successively

through a 10-cm water infrared filter and a long-pass glass filter in order to isolate $\lambda \geq 340$ nm.

Electron paramagnetic resonance (EPR) measurements

X-band EPR experiments were performed at room temperature using a Bruker ER 200 spectrometer (Bruker Analytische Messtechnik GmbH, Germany), as described elsewhere.²⁹ 2,2,6,6-tetramethylpiperidine-1-oxyl, (TEMPO, $g = 2.0051$), was used as a standard for the determination of g -factors. Amplitude signals were transformed into radical concentrations by double integration of the digitized first-derivative EPR signals, using the spectrum of an aqueous solution of the concentration standard, TEMPO, recorded at the same microwave power, modulation amplitude and amplification gain used in photolytic experiments. General instrumental conditions were: central field, 3436 G; sweep width, 60 G; scans 1–20; microwave power, 43 mW; modulation frequency, 100 kHz; time constant, 1–50 ms; sweep time, 1–5 s; modulation amplitude, 1.25 Gpp; receiver gain, 8×10^5 – 40×10^5 .

HPLC measurements

Analysis of DMPO consumption was performed using a HPLC system consisting of a gradient pump equipped with a UV-VIS photodiode array detector (UV2000-Thermo Separation Products), and a ODS-2, 5 μm , (Phenomenex, Luna), 25.0 cm \times 4.6 cm. Samples were eluted with methanol–water 20% (v/v). The solvent flow was kept constant at 1 mL min^{-1} .

Results and discussion

Spin trapping of phosphate radicals formed by peroxodiphosphate irradiation

Fig. 1(a) show a typical spectrum obtained upon excitation at $\lambda = 275 \pm 10$ nm of a $\text{K}_4\text{P}_2\text{O}_8$ solution in the presence of DMPO, at pH 4.0. The signal is characteristic of a persistent nitroxyl radical, with the β -H hyperfine constant close to the nitrogen hyperfine splitting. In addition, it shows the presence of two equivalent nuclei of spin $\frac{1}{2}$ (γ protons) and a relative small splitting due to the ^{31}P nucleus. Accordingly, the spectrum shown as Fig. 1(b) was simulated using $a^{\text{N}} = 14.6$ G, $a_{\beta}^{\text{H}} = 12.4$ G, $a_{\gamma}^{\text{H}} = 1.1$ G and $a^{\text{P}} = 0.5$ G. Consistently, a similar set of hyperfine coupling constants (with the exception of the P hfsc), was already found for the adduct between DMPO and $\text{SO}_4^{\bullet-}$ radicals.^{22,23}

$(\text{HO})_2\text{PO}_2\text{-DMPO}^\bullet$ was found to be very stable. Once the aliquots were extracted from the irradiation cell and placed in the EPR cavity, the spectra of the sample was repeatedly taken at different time intervals. By this way, we estimated that the life time under the trapping conditions ($[\text{DMPO}] = 0.1$ mM, $[\text{K}_4\text{P}_2\text{O}_8] = 25$ mM, pH = 4.0) was $\cong 12$ h.

Trapping efficiency of $(\text{HO})_2\text{PO}_2^\bullet$ by DMPO

Quantitative determination of phosphate radical concentrations requires the knowledge of the spin trapping efficiency, η , defined as the fraction of the radicals, R, reacting with DMPO to form the stable aminoxyl adduct indicated as DMPO-R in eqn. (1).²⁹ η may be experimentally determined as the quotient between the rate of radical trapping, R_{T} , and the rate of radical generation, R_{g} , as shown below.

Phosphate radicals were generated at a controlled rate, in the presence of DMPO, by UV photolysis of peroxodiphosphate ions at 275 ± 10 nm according to eqn. (2). In all experiments, DMPO concentration was kept lower than 0.3 mM thus assuring that it does not absorb at the irradiation wavelength (the molar absorption coefficient of DMPO at 275 nm

