

Kinetic study of the oxidation of phenolic derivatives of α,α,α -trifluorotoluene by singlet molecular oxygen [$O_2(^1\Delta_g)$] and hydrogen phosphate radicals

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The oxidation kinetics and mechanism of the phenolic derivatives of α,α,α -trifluorotoluene, 2-trifluoromethylphenol, 3-trifluoromethylphenol (3-TFMP), 4-trifluoromethylphenol and 3,5-bis(trifluoromethyl)phenol, mediated by singlet molecular oxygen, $O_2(^1\Delta_g)$, and hydrogen phosphate radicals were studied, employing time-resolved $O_2(^1\Delta_g)$ phosphorescence detection, polarographic determination of dissolved oxygen and flash photolysis. All the substrates are highly photo-oxidizable through a $O_2(^1\Delta_g)$ -mediated mechanism. The phenols show overall quenching constants for $O_2(^1\Delta_g)$ of the order of $10^6 \text{ M}^{-1} \text{ s}^{-1}$ in D_2O , while the values for the phenoxide ions in water range from 1.2×10^8 to $3.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The effects of the pH and polarity of the medium on the kinetics of the photo-oxidative process suggest a charge-transfer mechanism. 2-Trifluoromethyl-1,4-benzoquinone is suspected to be the main photo-oxidation product for the substrate 3-TFMP. The absolute rate constants for the reactions of $HPO_4^{\cdot-}$ with the substrates range from 4×10^8 to $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The 3-trifluoromethylphenoxy radical was observed as the organic intermediate formed after reaction of 3-TFMP with $HPO_4^{\cdot-}$, yielding 2,2'-bis(fluorohydroxymethyl)biphenyl-4,4'-diol as the end product. The observed results indicate that singlet molecular oxygen and hydrogen phosphate radicals not only react at different rates with the phenols of α,α,α -trifluorotoluene, but the reactions also proceed through different reaction channels.

Introduction

Numerous constituents of natural and atmospheric water contribute to the photochemical and/or thermal production of highly reactive species, such as HO^\cdot , $HO_2^\cdot/O_2^{\cdot-}$, singlet molecular oxygen [$O_2(^1\Delta_g)$], $CO_3^{\cdot-}$, $SO_4^{\cdot-}$, and organic peroxy radicals.^{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^\cdot and/or $SO_4^{\cdot-}$ radicals are among the most reactive and highly oxidative species, and their photochemical generation is being used as a benign method for detoxification of polluted water streams.³ The presence of inorganic components in the aqueous matrix is of importance in the chemistry related to these reactive species; HO^\cdot and/or $SO_4^{\cdot-}$ 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^\cdot and $SO_4^{\cdot-}$ radicals with phosphate ions yields phosphate radicals ($H_2PO_4^\cdot$, $HPO_4^{\cdot-}$, $PO_4^{\cdot 2-}$).^{4,5}

Despite its short lifetime of about 4 μs in water, singlet molecular oxygen, $O_2(^1\Delta_g)$, is present in steady-state concentrations in sunlit water which can exceed 10^{-14} M . Under such conditions, phenolic substrates present in natural water are very likely to be degraded by $O_2(^1\Delta_g)$ (for reviews, see ref. 6 and 7).

As both hydrogen phosphate radicals and singlet molecular oxygen may be present in sunlit phosphate-containing natural

waters, it is of environmental interest to study their reactivity towards model contaminants, such as phenols. These compounds are primary pollutants which are released into water streams and whose fate needs particular attention.

In a previous paper,⁸ we studied the reaction of HO^\cdot , $SO_4^{\cdot-}$ and phosphate radicals ($H_2PO_4^\cdot$, $HPO_4^{\cdot-}$, $PO_4^{\cdot 2-}$) with α,α,α -trifluorotoluene (TFT). TFT is a flammable, corrosive reagent used in the manufacture of high molecular weight polymers, in dielectric fluids and in dye chemistry, and, consequently, is of environmental concern. Phenolic species are primary oxidation products formed by reaction of TFT with HO^\cdot , $SO_4^{\cdot-}$, $H_2PO_4^\cdot$ and $HPO_4^{\cdot-}$ radicals.⁶

Here, we report a study on the reactions of $O_2(^1\Delta_g)$ and $HPO_4^{\cdot-}$ radicals with the phenolic derivatives of TFT: 2-trifluoromethylphenol (2-TFMP), 3-trifluoromethylphenol (3-TFMP), 4-trifluoromethylphenol (4-TFMP) and 3,5-bis(trifluoromethyl)phenol (3,5-TFMP).

Experimental

2-TFMP, 3-TFMP, 4-TFMP and 3,5-TFMP, Rose Bengal, KH_2PO_4 , K_2HPO_4 , and NaOH (99.99%) (all from Merck) were used as received. Furfuryl alcohol was purchased from Riedel de Haën. Distilled water ($>18 \Omega \text{ cm}^{-1}$, $<20 \text{ ppb}$ of organic carbon) was obtained from a Millipore system.

