Photodegradation of bisphenol A and related compounds under natural-like conditions in the presence of riboflavin: Kinetics, mechanism and photoproducts

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ABSTRACT

The aerobic riboflavin (Rf)-sensitized photodegradation of the endocrine disruptor 4,4′-isopropylidenebisphenol (bisphenol A, BPA), and of the related compounds 4,4′-isopropylidenebis(2,6-dibromophenol) and 4,4′-isopropylidenebis(2,6-dimethylphenol) has been studied in water and water–methanol mixtures through visible-light continuous photolysis, polarographic detection of oxygen uptake, stationary and time-resolved fluorescence spectroscopy, time-resolved near-IR phosphorescence detection and laser flash photolysis techniques. Bisphenols (BPs) quench excited singlet and triplet states of Rf, with rate constants close to the diffusion limit. BPs and dissolved molecular oxygen, employed in similar concentrations, competitively quench triplet excited Rf. As a consequence, superoxide radical anion and singlet molecular oxygen ($O_2(^1\Delta_g)$) are produced by electron- and energy-transfer processes, respectively, as demonstrated by auxiliary experiments employing selective quenchers of both oxidative species and the exclusive $O_2(^1\Delta_g)$ generator Rose Bengal. As a global result, the photodegradation of Rf is retarded, whereas BPs are degraded, mainly by an $O_2(^1\Delta_g)$-mediated mechanism, which constitutes a relatively efficient process in the case of BPA. Oxidation, dimerization and fragmentation products have been identified in the photooxidation of BPA. Results indicate that BPs in natural waters can undergo spontaneous photodegradation under environmental conditions in the presence of adequate photosensitizers.

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1. Introduction

Bisphenol A (BPA) is profusely used in the industrial production of epoxy resins, polycarbonate plastics and a variety of polymers (Katsumata et al., 2004; Zhan et al., 2006b) – materials widely employed in the packaging of foods, in the preparation of domestic bottles and envelopes, etc. Unfortunately, BPA is also a well-known endocrine disruptor agent that contaminates surface waters through waste waters of industries producing BPA or BPA-containing products, or by leaching or dissolution of discarded final products (Neamtu and Frimmel, 2006). This worrying situation has triggered the study of the induced or natural degradation – including the photochemical decomposition – of this contaminant in different types of waters (Cousins et al., 2002).

In the natural environment, BPA is degraded through two main oxidative pathways: biological processes and sensitized photooxidations. In waste waters, BPA is effectively oxidized by treatment with the enzyme laccase. Also, *p*-isopropenylphenol (Fukuda et al., 2001) and the dimer from the *o,o′*-coupling (*ortho* to OH) (Uchida et al., 2001) have been observed among the degradation products. With the enzyme tyrosinase, a BPA derivative with an additional *o*-OH group and its corresponding *o*-quinone have been suggested as reaction products, but their structures have not been confirmed (Andreescu et al., 2004).

Concerning the natural photochemical decomposition, BPA is colorless and cannot be degraded by direct irradiation with visible light. The irradiation of aqueous BPA solutions with UV light gives rise to its effective degradation and to the reduction of the estrogenic activity of the contaminated medium (Chen et al., 2006). In the presence of nitrate ions, *p*-isopropenylphenol, *p*-isopropylphenol, *p*-ethylphenol, *p*-hydroxyacetophenone, a BPA molecule with an additional oxygen, and some nitroaromatic compounds have been detected in the UV-irradiated medium (Zhan et al., 2006b). Similarly, irradiation of BPA in water with UV light in the presence of different amounts of hydrogen peroxide (Neamtu and Frimmel, 2006), or of hydrogen peroxide and Fe(II) (photo-Fenton process) (Katsumata et al., 2004), are also efficient methods for BPA photodegradation. Nevertheless, all these highly aggressive artificial photochemical methods are energetically expensive and, in general, only applicable to contaminated waters confined in containers.

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BPA can be degraded under visible light irradiation if some compounds (photosensitizers), able to absorb this light and to generate reactive oxygenated species, are present in the same aqueous environment. In nature, this photodegradation process may concur with the aerobic microbial process. Many dissolved organic compounds (humic substances) usually present in the natural aqueous medium can act as photosensitizers under solar irradiation (Chin et al., 2004), and *p*-isopropenylphenol, *p*-hydroxypropanoic acid, glycerol, hydroquinone and an oxidized BPA of unknown structure have been identified by GC–MS analysis of the irradiated solution (Zhan et al., 2006a).

Under laboratory conditions and in the presence of phthalocyanine complexes, BPA has been efficiently degraded under visible light irradiation through a pH-dependent process mediated by singlet molecular oxygen, $O_2(^1\Delta_g)$, yielding oxalic acid, maleic acid, *p*-isopropenylphenol and hydroquinone (Tai et al., 2005). On the other hand, mineralization has been observed in the visible light irradiation of aqueous solutions of BPA in the presence of TiO_2, probably via radical reactions that give rise to some of the former products (Watanabe et al., 2003).