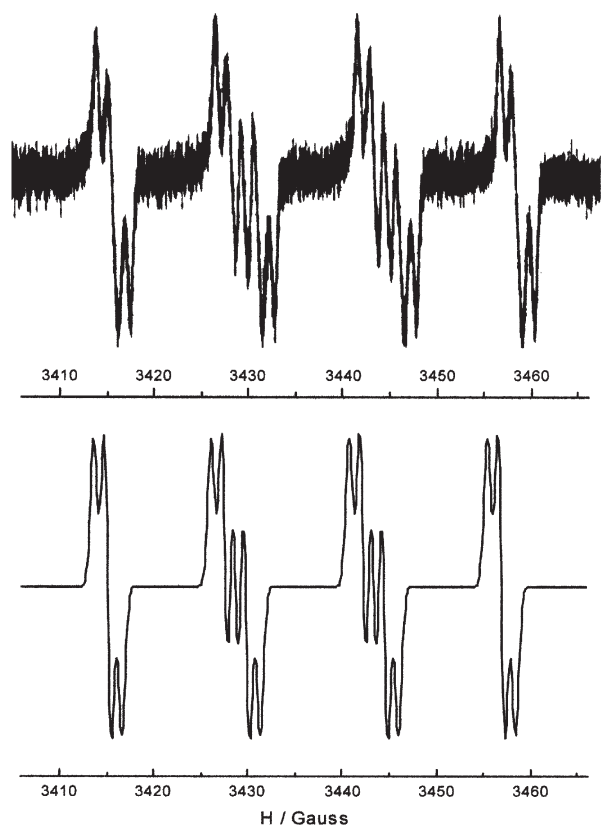


Fig. 1 (a) EPR spectra of the DMPO adduct formed on irradiation of a solution containing 25.0 mM $\text{K}_4\text{P}_2\text{O}_8$ and 0.3 mM DMPO at pH 4.0. Central field 3436 G, modulation amplitude 0.25 Gpp, gain 8×10^5 , scan time 1000 s. (b) Simulated spectrum using $a^{\text{N}} = 14.6$ G, $a_{\beta}^{\text{H}} = 12.4$ G, $a_{\gamma}^{\text{H}} = 1.1$ G and $a^{\text{P}} = 0.5$ G.

is $\sim 10 \text{ M}^{-1} \text{ cm}^{-1}$). As indicated in Fig. 2, $[(\text{HO})_2\text{PO}_2\text{-DMPO}^*]$ increases in a linear fashion during the first minutes of the monochromatic irradiation of 25 mM $\text{K}_4\text{P}_2\text{O}_8$ in the presence of 0.3 mM DMPO. Error bars represent typical dispersion observed in three to five repeated determinations. The rate of radical trapping, obtained from the slope of the plot in Fig. 2, is $R_{\text{T}} = 1.3 \times 10^{-7} \text{ Ms}^{-1}$.

On the other hand, the rate of radical generation, R_{g} under continuous irradiation, is given by:

$$R_{\text{g}} = 2\Phi_2 I a \quad (3)$$

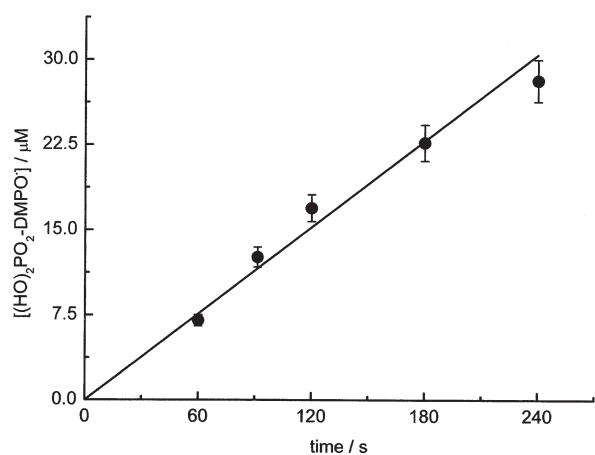


Fig. 2 $[(\text{HO})_2\text{PO}_2\text{-DMPO}]$ vs. time, as obtained by continuous irradiation of 25.0 mM $\text{K}_4\text{P}_2\text{O}_8$ and 0.3 mM DMPO at pH 4.0 at $\lambda = 275 \pm 10$ nm.

In the above expression, $2\Phi_2 = 1.6$,^{24,30} is the quantum yield of radical production in $\text{H}_2\text{P}_2\text{O}_8^{2-}$ photolysis, and $I_a = I_0 \times (1 - 10^{-A_{275}})$ is the rate of photon absorption, determined from the photon flow per unit volume, I_0 , and the absorbance of $\text{H}_2\text{P}_2\text{O}_8^{2-}$, A_{275} , at the irradiation wavelength, $\lambda = 275$ nm. From the experimental results we obtained $\eta = R_{\text{T}}/R_{\text{g}} = 0.35$, indicating that 35% of the generated radicals are trapped by 0.3 mM DMPO solutions.^{21,29}

Additionally, HPLC analysis of the aliquots indicates that the rate of DMPO consumption, $R_{\text{-DMPO}} = 1.25 \times 10^{-7} \text{ Ms}^{-1}$, determined from the slope of Fig. 3, was almost identical to the rate of radical trapping. This is taken as evidence that reaction (1) is the main—if not the only—fate of DMPO molecules, under the present experimental conditions.