The dissociation pK_a values of 2-TFMP and 3,5-TFMP were obtained from the spectrometric titration of $1.20 \times 10^{-4} \text{ M}$ aqueous solutions of the phenols with NaOH.

Singlet oxygen experiments

The values of the overall quenching rate constant, k_t , in several solvents were measured by time-resolved phosphorescence detection (TRPD). These experiments were performed with a Spectron SL400 Nd-YAG system generating 532 nm pulses (~8 ns pulse width). A quartz cell in a 90° geometry was used. The detection and acquisition systems are described elsewhere.⁹ The solvents employed were D₂O or D₂O–MeCN mixtures containing from 20 to 80% MeCN by volume. Solutions containing the sensitizer and the substrate in D₂O showed pD values of 5.5. For experiments involving phenoxide ions, the pD was adjusted to 12.5 by addition of NaOH. pD values were obtained by adding 0.4 to the measured pH values.¹⁰

For the measurement of dissolved oxygen consumption, continuous irradiation of the sensitizer contained in a closed 150 ml flask was performed with a Philips HPK 125 W lamp and the oxygen concentration measured with an oxygen-sensitive electrode (Orion 97-0899). These experiments employed H₂O as solvent. When required, the pH of the solutions was adjusted by addition of NaOH.

Rose Bengal was used as sensitizer in all the experiments. Absorbance values of $A^{532} = 0.2$ – 0.3 and substrate concentrations of <0.6 mM were employed in TRPD experiments, while oxygen consumption experiments had $A^{532} = 0.6$ and substrate and furfuryl alcohol concentrations of 0.5 mM.

Phosphate radical experiments

Potassium peroxodiphosphate was obtained electrochemically as described in the literature.¹¹

Phosphate radicals present two acid-base equilibria in aqueous solutions. In order to study the reactions of HPO₄^{•-}, the pH of the samples was adjusted with KH₂PO₄–K₂HPO₄ mixtures to 7.1 ± 0.1 . The ionic strength of the solutions was within the range 0.1–0.2 M. Flash photolysis experiments were carried out in a conventional apparatus (Xenon Co. model 720C) with modified optics and electronics.¹² 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 order to avoid product accumulation, each solution was irradiated only once. Signals arising from single shots were averaged.

Product analysis

Product analysis was performed by gas chromatography with an HP 5890 Series II Plus chromatograph equipped with a fused silica HP5-MS GC capillary column and coupled to an HP 5972A mass selective detector. The temperature program was 50 °C isothermal, then heating to 250 °C at 10 °C min⁻¹ and held at 250 °C for 5 min. Samples were taken from irradiated solutions in flash photolysis experiments. Because the very low yields of products obtained during irradiation with one flash of light are below the limits of detection of our chromatographic equipment (10⁻⁵ M), the organic products were concentrated in Sep-Pak C18-type cartridges and extracted with 2 ml diethyl ether. The injection volume was 1 μL. Extracts were injected without derivatization.

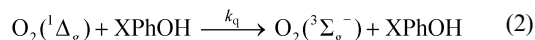
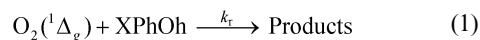
In order to favor the extraction of the organic products, solutions at pH >8 were neutralized with perchloric acid before concentration in the cartridges.

Results and discussion

Reactions of the substrates with singlet molecular oxygen

Scavenging of O₂(¹Δ_g) by phenols (XPhOH) takes place by two main pathways: (i) a chemical reaction with rate constant k_t (eqn. 1) and (ii) a physical interaction with quenching constant k_q (eqn. 2). In the latter equation, O₂(³Σ_g⁻) is the ground state of

molecular oxygen. The bimolecular rate constant for the overall process, $k_t = k_r + k_q$, includes the contribution of both reaction channels.



In order to separate the contribution of the phenols and phenoxide ions to k_t and k_r , the dissociation pK_a of the substrates is needed. For 3- and 4-TFMP, the pK_a values (Table 1) were calculated from the reported changes in normal free energy of dissociation with respect to phenol¹³ and the pK_a value of phenol.¹⁴ The pK_a values for 2-TFMP and 3,5-TFMP were calculated from the pH dependence of the absorbances at $\lambda_{\text{max}} = 240$ and 244 nm, respectively, where only the phenoxide ion absorbs, as shown in Fig. 1 for 2-TFMP. Fitting of the curve in the inset of Fig. 1 with eqn. 3,¹⁵ yields the corresponding pK_a

$$A = \varepsilon_{\text{PhO}^-} \lambda C_0 \frac{1}{10^{(\text{pK}_a - \text{pH})} + 1} \quad (3)$$

values depicted in Table 1. The values of the absorption coefficient of PhO⁻ at λ_{max} , are $\varepsilon_{\text{PhO}^-} = 7.3 \times 10^3$ and $1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for 2-TFMP and 3,5-TFMP, respectively, and the optical length is $l = 1 \text{ cm}$.