Riboflavin (Rf, vitamin B_2), a well-known natural pigment present as traces in waters of rivers, lakes and seas (Chacón et al., 1988), has been postulated as a possible sensitizer for the natural photooxidative degradation of contaminants (García and Amat-Guerri, 2005). The accepted photochemical mechanism of Rf sensitization, depicted in Scheme 1 for the photooxidation of a bisphenol (BP), is rath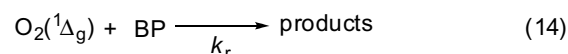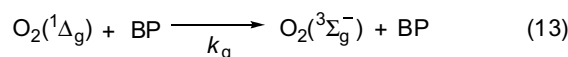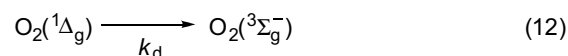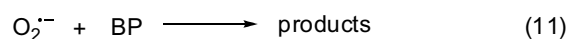er complex. Ground state Rf can associate with different compounds, including phenolic compounds (process (1)) (Massad et al., 2004). Upon absorption of a photon, Rf gives rise to its excited singlet state ($^1Rf^*$) and, through intersystem crossing, to its excited triplet state ($^3Rf^*$) (process (2)). $^3Rf^*$ can transfer energy or an electron to ground state oxygen, $O_2(^3\Sigma_g^-)$, in the aerated solution, generating $O_2(^1\Delta_g)$ (process (5), quantum yield 0.49) and superoxide radical anion ($O_2^{\cdot-}$) (process (6), quantum yield 0.009), respectively (Chacón et al., 1988; Krishna et al., 1991). $O_2(^1\Delta_g)$ can decay by collision with solvent molecules (process (12)), and can interact physically and/or chemically with the BP (processes (13) and (14), respectively). The species $O_2^{\cdot-}$ can be also produced through an indirect process via the reaction of an electron donor with $^3Rf^*$ (process (7)), giving rise to Rf-, which, through processes (8–10), eventually regenerates Rf with simultaneous BP degradation. $O_2^{\cdot-}$ can react with the BP, yielding oxidized products (process (11)).
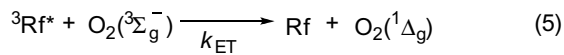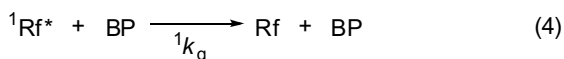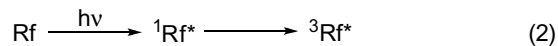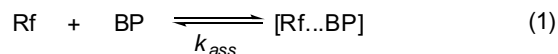
To our knowledge, no systematic kinetic or mechanistic studies have been carried out on the Rf-sensitized photodegradation of bisphenols (BPs). These studies could help to foresee the natural photochemical decay of the members of this family of contaminants and could contribute to the understanding of the mechanism involved in such a process and of its occurrence under environmental conditions. On this basis, the main aim of the present work was to study the experimental conditions that maximize the Rf-sensitized photodegradation efficiencies of BPA, 4,4′-isopropylidenebis(2,6-dibromophenol) (TBrBP) – a fire retardant (Luda et al., 2007) – and 4,4′-isopropylidenebis(2,6-dimethylphenol) (TMeBP) (see chemical structures in Table 1), with an additional focus on the analysis of BPA photodegradation products.

2. Materials and methods

2.1. Materials

Riboflavin (Rf) and superoxide dismutase (SOD) from bovine erythrocytes, were purchased from Sigma Chem. Co. BPA, TBrBP, TMeBP, Rose Bengal (RB), furfuryl alcohol (FFA), deuterium oxide (D_2O; 99.9 atom% D) and monodeuterated methanol (MeOD, 99.5 atom% D) were from Aldrich (Milwaukee, WI, USA). Sodium azide (NaN_3) was from Merck. All these compounds were used as received. Zinc tetraphenylporphyrine (ZnTPP) was prepared as described (Rossbroich et al., 1985). Methanol (MeOH, HPLC quality) was from Sintorgan (Buenos Aires, Argentine). Water was triply distilled. Buffered KH_2PO_4, $NaHCO_3$, and K_2HPO_4 solutions (each 0.01 M) were employed for pHs/pDs 7, 10 and 12, respectively (Hodgman et al., 1963). In all the cases, pHs/pDs were controlled with a MP220 Mettler-Toledo pH-meter.

$$Rf \;+\; BP \;\underset{k_{ass}}{\overset{}{\rightleftharpoons}}\; [Rf\ldots BP] \qquad (1)$$

$$Rf \;\xrightarrow{h\nu}\; {}^1Rf^* \;\longrightarrow\; {}^3Rf^* \qquad (2)$$

$$^1Rf^* \;\xrightarrow[^1k_d]{}\; Rf \qquad (3)$$

$$^1Rf^* \;+\; BP \;\xrightarrow[^1k_q]{}\; Rf \;+\; BP \qquad (4)$$

$$^3Rf^* \;+\; O_2(^3\Sigma_g^-) \;\xrightarrow[k_{ET}]{}\; Rf \;+\; O_2(^1\Delta_g) \qquad (5)$$

$$^3Rf^* \;+\; O_2(^3\Sigma_g^-) \;\xrightarrow[k_{eT}]{}\; Rf^{\cdot+} \;+\; O_2^{\cdot-} \qquad (6)$$

$$^3Rf^* \;+\; BP \;\xrightarrow[^3k_q]{}\; Rf^{\cdot-} \;+\; BP^{\cdot+} \qquad (7)$$

$$Rf^{\cdot-} \;+\; H^+ \;\longrightarrow\; RfH^{\cdot} \qquad (8)$$

$$2\,RfH^{\cdot} \;\longrightarrow\; RfH_2 \;+\; Rf \qquad (9)$$

$$RfH_2 + O_2(^3\Sigma_g^-) \rightarrow [RH_2^{\cdot+} + O_2^{\cdot-}] \rightarrow Rf + H_2O_2 \qquad (10)$$

$$O_2^{\cdot-} \;+\; BP \;\longrightarrow\; products \qquad (11)$$

$$O_2(^1\Delta_g) \;\xrightarrow[k_d]{}\; O_2(^3\Sigma_g^-) \qquad (12)$$

$$O_2(^1\Delta_g) \;+\; BP \;\xrightarrow[k_q]{}\; O_2(^3\Sigma_g^-) \;+\; BP \qquad (13)$$

$$O_2(^1\Delta_g) \;+\; BP \;\xrightarrow[k_r]{}\; products \qquad (14)$$
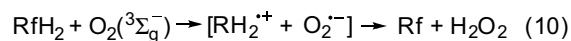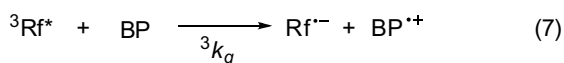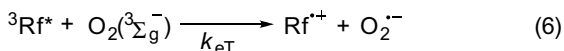
Scheme 1. Main kinetic processes in the visible light irradiation of a bisphenol (BP) in the presence of riboflavin (Rf).

Table 1
Rate constants ($M^{-1}\,s^{-1}$) for the quenching of $^1Rf^*$ (^1k_q) and $^3Rf^*$ (^3k_q) by Bisphenol A (BPA), 4,4′-isopropylidenebis(2,6-dibromophenol) (TBrBP) and 4,4′-isopropylidenebis(2,6-dimethylphenol) (TMeBP), in MeOH–water 1:1 v/v; and quantum yield for the generation of the species RfH· ($\Phi_{RfH\cdot}$)

Compound	R	$^1k_q/10^9$	$^3k_q/10^9$	Φ_{RFH}
BPA	H	5.32	2.1 ± 0.2	0.28 ± 0.02
TBrBP	Br	2.93	1.4 ± 0.1	0.25 ± 0.01
TMeBP	Me	5.99	1.7 ± 0.3	0.39 ± 0.02
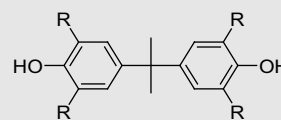
2.2. Absorption and fluorescence measurements