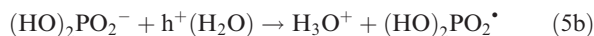
The heterogeneous phosphate/DMPO/TiO₂ system

The irradiation of a TiO₂ suspension in the presence of DMPO, yields the well-characterized HO-DMPO^{*} complex ($a^{\text{N}} = a_{\beta}^{\text{H}} = 15.3$ G),^{8,29,31,32} by reaction of the spin trap with the photoproducted intermediates, h^+ or OH:



In a previous work, we briefly explored the effect of phosphate addition ($0.01 \leq [\text{H}_2\text{PO}_4^-]/\text{mM} \leq 0.3$) on the rate of formation of HO-DMPO^{*}, $R_{\text{HO-DMPO}^*}$, in irradiated TiO₂ sols ($\lambda \geq 330$ nm), at pH = 4.0, and $[\text{DMPO}] = 0.3$ mM.⁸ Fig. 4 shows the extension of our previous study to higher phosphate concentration, up to 0.1 M.

The inhibition in adduct formation rates may result from a physical blockage of the surface active sites, and/or because the oxidizing species (h^+ , OH^*) are intercepted by phosphate ions:



Taken the specific homogeneous rate constants as a guide, $k_{4a} = 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$,²¹ and $k_{5a} = 2.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$,¹⁰ we inferred that reaction (5a) can hardly compete with reaction (4a), under present experimental conditions, since the condition $k_{5a} [\text{OH}^*][(\text{HO})_2\text{PO}_2^-] > k_{4a} [\text{OH}^*][\text{DMPO}]$ is attained at a ratio $[(\text{HO})_2\text{PO}_2^-]/[\text{DMPO}] > 1.4 \times 10^5$. If the above reasoning holds in the heterogeneous media, phosphate oxidation

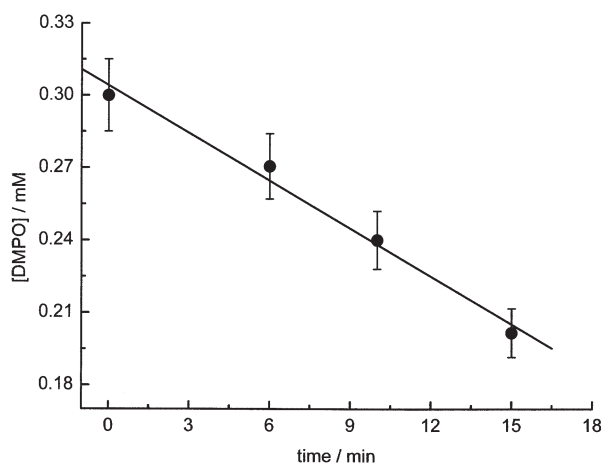


Fig. 3 $[\text{DMPO}]$ consumption during the homogeneous trapping of phosphate radicals determined by HPLC analysis in the same conditions of Fig. 2. $[\text{K}_4\text{P}_2\text{O}_8] = 25$ mM, $[\text{DMPO}] = 0.3$ mM, pH 4.0.

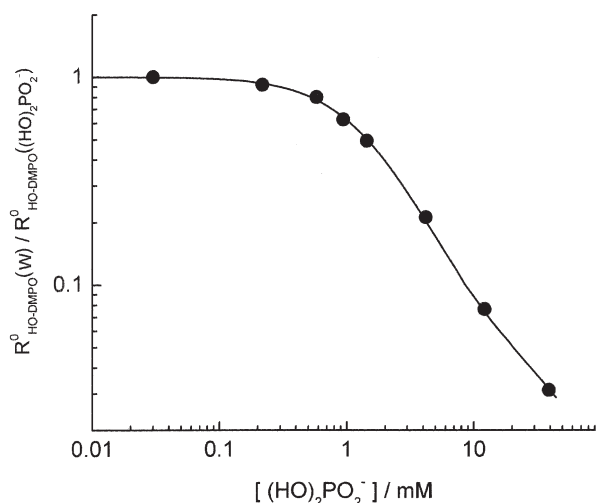


Fig. 4 Phosphate dependence on the ratio between the initial rates of HO-DMPO[•] formation, obtained by excitation of TiO₂ sols ($\lambda \geq 330$ nm), at pH = 4.0, and [DMPO] = 0.3 mM, in pure water, $R_{\text{HO-DMPO}}^0(\text{W})$, and in the presence of phosphate anions, $R_{\text{HO-DMPO}}^0((\text{HO})_2\text{PO}_2^-)$.