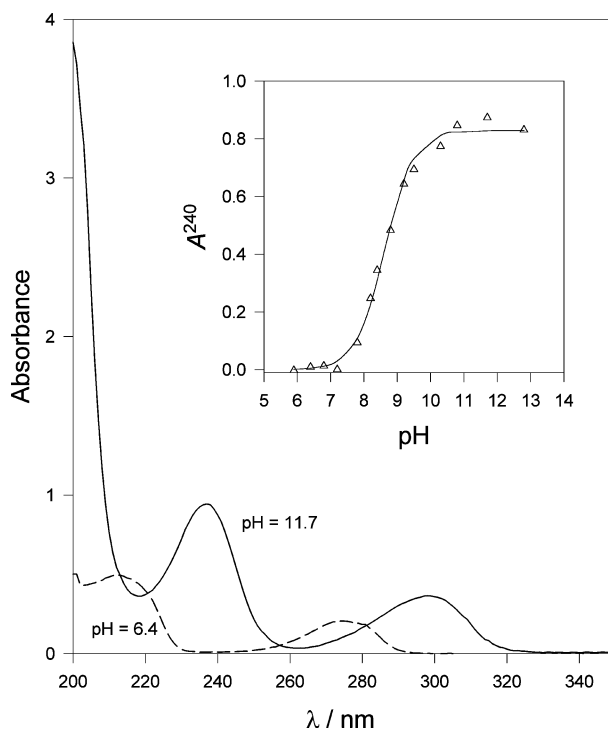


Fig. 1 Absorption spectra of 2-TFMP at pH 6.4 (---) and of its phenoxide ion at pH 11.7 (—). Inset: absorbance at 240 nm vs. pH. The solid line shows the fitting of the data to eqn. 3.

Typical singlet oxygen phosphorescence traces obtained at 1270 nm are shown in Fig. 2 (inset A).

The lifetime of singlet oxygen in the solutions containing the sensitizer, τ_{Δ} , was found to decrease with increasing concentration of added substrate, according to eqn. 4.¹⁰

$$1/\tau_{\Delta} = 1/\tau_{\Delta}^0 + k_t[S] \quad (4)$$

where S denotes the substrate XPhOH or XPhO⁻ and τ_{Δ}^0 is the lifetime of singlet oxygen in the absence of S. Typical plots of $1/\tau_{\Delta}$ vs. [S] are shown in Fig. 2. The value of τ_{Δ}^0 in D₂O obtained from the plots was in very good agreement with those reported

Table 1 pK_a values of the phenolic derivatives of TFT in water, k_t for XPhOH and XPhO⁻ in D₂O and k_r for XPhO⁻ in water

Substrate	pK_a	$k_t(\text{XPhOH})/10^6 \text{ M}^{-1} \text{ s}^{-1}$	$k_t(\text{XPhO}^-)/10^8 \text{ M}^{-1} \text{ s}^{-1}$	$k_r(\text{XPhO}^-)/\text{M}^{-1} \text{ s}^{-1}$
2-TFMP	8.62 ± 0.04^a	5 ± 2	2.0 ± 0.4	$(1.11 \pm 0.09) \times 10^8$
3-TFMP	8.84 ± 0.02^b	3.5 ± 0.2	3.6 ± 0.8	$(1.30 \pm 0.08) \times 10^8$
4-TFMP	8.56 ± 0.02^b	4 ± 2	1.18 ± 0.06	$(1.9 \pm 0.1) \times 10^7$
3,5-TFMP	8.16 ± 0.03^a	3.2 ± 0.8	1.8 ± 0.2	$(6.5 \pm 0.8) \times 10^7$

^a This work. ^b Calculated from ΔG values reported in ref. 13 and the pK_a value of phenol.¹⁴