Ground state absorption spectra were registered in a Hewlett Packard 8452 A diode array spectrophotometer. Steady-state fluorescence was measured with a Spex Fluoromax spectrofluorimeter at 25 ± 1 °C in air-equilibrated solutions. Excitation and emission wavelengths for Rf were 445 and 515 nm, respectively. Fluorescence lifetimes were determined with a time-correlated single photon counting (SPC) technique on an Edinburgh FL-9000CD instrument equipped with a blue LED (PicoQuant PLS-8-2-208). Excitation and emission wavelengths for Rf were 450 and 515 nm, respectively. In both stationary and time-resolved fluorescence measurements, a classical Stern–Volmer treatment of the data were applied through equations $I_0/I = 1 + K_{SV}$ [BP], and $^1\tau_0/^1\tau = 1 + {}^1k_q \, {}^1\tau_0$ [BP], where I and I_0 are the respective fluorescence intensities of Rf in the presence and in the absence of a BP, and $^1\tau$ and $^1\tau_0$ are the respective fluorescence lifetimes. K_{SV} is the Stern–Volmer constant.

2.3. Continuous photolysis

Continuous aerobic photolysis of aqueous solutions containing Rf plus BP, or RB plus BP, were carried out in a PTI unit provided with a high pass monochromator and a 150-W Xe lamp, irradiating at 440 ± 10 nm, or, for non-monochromatic irradiation (>400 nm), in a home-made photolyser with a 150-W quartz–halogen lamp with a cut-off filter. Another home-made photolyser was used for the irradiation of Rf-containing solutions, using six blue light emitting diodes (LEDs, λ_{max} 467 nm, polarization current 30 mA) directly irradiating the magnetically stirred solution.

The reactive rate constant, k_r, for the reaction of $O_2(^1\Delta_g)$ with each BP (process (14)) was determined as previously described (Scully and Hoingé, 1987), using the expression slope/slope$_R$ = k_r [BP]/k_{rR} [R], for which the knowledge of the reactive rate constant for the photooxidation of a reference compound, R, at similar concentration, is required, and where slope and slope$_R$ are the respective slopes of the first-order plots of BP and R consumption, or oxygen consumption by the same compounds, under sensitized irradiation. Oxygen uptake in water was monitored with a 97-08 Orion electrode. Employing RB as a sensitizer, it was assumed that the reaction of $O_2(^1\Delta_g)$ with each BP is the only way of oxygen consumption. The reference R was FFA, with a reported pH-independent k_{rR} value in water of $1.2 \times 10^8 \ M^{-1} \ s^{-1}$ (Wilkinson et al., 1995). In MeOH–H$_2$O 1:1, v/v, the k_{rR} employed was $6.2 \times 10^7 \ M^{-1} \ s^{-1}$, as determined in the present work (see latter).

2.4. Laser flash photolysis experiments

Argon-saturated aqueous solutions of Rf 0.04 mM were irradiated with a flash photolysis apparatus. A ns Nd:YAG laser system (Spectron) at 355 nm was used for excitation, employing a 150-W Xenon lamp as a source for the analyzing light. The detection system comprised a PTI monochromator and a red-extended photomultiplier (Hamamatsu R666). The signal, acquired and averaged by a digital oscilloscope (Hewlett–Packard 54504 A), was transferred via a HPIB parallel interface to a PC where it was analyzed and stored. The disappearance of $^3Rf^*$, a species generated by the 355 nm pulse, was monitored from the first-order decay of the absorbance at 670 nm, a zone where the interference from other possible species is negligible. The decay was measured at low Rf concentration (typically 0.05 mM) and at low enough laser energy to avoid self-quenching and triplet–triplet annihilation. The rate constant for the interaction $^3Rf^*$-BP (process (7)) was determined by the Stern–Volmer expression $1/^3\tau = (1/^3\tau_0) + {}^3k_q$ [BP], where $^3\tau$ and $^3\tau_0$ are the experimentally determined lifetimes of $^3Rf^*$ in the presence and in the absence of BP, respectively.

Quantum yields of RfH generation (Φ_{RFH^-}) by electron transfer (process (7)), followed by protonation (process (8)) were determined relative to the triplet yield of zinc tetraphenylporphyrin in benzene ($\Phi_T = 0.83$) (Hurley et al., 1983), employing the expression $\Phi_{RFH^-} = \Phi_T \ A(RfH^-) \ \varepsilon_T/A(T) \ \varepsilon_{RfH}$ (Bertolotti et al., 1999), where $A(RfH^-)$ is the absorbance of RfH$^-$ at 570 nm, $A(T)$ is the absorbance of $^3Rf^*$ at 470 nm immediately after the laser pulse, and ε_T is the molar absorption coefficient of zinc tetraphenylporphyrin triplet ($7.3 \times 10^4 \ M^{-1} \ cm^{-1}$) (Hurley et al., 1983).

2.5. Time-resolved phosphorescence detection (TRPD) of $O_2(^1\Delta_g)$

The overall quenching rate constant of $O_2(^1\Delta_g)$ deactivation by each BP (k_t, the sum of k_q plus k_r, processes (13) and (14), respectively, Scheme 1) was determined using a previously reported system (Massad et al., 2005). Briefly, a Nd:YAG laser (Spectron) was used for the excitation (532 nm) of the sensitizer RB (Abs$_{532}$ = 0.4), and the emitted radiation ($O_2(^1\Delta_g)$) phosphorescence at 1270 nm) was detected at right angles using an amplified Judson J16/8Sp germanium detector, after passing through two Wratten filters. The output of the detector was coupled to a digital oscilloscope and to a personal computer for the signal processing. Usually, 16 shots were needed for averaging, so as to achieve a good signal to noise ratio, from which the decay curve was obtained. Air-saturated solutions were employed in all the cases. In the dynamic determinations, D$_2$O and MeOD, instead of H$_2$O and MeOH, were used as solvents in order to enlarge the lifetime of $O_2(^1\Delta_g)$ (Wilkinson et al., 1995). The $O_2(^1\Delta_g)$ lifetimes were evaluated in the presence (τ) and in the absence (τ_0) of the quencher, and the data were plotted as a function of concentration, according to a simple Stern–Volmer treatment, $1/\tau = 1/\tau_0 + k_t$ [BP].