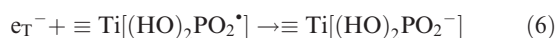
in the presence of DMPO should rather take place by direct hole capture, thus preventing OH[•] generation.

In any case, in light of the results presented in the previous section, if (HO)₂PO₂[•] radicals are formed, they are expected to become trapped by DMPO, *i.e.*, the decrease in HO-DMPO[•] should be simultaneous with the growth of the signal attributable to (HO)₂PO₂-DMPO[•]. Notice that the EPR spin trapping technique allows the monitoring of the species at extremely small conversions, *i.e.*, the determination of *initial rates* in which posterior events such as adduct decay are not involved.^{8,10,18,29,31,32}

The full characterization of the adduct between DMPO and phosphate radicals, guided us to perform a careful search for its paramagnetic signal. However, we found no evidence of (HO)₂PO₂-DMPO[•] in the whole range of our experimental conditions ($0.02 \leq [(\text{HO})_2\text{PO}_2^-] / \text{mM} \leq 100$) during the continuous monitoring of the irradiated samples, despite HO-DMPO[•] was nearly completely inhibited at the higher explored phosphate concentrations (see Fig. 4). Considering a generous detection limit for phosphate adduct, [(HO)₂PO₂-DMPO[•]] = 0.5 μM , our experiments indicate that less than $(0.5/\eta) \mu\text{M}$ of (HO)₂PO₂[•] are accumulated during the continuous monochromatic irradiation of TiO₂ suspensions, ($\lambda = 303 \pm 10$ nm, $I_a = 4.0 \times 10^{-6}$ Einstein L⁻¹ s⁻¹). Using these figures we estimated a conservative upper limit for the quantum yield of (HO)₂PO₂[•] production, $\Phi = 2.0 \times 10^{-4}$.

The displacement of the surface hydroxyl groups by specifically adsorbed ions is known to affect the nature of the surface states of the TiO₂ particles and the dynamics of the interfacial redox reactions.^{2,3,33,34} Nevertheless, taken as a guide the reversible homogeneous redox potential for the generation of phosphate radical, ($E^0((\text{HO})_2\text{PO}_2^{\bullet}) / (\text{HO})_2\text{PO}_2^-) = 2.52$ V vs. NHE),^{35,36} and the valence band edge potential, ($E_{\text{vb}} = 2.9$ V, vs. NHE), the derived yield looks unexpectedly low.²⁹

A plausible explanation for the results on Fig. 4 and the lack of observation of (HO)₂PO₂-DMPO[•] is that complexed phosphate anions, $\equiv\text{Ti}[(\text{HO})_2\text{PO}_2^-]$, are involved in a net null cycle consuming photogenerated holes and electrons (reactions 5(b)+6)



However, it should be stressed that the upper limit for phosphate radical production is derived from direct evidence, *i.e.*, independent of the actual mechanism of inhibition.

Conclusions

We generated phosphate radicals by homogeneous UV photolysis of peroxodiphosphate anions in the presence of DMPO and we fully characterized the adduct formed between (HO)₂PO₂[•] and the spin trap, for the first time. These results were used to quantitatively explore the involvement of (HO)₂PO₂[•] radicals in UV irradiated TiO₂ particles in the presence of (HO)₂PO₂⁻ anions.

At variance with previous suggestions,¹ the low upper bound for the yield of (HO)₂PO₂[•] determined in this work, $\Phi = 2.0 \times 10^{-4}$, rules out the contribution of this radical to the oxidation of organic compounds in photocatalytic TiO₂ / (HO)₂PO₂⁻ systems.

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- 35 The value ($E^0((\text{HO})_2\text{PO}_2^*/(\text{HO})_2\text{PO}_2^-) = 2.5$ V corresponds to pH 4.0. It was evaluated from $E^0((\text{HO})_2\text{PO}_2^*, \text{H}^+/\text{H}_3\text{PO}_4) = 2.65$ V,⁵ and $\text{p}K_{a_1}(\text{H}_3\text{PO}_4) = 2.15$.
- 36 The standard free energy for the interfacial oxidation of phosphate anions involves the redox potential of the surface coordinated species and not its homogeneous counterpart.