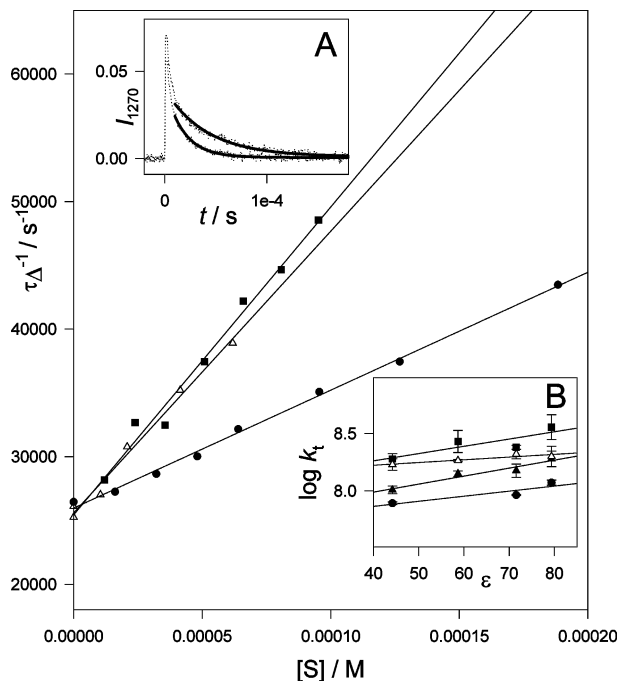


Fig. 2 Plot of $1/\tau_A$ vs. substrate concentration, $[S]$, in 1:4 MeCN–D₂O containing 0.01 M NaOH for 2-TFMP (Δ), 3-TFMP (\blacksquare) and 4-TFMP (\bullet). Inset A: phosphorescence decay obtained from a Rose Bengal solution ($A^{532} = 0.2$) in the absence (upper trace) and presence of 3.63×10^{-4} M 4-TFMP (lower trace) in 4:1 MeCN–D₂O. The solid lines show the fitting to a single exponential decay. Inset B: dependence of $\log k_t$ on the dielectric constant of the medium.

in the literature.¹⁶ The values of k_t for XPhOH and XPhO⁻ in D₂O are listed in Table 1.

The values of k_t measured in different D₂O–MeCN mixtures for XPhO⁻ was found to increase with the dielectric constant of the solvent, as shown in Fig. 2(inset B) for all the phenoxides studied here. The dielectric constant (ϵ) of a H₂O–MeCN mixture can be calculated as $1/\epsilon = (1.26 \times 10^{-2}) + x_{\text{MeCN}}(1.73 \times 10^{-2})$, where x_{MeCN} is the molar fraction of acetonitrile.¹⁷ The latter equation was used here for the D₂O–MeCN mixtures due to the very similar dielectric constants of H₂O and D₂O [$\epsilon(\text{D}_2\text{O}) = 77.9$, $\epsilon(\text{H}_2\text{O}) = 78.3$ at 25 °C].¹⁸

Oxygen consumption experiments performed under continuous irradiation in the presence of substrate S yield information on k_r . If reaction 1 is the only sink of molecular oxygen and one mole of substrate is assumed to react with one mole of oxygen,⁶ the rate of molecular oxygen consumption, $-d[\text{O}_2]/dt$, is given by eqn. 5.

$$-d[\text{O}_2]/dt = k_r[\text{S}][\text{O}_2(^1\Delta_g)]_{\text{ss}} \quad (5)$$

where $[\text{O}_2(^1\Delta_g)]_{\text{ss}}$ is the steady-state concentration of $\text{O}_2(^1\Delta_g)$. For low oxygen consumption, $[\text{O}_2(^1\Delta_g)]_{\text{ss}}$ may be considered constant and integration of eqn. 5 leads to eqn. 6.

$$\ln([\text{O}_2]/[\text{O}_2]_0) = -k_r t [\text{O}_2(^1\Delta_g)]_{\text{ss}} \quad (6)$$

Eqn. 6 predicts a pseudo-first-order slope proportional to k_r . Thus, the ratio of these slopes to those obtained from com-

parative experiments under identical experimental conditions, but with a reference substrate for which k_r is known, allows determination of k_r for each of the substrates studied here.²⁰ The value of $k_r = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ¹⁵ for furfuryl alcohol is pH independent. This compound is thus an appropriate reference for a study of the pH effect on k_r for the phenolic substrates. Fig. 3 shows typical first-order oxygen uptake plots for furfuryl alcohol and 3-TFMP at two different pH values. The pH dependence of k_r , as shown in the inset of Fig. 3 for 3-TFMP, may be fitted to eqn. 7, where $k_t(\text{XPhOH})$ and $k_t(\text{XPhO}^-)$ are the values of k_t for the phenol and phenoxide ion, respectively. From the fittings, $k_t(\text{XPhOH})$ is estimated to be $\leq 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for all the phenols studied here and the values of $k_t(\text{XPhO}^-)$ are shown in Table 1.