2.6. Analysis of photoproducts from BPA

Solutions of 0.42 mM Rf and 2.15 mM BPA in H$_2$O–MeCN 95:5, v/v (50 ml) or in MeOH (50 ml) were irradiated for 6 h in a Pyrex vessel using the above described blue LED photolyser. Then, the solvent was removed by lyophilization and the residues (ca. 1 mg each) were treated with H$_2$O (1 ml) or MeOH (1 ml), respectively, filtered and analyzed. HPLC–MS analysis was carried out in a Thermo Electron apparatus provided with a Surveyor pump, a Surveyor PDA and a LCQ Deca ion trap mass spectrometer with an electrospray interface. Column: Hypersyl HyPurity C18 (100×2.1 mm, 3 μm, 190 Å pore size silica, endcapped) at room temperature. Mass spectrometer spray voltage: 5 kV; capillary temperature: 275 °C; nitrogen (99.5% purity) as sheath (0.6 l min^{-1}) and as auxiliary (6 l min^{-1}) gas. External mass calibration was carried out with the calibration mixture provided by the manufacturer. Mass spectra were recorded in both positive and negative ion modes, scanning from m/z 50–800. PAD was recorded from 230 to 600 nm. Conditions of isocratic elution: MeOH–H$_2$O 1:1, v/v plus 0.1% formic acid as eluent, flow rate 0.1 ml min^{-1}, injection of 5 μl of sample solution, room temperature, total time 12 min. Conditions of gradient elution: as above, except for an initial elution for 3 min with MeOH–H$_2$O 1:9, v/v plus 0.1% formic acid, then changing to 9:1 plus 0.1% formic acid for 10 min, and then for 7 min with the last eluent.

HPLC analysis for the detection of BPA in freshly irradiated samples was carried out with an Agilent 1100 chromatograph equipped with a 5-μm C18 reverse phase column (4.6×150 mm) and a diode array detector, using isocratic elution at room temperature with H$_2$O–MeCN 1:1, v/v plus 0.1% formic acid al eluent, at a flow rate of 1 ml min^{-1}, injecting 20 μl. Under these conditions, BPA (R_t = 3.7 min) was identified by its UV–vis spectrum and by comparison with a pure sample.

Direct GC–MS analysis of the reaction mixtures was performed using an HP-5890 gas chromatograph coupled to an HP-5971 mass detector (Hewlett–Packard). Samples were injected in the splitless mode (0.5 min) at 280 °C. A methylpolysiloxane column (30 m × 0.22 mm i.d. × 0.25 d.f.) with helium as carrier gas was programmed from 70 to 270 °C at a rate of 4 °C min^{-1}. Transfer line temperature was 280 °C. Ionization was carried out by electron impact (EI) at 70 eV, and the mass range (38–550 m/z) was scanned in 0.9 s.

3. Results

3.1. Interactions Rf–BPs and ^{1}Rf*–BPs

Rf is probably the most extensively studied biomolecule as regards its complexation ability along with other molecules of biological and environmental relevance, including hydroxyaromatic compounds (Massad et al., 2004a). The absorption spectrum of 0.03 mM Rf in MeOH suffers a number of shape perturbations in the presence of a BP (examined upto 0.1 M BP) that do not obey to the simple addition of the individual spectra of the components of the mixture. The spectral changes must be ascribed to the formation of the Rf–BP complex (process (1)).

In water, Rf presents an intense fluorescence emission band centered at 515 nm, with a reported fluorescence quantum yield value (Φ_f) of 0.25 (Heelis, 1982). In the presence of a BP, the fluorescence quenching of excited singlet Rf (^{1}Rf*) produces a decrease in the steady-state emission intensity, but the shape of the emission spectrum does not change. The fluorescence decay of Rf in the absence and in the presence of a BP, as determined by the SPC technique, was monoexponential. Fig. 1 (panel I, inset) shows the respective Stern–Volmer plots obtained from stationary and time-resolved methods. The first one presents a neat positive curvature, whereas the plot for the time-resolved data is linear. This behavior corresponds to the typical case in which the fluorescent probe is simultaneously quenched by in-dark association with its ground state and by collision with its excited singlet state. These systems can be treated (Lakowicz, 1999) by using the modified Stern–Volmer equation $I_0/I = (1 + K_D[Q])(1 + K_{ass}[Q])$, where I_0 and I are the fluorescence intensities of Rf in the absence and in the presence of a quencher, Q, such as a BP, $K_D = {}^1k_q\,{}^1\tau_0$ accounts for the dynamic component of the fluorescence quenching, and K_{ass} is the association constant (process (1)). K_D was calculated with $^1\tau_0 = 5.6$ ns Heelis, 1982 and the ^1k_q values shown in Table 1, were all determined from independent time-resolved experiments. For BPA, TBrBP and TMeBP, K_{ass} values of 1.6 ± 0.1, 2.0 ± 0.2 and 6.1 ± 0.1 M^{-1}, respectively, were deduced by non-linear least square fitting of the former equation.

3.2. Photodegradation kinetics

The Rf-sensitized photoirradiation of air-equilibrated pH 7 aqueous or aqueous–methanolic solutions of each BP ($\lambda_{irr} > 400$ nm) produces changes in the spectral region of the BP absorption (a representative plot for BPA in water is shown in Fig. 1,
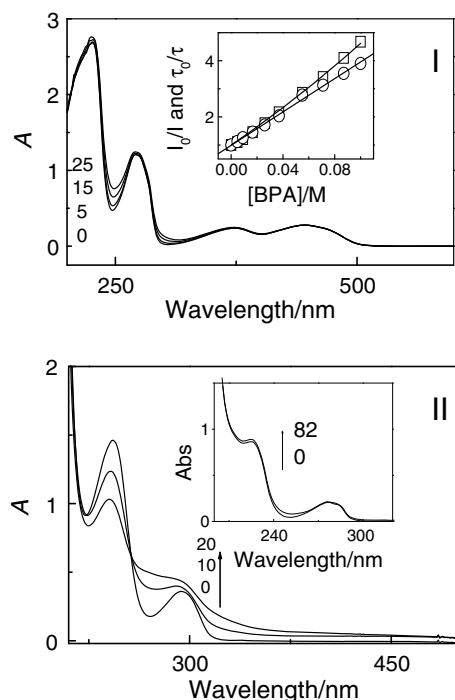
Fig. 1. Panel I: changes in the UV–vis absorption spectra of a pH 7 aqueous solution of 0.023 mM riboflavin (Rf) plus 0.17 mM Bisphenol A (BPA), taken vs. solvent, upon irradiation ($\lambda_{irr} > 400$ nm) under air-saturated conditions; inset: Stern–Volmer plots for the stationary (□) and time-resolved (○) fluorescence quenching of ^{1}Rf* by BPA in pH 7 water. Panel II: changes in the UV–vis absorption spectra of a pH 12 aqueous solution of Rose Bengal (RB) (A(549) = 0.41) plus 0.19 mM BPA, taken vs. RB (A(549) = 0.41), upon irradiation under the same conditions of panel I (main); inset: changes in the UV–vis absorption spectra of a methanol–water 1:1, v/v solution of RB (A(549) = 0.35) plus 0.16 mM BPA, taken vs. RB (A(549) = 0.35), upon irradiation under the same conditions of panel I (main). Numbers in the spectra represent irradiation times (min).
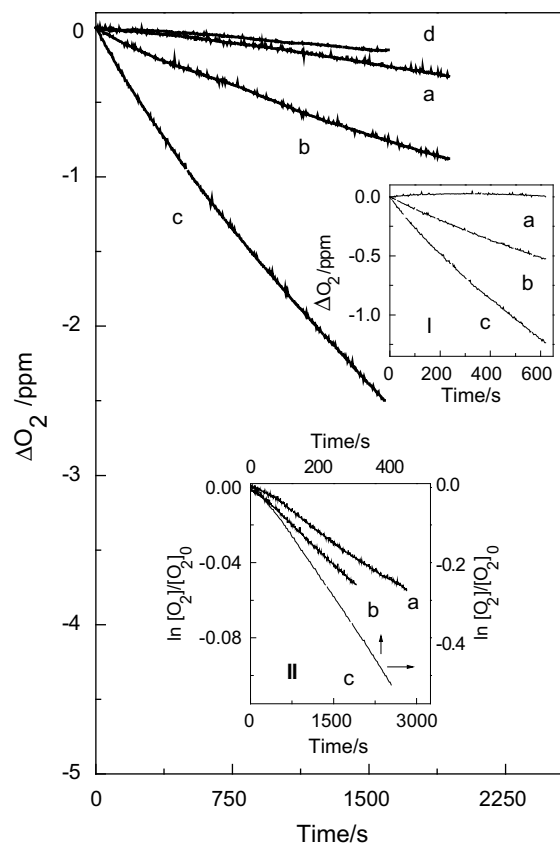
Fig. 2. Oxygen uptake in the visible-light irradiation of MeOH–H$_2$O 1:1, v/v solutions containing 0.02 mM Rf plus: (a) 0.5 mM TBrBP; (b) 0.5 BPA mM; (c) 0.5 mM TMeBP; (d) 0.5 mM BPA plus 2 mM NaN$_3$. Inset I: rates of oxygen consumption of a MeOH–H$_2$O 1:1 v/v solution containing 0.028 mM Rf plus: (a) 0.38 μM SOD; (b) 0.5 mM BPA; and (c) 0.5 mM BPA plus 0.38 μM SOD. Inset II: First-order plots of oxygen uptake in the visible-light irradiation of MeOH–H$_2$O 1:1, v/v solutions containing RB (A(549) = 0.32) plus: (a) 0.5 mM TBrBP; (b) 0.5 mM TMeBP; (c) 0.5 mM FFA.

panel I) and also in the absorption bands of the sensitizer, the latter only after prolonged irradiation.

In parallel, the photoirradiation of aerated solutions of 0.02 mM Rf plus 0.5 mM BP in MeOH–H$_2$O 1:1, v/v gave rise to oxygen consumption (Fig. 2). The rates for the three studied BPs are shown in Table 2. The presence of 0.38 μM SOD increased the rate of oxygen consumption (a representative example is shown in Fig. 2, inset I). SOD specifically produces the dismutation of the species O$_2^-$ through process (15). The same experiment, performed in the presence of 2 mM NaN$_3$, instead of SOD, reduced the rate of oxygen consumption, by a factor of 4.5 in the case of BPA, as compared to the run in the absence of NaN$_3$ (Fig. 2, main). This salt is an exclusive physical quencher of O$_2$($^1\Delta_g$) (Wilkinson et al., 1995).

$$2O_2^- + 2H^+ \xrightarrow{SOD} O_2(^3\Sigma_g^-) + H_2O_2 \qquad (15)$$

In deoxygenated solutions, the presence of a BP in the mM concentration range produced a decrease in the rate of Rf consumption, as evaluated by monitoring the rates of absorbance decrease of the 445 nm absorption band of Rf. Since photodegradation of Rf is known to proceed from its electronically excited states (Heelis, 1982), the above mentioned delay in the photodegradation rate of Rf constitutes an indication of the quenching of the excited states of the pigment by BPs.

All this experimental evidence indicates that under visible light irradiation the overall interaction Rf–BP must include the participation of electronically excited states of Rf and, according to the oxygen uptake experiments, dissolved ground state oxygen and/or reactive oxygenated species formed in the medium.

3.3. Interactions ^{3}Rf*–BPs

As a first approximation to the knowledge of the involved reaction mechanism, the specific interactions of ^{3}Rf* with each BP were studied by laser flash photolysis experiments (the interactions ^{1}Rf*–BP can be quantified by the constant K_{ass}). In MeOH–H$_2$O 1:1, v/v, the ^{3}Rf* lifetime was neatly reduced by the presence of a BP, demonstrating the occurrence of interaction between both species. For each BP, its bimolecular rate constant ^3k_q (process (7), Table 1) was graphically obtained (not shown). In the particular case of BPA, its interaction with ^{3}Rf* was studied by recording the transient absorption spectra. In the absence of BPA, a spectrum similar to the expected one for ^{3}Rf* was observed after the laser pulse (Haggi et al., 2002), while in the presence of 0.5 mM BPA

(ca. 94% ^{3}Rf* quenched by BPA) the shape of the long-lived absorption is in good agreement with that reported for the semiquinone radical RfH· (Lu et al., 2004). At pH 7, the radical RfH· (pK_a = 8.3) must be formed (process (8)), after protonation of the species Rf$^-$ (process (7)) Lu et al., 2000. RfH· has been formerly detected as a product of electron transfer processes to ^{3}Rf* from several electron-donor substrates of environmental and biological importance (Haggi et al., 2002). Determined quantum yields for RfH· generation ($\Phi_{RfH·}$) in the presence of each BP as electron donor are shown in Table 1.

3.4. Quenching of O$_2$($^1\Delta_g$)

All experiments involving possible O$_2$($^1\Delta_g$)-mediated processes at pH 7, 10 and 12 were carried out in the presence of the exclusive O$_2$($^1\Delta_g$)-generator dye RB. Rf was not used in these kinetic determinations in order to avoid interferences by other oxidative species generated in the medium, and because Rf suffers a rapid photodegradation at pH 9 (Heelis, 1982). RB is the sensitizer most frequently employed in O$_2$($^1\Delta_g$) reactions, producing O$_2$($^1\Delta_g$) with a quantum yield of 0.81 in MeOH (Amat-Guerri et al., 1990).