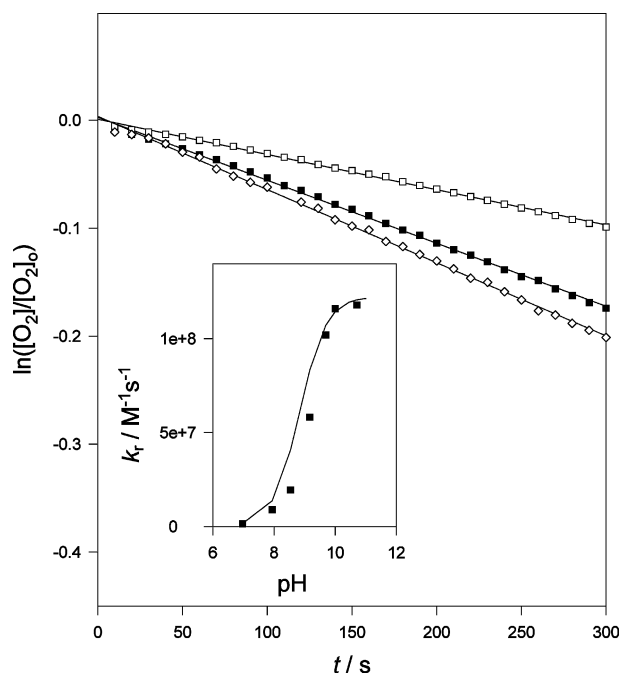


Fig. 3 First-order plots for oxygen uptake obtained with Rose Bengal solutions ($A^{532} = 0.6$) containing 5×10^{-4} M 3-TFMP at pH 9.69 (\blacksquare) and at pH 9.17 (\square), and FFA at pH 11.93 (\diamond). Inset: pH effect on k_r for 3-TFMP. The solid line shows the fitting of the data to eqn. 7.

$$k_r = k_t(\text{XPhO}^-) \cdot \left(\frac{10^{(pK_a - \text{pH})}}{10^{(pK_a - \text{pH})} + 1} \right) + k_t(\text{XPhOH}) \cdot \left(\frac{1}{10^{(pK_a - \text{pH})} + 1} \right) \quad (7)$$

Both the values of k_t and k_r obtained here for the phenolic derivatives of TFT indicate that, in all cases, the phenoxide ions are much better singlet oxygen quenchers than the corresponding phenols (see Table 1) and that the efficiency of the overall quenching process is increased with increasing solvent polarity [see Fig. 2(inset B)].

The values of k_t measured here in D₂O for the phenolic derivatives of TFT are of the same order as those reported for phenol and its monosubstituted derivatives ($k_t > 10^6 \text{ M}^{-1} \text{ s}^{-1}$)²¹ and higher than that reported for TFT ($1.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$).²²

The k_t values for 2-TFMP, 3-TFMP and 4-TFMP fall in the Hammett free-energy correlation of $\log k_t$ vs. the σ parameters observed for monosubstituted phenols, XPhOH, (Fig. 4), taking phenol as the parent compound ($\sigma = 0$) and $\sigma = 0.45, 0.43$ and 0.54 for CF_3 substituents in the *ortho*, *meta* and *para* positions, respectively.¹⁹ The observed negative slope value, ρ , suggests electrophilic attack of singlet oxygen on the aromatic substrate.

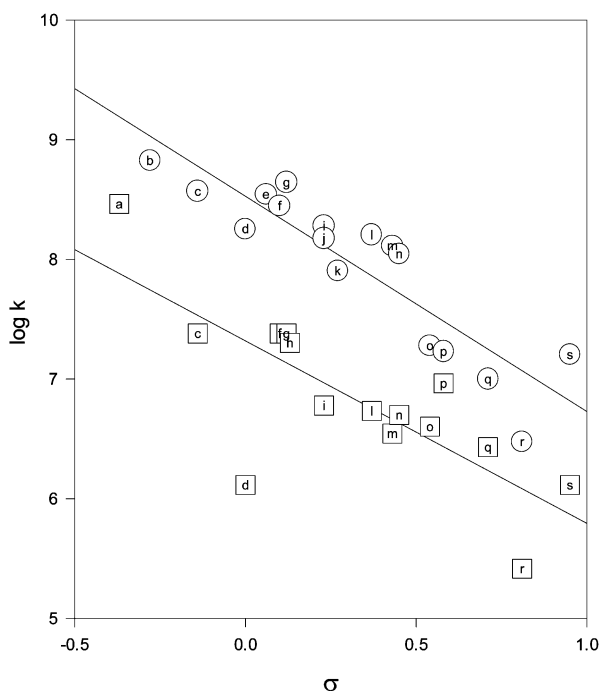
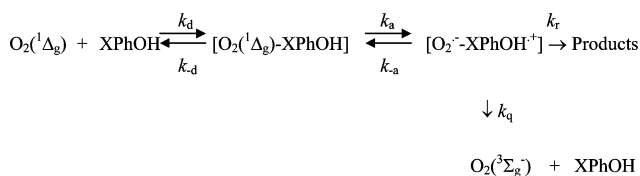


Fig. 4 Hammett free-energy correlation of $\log k_t$ for monosubstituted phenols, XPhOH, (\square) and of $\log k_t$ for monosubstituted phenoxide ions, XPhO⁻, (\circ) vs. the σ parameters: X = *p*-OH (a); *p*-OCH₃ (b); *p*-CH₃ (c); H (d); *p*-F (e); *m*-OCH₃ (f); *o*-OCH₃ (g); *m*-OH (h); *p*-Cl (i); *p*-Br (j); *p*-I (k); *m*-Cl (l); *m*-CF₃ (m); *o*-CF₃ (n); *p*-CF₃ (o); *o*-Cl (p); *m*-NO₂ (q); *p*-NO₂ (r); *o*-NO₂ (s). The rate constants were taken from ref. 16 for most compounds. The rate constants for *m*-, *o*- and *p*-CF₃ were taken from this work. The σ parameters are from ref. 19.

The reactive constant values, k_r , for the phenoxide ions of 2-TFMP, 3-TFMP and 4-TFMP fall in the Hammett free-energy correlation of $\log k_r$ vs. the σ parameters (Fig. 4) observed for monosubstituted phenoxide ions (XPhO⁻), also showing a negative slope. On the other hand, although the published k_t values are very dispersed and no Hammett correlation is observed, the k_t values obtained here decrease with the increasing electron-accepting effect of the CF_3 substituents in the *ortho*, *meta* and *para* positions on the phenolic ring, in agreement with their σ parameters. Moreover, the presence of an additional CF_3 electron-acceptor group, as in 3,5-TFMP, further decreases k_t with respect to 3-TFMP. Similar observations hold for k_t and k_r of the respective phenoxide ions.

The previous observations are in agreement with the electrophilic character of singlet molecular oxygen. Therefore, the present data further support the charge-transfer mechanism proposed for $\text{O}_2(^1\Delta_g)$ quenching by phenols shown in Scheme 1.²³⁻²⁶



Scheme 1 Charge-transfer mechanism proposed for the quenching of $\text{O}_2(^1\Delta_g)$ by phenols.

In this scheme, k_d and k_{-d} are the diffusion-controlled rate constants for formation and decomposition of the precursor complex $[\text{O}_2(^1\Delta_g)\text{-XPhOH}]$ and k_a and k_{-a} are the rate constants for the charge transfer from phenol to $\text{O}_2(^1\Delta_g)$.

The value of k_r for 4-TFMP in water falls in the curve describing the Marcus treatment for the chemical quenching of singlet molecular oxygen by phenols,²⁶ taking the reported redox potential, E^0 (XPhO⁻/XPhOH = 0.954 V²⁷), for this substrate. This behavior provides further support for the view that the phenolic derivatives of TFT react with singlet molecular oxygen according to the mechanism depicted in Scheme 1.

In order to identify the products of the reaction of $\text{O}_2(^1\Delta_g)$ with the phenoxide of 3-TFMP, aqueous solutions containing Rose Bengal ($A^{532} = 0.6$) and 5×10^{-4} M 3-TFMP at pH 11 were irradiated under steady-state conditions. Comparison of the UV-visible absorption spectra before and after irradiation shows depletion of the phenoxide absorption band ($\lambda_{\text{max}} \approx 300$ nm) upon irradiation and the concomitant formation of two absorption bands with λ_{max} around 220 and 265 nm due to the reaction products (Fig. 5). These new bands may be assigned to 2-trifluoromethyl-1,4-benzoquinone, since, upon substitution, the 1,4-benzoquinone bands at 240 and 278 nm are expected to be shifted: to visible wavelengths for electron-donating substituents and to the UV region for electron acceptors. Despite our effort to identify the observed product by GC-MS, no products were detected by this technique with our experimental set-up and sample manipulation procedure. An important conclusion from the GC-MS experiments is that condensation products of the organic substrates are not formed in the reaction of 3-TFMP with singlet oxygen.

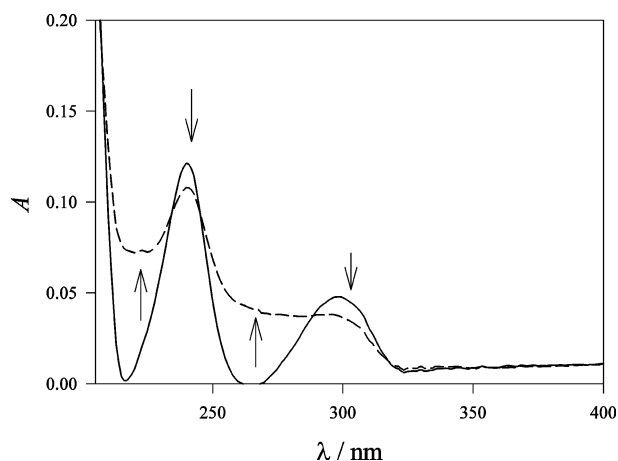


Fig. 5 Absorption spectra of a Rose Bengal ($A^{532} = 0.6$) solution containing 5×10^{-4} M 3-TFMP at pH 11 before (—) and after (---) 3 h irradiation.