Photoirradiation of solutions of RB (A(549) = 0.41) plus 0.19 mM BP with visible light, in MeOH–H$_2$O 3:7, v/v or in water solutions with pH 10 or 12, produces changes in the absorption spectrum of the particular BP (Fig. 1, panel II), as well as oxygen consumption. The presence of a BP in the sub-mM concentration range quenches the IR phosphorescence emission of O$_2$($^1\Delta_g$), as detected by TRPD experiments (see above). It is well known that phenols and polyphenols interact with O$_2$($^1\Delta_g$) through processes that are highly dependent on the degree of ionization of the OH groups (García et al., 1994). The rate constant k_t for the overall interaction O$_2$($^1\Delta_g$)-BP was independently determined in MeOD–D$_2$O 1:1, v/v and in pD 10 and pD 12 D$_2$O (Table 2), through a Stern–Volmer treatment. These experiments unambiguously demonstrate the existence of this interaction, which may be physical in nature (process (13)) and/or chemically reactive (process (14)). The k_t values, as determined by TRPD (Table 2), do not depend on the type of sensitizer or on potential interactions of the substrate with excited states of the sensitizer involved in the O$_2$($^1\Delta_g$) generation.

The presence of 0.5 μM SOD in MeOD–D$_2$O 1:1, v/v, i.e., similar conditions as used in auxiliary O$_2^-$ tests experiments (see above, Section 3.2), did not change the lifetime of RB-generated O$_2$($^1\Delta_g$). In parallel, a rate constant $k_t = 9.5 \times 10^8$ M^{-1} s^{-1} was determined in MeOD–D$_2$O 1:1, v/v for the quenching of RB-generated O$_2$($^1\Delta_g$) by NaN$_3$, a value in excellent agreement with published data (Wilkinson et al., 1995).

The rate constant k_r for each BP was determined by monitoring oxygen consumption upon photoirradiation of RB–BP mixtures, following a described method (Scully and Hoingé, 1987) (Fig. 2, inset II and Table 2). The calculated k_r/k_t ratios represent a measure of the efficiency of the degradation pathway via reaction with O$_2$($^1\Delta_g$). The k_r value herein found for BPA in pH 12 aqueous solution ($k_r = 2.0 \times 10^8$ M^{-1} s^{-1}) is in excellent coincidence with the only published data ($k_r = 2.1 \times 10^8$ M^{-1} s^{-1}) on the interaction O$_2$($^1\Delta_g$)-BPA (Tai et al., 2005).

3.5. Photoproducts

Table 3 shows the results of the HPLC–MS analysis of a photolysed MeOH solution of BPA, using ESI− under isocratic elution. The use of ESI+ and isocratic or gradient elution for the analysis of this sample also allowed the detection of some of the compounds in the Table. The same holds for the analysis of samples photolysed in water using ESI+ or ESI− and isocratic or gradient elution. The absence of BPA in the analytical results in Table 3 indicates that, as a consequence of the presence of Rf, the photooxida-

Table 2
Rate constants (M^{-1} s^{-1}) for overall (k_t) and reactive (k_r) quenching of O$_2$($^1\Delta_g$), and relative rates of oxygen consumption (ΔO$_2$) upon RB- or Rf-sensitization, by Bisphenol A and related compounds. Literature data for phenol are included for comparison

Compound	Solvent[a]	$k_t/10^8$	$k_r/10^8$	k_r/k_t	ΔO$_2$ (RB)	ΔO$_2$ (Rf)
BPA	Methanol–water[b]	0.017	0.003	0.20	0.20	
	H$_2$O pH 7					0.29
	Water pH/pD 10	4.8	1.01	0.21		
	Water pH/pD 12	7.4	2.0	0.27		
TBrBP	Methanol–water[b]	0.64	0.009	0.01	0.60	
	H$_2$O pH 7					0.46
	H$_2$O pH 12		1.5			
TMeBP	Methanol–water[b]	0.33	0.012	0.04	1.00	
	H$_2$O pH 7					1.00
	H$_2$O pH 12		1.4			
phenol	MeOD	0.014[c]				
	D$_2$O pD 10	2.4[d]				

[a] In the determinations of k_t, water is D$_2$O and methanol is MeOD, and in the rest of determinations water is H$_2$O and methanol is MeOH.
[b] 1:1, v/v mixture.
[c] From Haggi et al. (2002).
[d] From Tai et al. (2005).

Table 3
Analysis of the products from the Rf-sensitized photooxidation of bisphenol A (BPA) in methanol by HPLC–MS (MeOH–H$_2$O 1:1 v/v plus 0.1% formic acid; isocratic elution; ESI-mode). Retention times (R_t), [M−H]$^-$ values (M: molecular mass), and wavelengths of maximum absorption (λ_{max}) of the main signals are shown

Compound	R_t (min)	[M−H]$^-$	λ_{max} (nm)	Assignment
1	3.80	375	383, 450	Riboflavin
2	3.80	241	l.a.[a]	[M]$_{BPA}$ − 2 + 16
3	4.74	243	280	[M]$_{BPA}$ + 16
4	5.24	243	264	[M]$_{BPA}$ + 16
5	5.97	241	353, 385	Lumichrome
6	5.97	453	274	(2 × [M]$_{BPA}$) − 2
7	7.26	483	l.a.[a]	(2 × [M]$_{BPA}$) − 4 + 32
8	7.85	487	l.a.[a]	(2 × [M]$_{BPA}$) + 32
9	8.28	467	l.a.[a]	(2 × [M]$_{BPA}$) − 4 + 16
10	8.72	469	l.a.[a]	(2 × [M]$_{BPA}$) − 2 + 16
11	11.84[b]	453	286	(2 × [M]$_{BPA}$) − 2
12	19.05[b]	453	278	(2 × [M]$_{BPA}$) − 2

[M]$_{BPA}$ = molecular mass of BPA (228).
[a] l.a., low absorption.
[b] Major peaks.

tion process continues in partially photolysed samples kept in solution under normal laboratory conditions. BPA was easily identified in freshly photolysed samples using other HPLC conditions (see above).