Formation of 2-trifluoromethyl-1,4-benzoquinone is in agreement with the work of Li and Hoffman,¹⁴ who detected 1,4-benzoquinone as the only product for the reaction of $\text{O}_2(^1\Delta_g)$ with phenol. The formation yields of 1,4-benzoquinone depend on solvent, pH, temperature and on the concentrations of molecular oxygen and phenol. The proposed mechanism¹⁴ involves the formation of a singlet oxygen-phenol adduct, leading to an endoperoxide which further rearranges to a hydroperoxycyclohexadienone. The latter intermediate may finally lose water to yield 1,4-benzoquinone.

Reactions of the substrates with hydrogen phosphate radicals

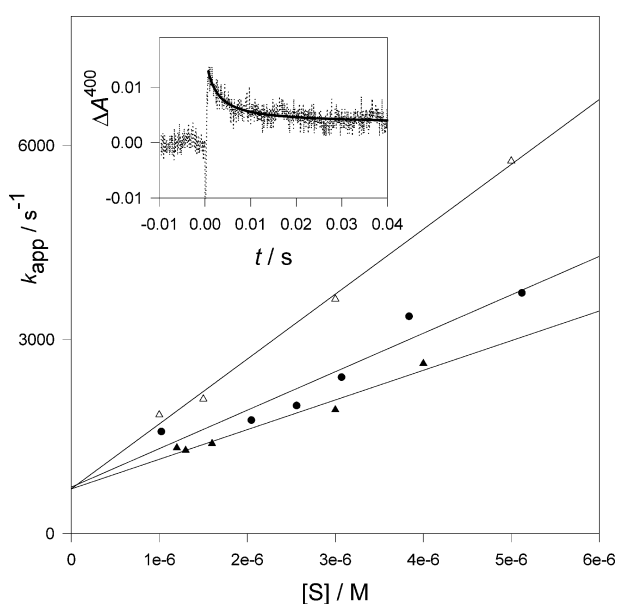
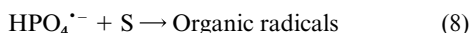
The reactions of $\text{HPO}_4^{\cdot-}$ radicals with the substrates (reaction 8), are conveniently studied by following the $\text{HPO}_4^{\cdot-}$ radical decay rate as a function of added solute concentration. Photolysis experiments of $\text{P}_2\text{O}_8^{4-}$ solutions of pH 7.1, in the presence of low concentrations of substrates ($[\text{S}] < 1 \times 10^{-5}$ M) showed absorption traces at $\lambda > 400$ nm, whose spectrum immediately

Table 2 Rate constants for the reactions of $\text{HPO}_4^{\cdot-}$ with various substrates

Substrate	$k_8/\text{M}^{-1} \text{s}^{-1}$
TFT	$(2.7 \pm 0.5) \times 10^6$ ^a
2-TFMP	$(1.00 \pm 0.05) \times 10^9$
3-TFMP	$(7 \pm 1) \times 10^8$
4-TFMP	$(5.9 \pm 0.9) \times 10^8$
3,5-TFMP	$(4.4 \pm 0.9) \times 10^8$
Phenol	$(5.3 \pm 0.4) \times 10^8$ ^b

^a From ref. 11. ^b From ref. 28.

after the flash of light matched that of the hydrogen phosphate radicals. The absorption traces showed faster decay kinetics with increasing concentrations of the organic substrates and could be fitted well to a first-order law with an apparent rate constant, k_{app} . The slopes of the linear plots of k_{app} vs. substrate concentration (see Fig. 6) yield the bimolecular rate constants k_8 .¹¹ Table 2 shows the values of k_8 for the substrates studied in this work, and those for phenol and TFT for comparative purposes.

**Fig. 6** Apparent rate constants, k_{app} , for the decay of $\text{HPO}_4^{\cdot-}$ radicals in the presence of: 2-TFMP (Δ), 4-TFMP (\bullet), and 3,5-TFMP (\blacktriangle). Inset: Trace obtained at $\lambda = 400$ nm with 1.4×10^{-3} M $\text{K}_4\text{P}_2\text{O}_8$ solution at pH 8 in the presence of 5.7×10^{-4} M 3-TFMP.

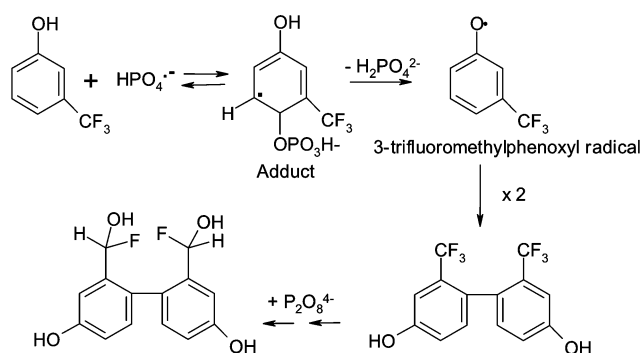
Previous studies showed that the bimolecular rate constants k_8 obtained for the reactions of several aromatic substrates with $\text{HPO}_4^{\cdot-}$ radicals correlate with the electron-withdrawing ability of the substituent, as expected from the electrophilicity of these radicals.²⁸ The good correlation reported between $\log k_8$ and the substituent Hammett parameter, σ^+ ,²⁸ implies that the transition state of the reaction has either significant polar character or important resonance interaction with the substituents. The proposed mechanism²⁸ considers formation of an adduct between the phosphate radicals and the aromatics, which may decay by different reaction channels, leading to either hydroxycyclohexadienyl radicals, phenoxy radicals or the substrate radical cation. The k_9 values measured here decrease in the order $\text{PhOH} > 3\text{-TFMP} > 2\text{-TFMP} > 4\text{-TFMP}$, following the increase in the σ parameters observed when the CF_3 group is in the *meta*, *ortho* and *para* positions of the phenolic ring (*vide supra*); all these rate constants are higher than that of TFT, in agreement with the expected behavior for the phosphate radicals. Moreover, the presence of an additional CF_3 in 3,5-TFMP

further decreases k_9 with respect to the phenolic derivatives with only one CF_3 group.

In order to obtain further information on reaction 8, the nature of the organic intermediates was determined. For this purpose, flash-photolysis experiments of peroxodiphosphate solutions of pH 7.1 in the presence of 3-TFMP concentrations of $>5 \times 10^{-4}$ M were performed. Under such experimental conditions, depletion of $\text{HPO}_4^{\cdot-}$ radicals takes place within less than 100 μs and formation of transient species absorbing in the wavelength region from 300 to 450 nm due to the organic radicals formed through reaction 8 were observed. The decay rates of the traces obtained in the 280–450 nm region are independent of the dissolved oxygen concentration and follow second-order kinetics with $2k/e = (4.8 \pm 1.0) \times 10^5 \text{ cm s}^{-1}$ (see inset of Fig. 6). The analysis of the traces at lower wavelengths is more complex due to formation of reaction products which absorb in this region. These observations are in agreement with the absorption spectra of the irradiated solutions showing depletion of the band with $\lambda_{\text{max}} = 280$ nm and the concomitant formation of bands at $\lambda \approx 240$ and 300 nm due to stable reaction products (inset of Fig. 5). The observed spectrum is assigned to 2,2'-bis(fluorohydroxymethyl)biphenyl-4,4'-diol, which was the only reaction product detected by GC-MS.

Phenoxy radicals show characteristic absorption maxima at 300 nm (ϵ^{300} of the order of $5300 \text{ M}^{-1} \text{ cm}^{-1}$) and lower intensity at 400 nm (ϵ^{400} of the order of $1600 \text{ M}^{-1} \text{ cm}^{-1}$). The traces observed at 400 nm show decay oxygen-independent lifetimes of the order of milliseconds and are assigned to the 3-trifluoromethylphenoxy radical^{29–32} (see inset of Fig. 6). Recombination of the latter radicals leads to the formation of 2,2'-bis(trifluoromethyl)biphenyl-4,4'-diol, which may further undergo fluorine atom loss in subsequent thermal reactions with peroxodiphosphate, leading to the observed product, as was also reported for the oxidized products of TFT.⁷

The proposed mechanism shown in Scheme 2 considers the observed intermediate and product and the reported behavior of phosphate radicals towards aromatic substrates.²⁸ 3-Trifluoromethylphenoxy radicals are formed from the phosphate radical adduct of 3-TFMP *via* loss of hydrogen phosphate ions. Recombination of phenoxy radicals leads to the biphenyl reaction product.

**Scheme 2** Proposed mechanism for the reaction of $\text{HPO}_4^{\cdot-}$ with 3-TFMP.

Conclusions

The mechanism of the singlet oxygen reactions with the substrates involves the electrophilic attack of $\text{O}_2(^1\Delta_g)$ on the aromatics through a charge-transfer mechanism, which, in the case of 3-TFMP at least, leads to an addition intermediate which evolves to 2-trifluoromethyl-1,4-benzoquinone. On the other hand, the reaction of the same substrates with hydrogen phosphate radicals, which are also electrophilic in nature, leads to radical adducts, yielding organic radicals which then form condensation products different from those observed in the reactions with singlet oxygen.

The dissimilar reactivity of singlet oxygen and inorganic radicals towards organic molecules was also recently demonstrated for substrates of biological interest, such as nucleobases,³³ lipids³⁴ and peptides.³⁵

Singlet oxygen is much less reactive towards undissociated trifluoromethylphenols than the HPO_4^{2-} radicals, however, its reaction products are much more oxidized than the biphenyls obtained with the latter radicals and, therefore, more prone to undergo further biological mineralization. This conclusion is of relevance to the choice of suitable waste-water procedures for the elimination of phenolic contaminants.

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