4. Discussion

4.1. Kinetic analysis

Oxygen uptake results, spectroscopic evidence in the Rf-sensitized photoprocesses and auxiliary specific O$_2^-$ and O$_2$($^1\Delta_g$) experiments strongly support the effective participation of both reactive oxygenated species in the degradation of BPs through a relatively complex mechanism. The spectral changes due to in-dark association between Rf and OH-aromatic compounds, via processes driven by a charge transfer mechanism (Massad et al., 2004a), are very similar in shape to those described herein for the systems Rf–BP. The relatively low values obtained for the association constants indicate that these in-dark complexations do not significantly affect the Rf-photosensitizing ability of Rf, at least at the BP concentrations employed in the present work.

As in the case of phenol (reported values: $^1k_q = 4.10 \times 10^9$ M^{-1} s^{-1}, $^3k_q = 4.8 \times 10^8$ M^{-1} s^{-1}) (Haggi et al., 2004), considered a simplified model compound, BPs interact with excited singlet and triplet states of Rf, ^{1}Rf* and ^{3}Rf*, respectively. Nevertheless, according to the fluorescence quenching data, a BP concentration of 0.5 mM -much higher than the concentrations employed in the Rf-sensitized experiments- would only produce a decrease in ^{1}Rf* lifetime of much less than 1%. Hence, the participation of ^{1}Rf* in the photodegradation of BPs must be totally disregarded.

On the other hand, ^{3}Rf* is efficiently quenched by BPs. As demonstrated by laser flash photolysis experiments, the species RfH$^•$ is generated in this interaction, with quantum yields in the range 0.25–0.39 as upper limit values, depending on the particular BP. The bimolecular decay of RfH$^•$ is known to proceed through a disproportionation reaction yielding Rf and fully reduced Rf (RfH$_2$) (process (9)). In the presence of O$_2$($^3\Sigma_g^-$), RfH$_2$ is reoxidized, giving rise to RfH$_2^+$ and O$_2^-$, and, eventually, to Rf and H$_2$O$_2$ (process (10)) Lu et al., 1999; 2004. The thermodynamic feasibility of the electron transfer process (7) for the case of Rf-BPA can be evaluated by means of the Gibbs free energy for electron transfer, $\Delta_{ET}G_0 = E_{0(BPA/BPA+)} − E_{0(Rf/Rf−)} − E_{Rf}^* + C$, where $E_{0(BPA/BPA+)}$, (0.9 V in MeCN) (Ngmundi et al., 2003; Mendez et al., 2006) is the standard electrode potential of the donor cation radical, $E_{0(Rf/Rf−)}$ is the standard electrode potential of the acceptor Rf (−0.80 V), E_{Rf}^* is the ^{3}Rf* en-

ergy (2.17 eV), and C is the coulombic energy term (−0.06 V) Porcal et al., 2003. The so-calculated $\Delta_{ET}G_0$ value (−0.53 V) indicates that process (7) may be operative and, consequently, that the species O$_2^-$ could be formed by electron transfer from Rf (process (10)), if process (7) is kinetically competitive with the O$_2$($^1\Delta_g$) generation (process (5)). Considering the k_{ET} value of process (5) in MeOH (1.2×10^9 M^{-1} s^{-1}, i.e., 1/9 of the diffusional value) Koizumi et al., 1978 and a mean ^3k_q value for the BPs of 1.7×10^9 M^{-1} s^{-1} (Table 1), it can be deduced that, for the same concentrations of BP and dissolved O$_2$($^3\Sigma_g-$), the rate constant values for the generation of both RfH$^•$ (vía Rf$^{•-}$, process (8)) -RfH$^•$ is the initial O$_2^{•-}$ precursor- and O$_2$($^1\Delta_g$) (process (5)) are practically the same.

In the continuous irradiation experiments employing Rf as a sensitizer, the increase of the rate of oxygen uptake due to the presence of SOD (Fig. 2, inset I) supports the involvement of the species O$^{•-}$ in the proposed mechanism. A O$_2$($^1\Delta_g$)-mediated photooxidation of the protein SOD as a potential source for oxygen consumption must be disregarded (see above, Section 3.4). It has been reported that SOD can either inhibit or stimulate the O$_2^-$-mediated oxidation of different substrates (Afanaśev, 1989). Thus, SOD stimulates the oxidation of some hydroquinones as well as gallic acid and hydroxyanthranilic acid, among other hydroxy-aromatic compounds (Afanaśev, 1989), being H$_2$O$_2$ the oxidative species. H$_2$O$_2$ appears as a product of O$_2^-$ dismutation (process (15)), contributing in this way to oxygen consumption. A similar behavior can be assumed in the case of BPs.

In the visible-light irradiation of systems Rf-BPA in MeOH–H$_2$O 1:1, v/v, in the presence of 2 mM NaN$_3$, the O$_2$($^1\Delta_g$) lifetime should be reduced by a factor of ca. 15. This value was calculated through a simple Stern–Volmer treatment employing the k_t value herein found and a O$_2$($^1\Delta_g$) lifetime of 7 μs (τ_0). However, the rate of oxygen uptake by BPA under these conditions was only reduced by a factor of ca. 4.5 (Fig. 2, main). This fact strongly supports the existence of at least a second pathway for oxygen consumption different from the O$_2$($^1\Delta_g$)-driven process, possibly represented by the O$_2^-$-mediated mechanism.

The quenching of O$_2$($^1\Delta_g$) by phenols and hydroxy-*N*-heteroaromatic compounds in polar and non-polar solvents has been extensively reviewed (García et al., 1994; 2005). The hydroxy substituent increases the electron donor ability of the aromatic compound towards the electrophilic species O$_2$($^1\Delta_g$), with regard to the non-substituted compound. This has been explained on the basis of a mechanism involving an intermediate complex possessing charge-transfer character (García et al., 1994). The deactivation of the encounter complex will merely lead to physical quenching (process (13), Scheme 1), whereas complete electron transfer will produce chemical oxidation of the substrate (process (14)).

The efficiency of the photooxidation reaction with O$_2$($^1\Delta_g$) (ratio k_r/k_t) in MeOH–H$_2$O 1:1, v/v is higher in BPA than in the other two BPs (Table 2). In the case of TBrBP, with the highest k_t value and the lowest photooxidation efficiency, this can be explained on the basis of the heavy atom effect due to the presence of four bromine atoms, an effect that increases the value of the O$_2$($^1\Delta_g$) physical quenching, k_q (process (13)). This quenching is a singlet-to-triplet intersystem crossing followed by relaxation of the generated, vibrationally excited O$_2$($^3\Sigma_g-$) molecule. An interesting case on this effect, and probably the only clear experimental example, has been studied by our group for a series of tyronine derivatives (Miskoski et al., 2005).

The rate constants k_t and k_r of the studied BPs increase with the ionization of the OH groups, a property well described for hydroxy-aromatic compounds (García et al., 1994; 2005). Besides, in the case of BPA, the k_r/k_t ratios show that the reactive quenching component of the interaction with O$_2$($^1\Delta_g$) increases with the pH value of the medium. This effect has been extensively discussed for phenols and monohydroxylated *N*-heteroaromatic compounds (Luiz

et al., 1993; García et al., 2005). Results in Table 2 also indicate that the presence of substituents in the aromatic rings of the BPs increases both k_t and k_r values.

Both the photooxidation rate k_r of each BP (under sensitization with RB in MeOH–H_2O 1:1, v/v) and the relative rates of oxygen uptake (under the same conditions, or under sensitization with Rf in H_2O, pH 7) increase in a parallel fashion with the electron-releasing ability of the substituents, in the order BPA < TBrBP < T-MeBP. This suggests similar main photooxidation mechanisms with both sensitizers, possibly represented by the $O_2(^1\Delta_g)$-mediated reaction (Table 2). In the photooxidation of BPs with Rf, the experimental evidence points to the involvement of the reactive species $O_2(^1\Delta_g)$ (mainly) and O_2^-, in contrast with the same processes in other phenolic compounds in neutral water (Haggi et al., 2004), where the interaction with $O_2(^1\Delta_g)$ was only physical in nature, being the O_2^- pathway the responsible of substrate and oxygen consumption.

4.2. Photoproducts from BPA

Visible-light irradiation of water or MeOH solutions of BPA in the presence of Rf gives rise to products formed by oxidation and/or dimerization reactions of the substrate, as the corresponding quasi-molecular ions in the HPLC–MS analysis indicate. In MeOH solution and under ESI- conditions, twelve compounds were observed (Table 3). Compounds **2**–**4** come from the addition of one oxygen atom to BPA (in the case of 2 with the concomitant loss of two hydrogen atoms); three dimeric products, compounds **6**, **11** and **12** (**11** and **12** being by far the most important products in the mixture) result from the elimination of two hydrogen atoms between two molecules of BPA; and other four dimers (traces) (compounds **7**–**10**) result from the addition of oxygen atoms to two molecules of BPA, with hydrogen elimination in the cases of compounds **7**, **9** and **10**. Rf (**1**) and lumichrome (**5**, the main photodegradation product from Rf) have also been detected in the analyzed mixture. In general, all the former compounds were better observed under ESI- conditions, and the dimers were preferentially detected in the photo-oxidized mixture in MeOH.

The molecular weight of each degradation product – available from the MS-ESI spectra – and the corresponding UV data do not allow an unequivocal assignment of chemical structure. Moreover, some products appeared as traces, producing peaks with very low UV absorption. However, considering the compounds formerly detected in the degradation of BPA under different experimental conditions, and assuming that similar reactions are involved in the

case of the Rf-sensitized photooxidation, it is possible to propose structures for some of the compounds in Table 3. Thus, compound **2** could be an o-quinone (Scheme 2) (Andreescu et al., 2004), compounds **3** and **4** could be o-hydroxy- and m-hydroxy-BPA, respectively Gözmen et al., 2003, and compounds **6**, **11** and **12**, with maximum absorption close to that of BPA in water (276 nm), could have dimeric structures formed by o,o'- (Uchida et al., 2001), o,m'-, and m,m'-coupling between phenol rings of two molecules of BPA. These dimeric compounds must be formed through the generation of radicals at the o- or m-position of BPA via processes (11) and (14) (Scheme 1), although the involvement of process (7) cannot be discarded.

Two other products were detected by HPLC–MS analysis with gradient elution: p-isopropylphenol (R_t = 11.17 min, ESI-, λ_{max} = 271 nm) and p-isopropenylphenol (R_t = 17.36 min, ESI+, λ_{max} = 278 nm), observed in samples photolysed in water and methanol, respectively, and identified by their corresponding molecular masses and UV absorption spectra. On the other hand, direct GC–MS analysis of the sample from water allowed the detection of traces of the volatile products phenol (at 6.0 min), p-isopropenylphenol (at 9.5 min, MS spectrum as described) (Fukuda et al., 2001), and BPA (at 25.4 min).

5. Conclusions

Under visible light irradiation in the presence of Rf as a dye sensitizer, BPA, TBrBP and TMeBP react with the oxidative species $O_2(^1\Delta_g)$ and O_2^-, both generated through the interaction of excited triplet Rf with ground state molecular oxygen, via a relatively complex mechanism. In the case of BPA, oxidation, fragmentation and dimerization products have been identified in the photo-oxidized mixtures. According to oxygen uptake experiments, the overall process seems to be mainly driven by the reaction with $O_2(^1\Delta_g)$, a reaction very much faster in alkaline media. In a natural environment, these processes are certainly a factor in the removal of BP-contaminants by the combined action of dissolved oxygen, dissolved natural sensitizers such as Rf, and solar light. From the results herein shown, it can be concluded that BPA and related compounds are susceptible to spontaneous photodegradation under usual environmental conditions by an energetically efficient, although relatively time-demanding process. Additionally, the dye RB and, in all likelihood, similar efficient $O_2(^1\Delta_g)$-generators, could be used for a faster non-natural photodegradation of BPs in aqueous solutions under controlled conditions.

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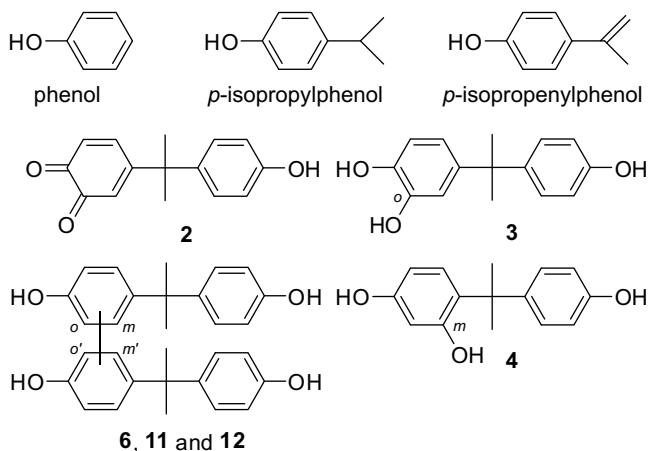
Scheme 2. Confirmed (upper row) and tentative structures of the detected products in the riboflavin-sensitized photodegradation of bisphenol A.

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