



Photosensitized degradation in water of the phenolic pesticides bromoxynil and dichlorophen in the presence of riboflavin, as a model of their natural photodecomposition in the environment

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ABSTRACT

Within the context of environmentally friendly methods for the elimination of surface-water pollutants, the photodegradation of the phenolic pesticides bromoxynil (BXN) and dichlorophen (DCP) under simulated natural conditions has been studied. The work was done in the presence of the visible-light absorber photosensitizer riboflavin (Rf), usually present in trace quantities in natural waters. Under aerobic conditions, an efficient photooxidation of both pesticides was observed. The relatively intricate photochemical mechanism involves pesticide and oxygen consumption and, to a lesser extent, Rf degradation. The kinetic and mechanistic study supports that both H_2O_2 and singlet molecular oxygen, $\text{O}_2(^1\Delta_g)$, are involved in the process. Kinetic data for the $\text{O}_2(^1\Delta_g)$ -mediated oxidation indicate that BXN and DCP are photodegraded with this species faster than the parent compound phenol, very frequently employed as a model for aquatic contaminants, likely due to their lower pK_a values. This observation allows the design of phenolic pesticides with different photodegradation rates under environmental conditions.

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1. Introduction

Significant amounts of agricultural pesticides are usual contaminants of surface waters and soils [1] and their use in crop protection is conditioned by their persistence in the environment. Consequently, their thermal, microbiological and photochemical pathways of degradation are topics of particular research interest. A pesticide that absorbs the sunlight can be spontaneously degraded by photochemical processes initiated from the electronically excited compound, such as the breakage of molecular bonds, the direct reaction with ground state oxygen in the medium, and the reaction with reactive oxygen species (ROS), such as singlet molecular oxygen, $\text{O}_2(^1\Delta_g)$, superoxide radical anion ($\text{O}_2^{\bullet-}$) and hydrogen peroxide (H_2O_2), generated by energy transfer or electron transfer from the excited contaminant to oxygen. When the pesticide does not absorb (or absorbs little) any wavelength of the sunlight, its degradation in an aquatic natural environment can also be carried out through its reaction with ROS if another light-absorbing compound – a photosensitizer – is present in the medium. Traces of sensitizers are usually present in water

courses, lakes and seas. Among them, humic acids (HA) [2] and, in special, the pigment riboflavin (Rf) [3,4] are relevant in the sensitized photooxidation of contaminants. However, upon visible light irradiation and in the absence of interacting compounds, the contribution of HA to the generation of ROS is very small, if compared with that of Rf [5,6]. Both HA and Rf generate $\text{O}_2(^1\Delta_g)$, but with very different quantum yields, 0.04 (upper limit) [7] and 0.47 [8], respectively, and Rf also generates $\text{O}_2^{\bullet-}$ (quantum yield 0.009) [9].

Phenolic pesticides and, in general, hydroxyaromatic pesticides are usually colorless, and their phototransformation under natural or artificial conditions has received considerable attention in the last decades [10–14]. In the presence of Rf, it has been reported that the parent compound phenol and several substituted phenols can be efficiently degraded under visible irradiation, and that the photodegradation occurs mainly through radical-driven reactions, whereas in some cases $\text{O}_2(^1\Delta_g)$ -mediated oxidations are also involved [15–17].

In the present work, we have studied the kinetics and the photochemical mechanism of the Rf-sensitized photodecomposition of the phenolic pesticides bromoxynil (BXN) and dichlorophen (DCP), both generically named PP in the following. The chosen colorless compounds exhibit characteristics that make them different from other phenolic pesticides: (a) BXN shows an extremely low pK_a value for the ionization of its OH group ($\text{pK}_a = 3.86$) [1], as compared

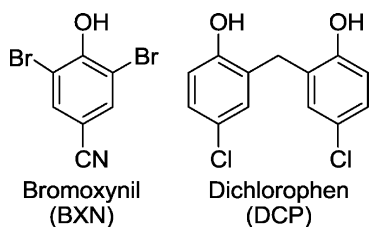
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to phenol ($pK_a = 9.89$) [18] and most phenolic pesticides, usually in the range 9–11 [19]; and (b) DCP has two phenol groups, with pK_a values of 7.66 and 11.60 [1], whereas most phenolic pesticides are monohydroxylated compounds. Taking into account that both the presence of a phenol group in a pesticide and its ionization play a crucial role on kinetic and mechanistic aspects of its photodegradation [11], the former characteristics make BXN and DCP interesting candidates for a photochemical study.

Few works have been devoted to the environmental fate of BXN and DCP, and their main purpose was the identification of final products. In general, phenolic compounds react with ROS, in special with $O_2(^1\Delta_g)$, usually yielding quinones and/or polyhydroxylated compounds [11,20–22]. In the direct photolysis of DCP in an acid medium, 4-chloro-4-hydroxymethylene-diphenol and a benzoquinone were respectively identified under anaerobic and aerobic conditions [23]. The photodegradation of DCP has also been investigated in the form of a dispersion in sand [24], being the primary photoproducts similar to those found in aqueous solution. The laccase-mediated oxidation of several halogenated pesticides, including BXN and DCP, has been recently studied [25], looking for the reduction of their environmental impact.

In synthesis, no systematic kinetic or mechanistic study has been carried out on the sensitized photooxidation process applied to PPs, although these studies could help to foresee the environmental decay of these compounds. The present research was undertaken in order to know the fate of both pesticides under natural-like photoirradiation in the presence of Rf, as well as to gain insight into the structure–photodegradability correlation of phenolic pesticides in general.



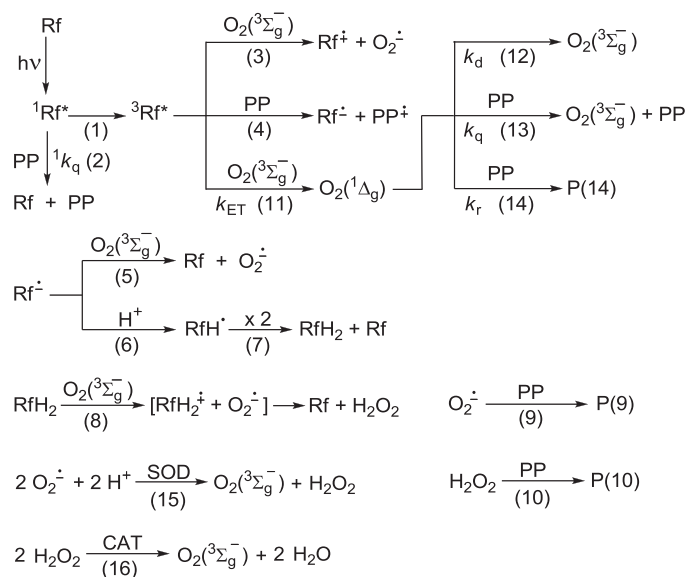
2. Materials and methods

2.1. Materials

Bromoxynil (3,5-dibromo-4-hydroxybenzotrile), dichlorophen (2,2'-methylenebis(4-chlorophenol)), riboflavin, Rose Bengal (RB), sodium azide (NaN_3), superoxide dismutase (SOD) from bovine erythrocytes and catalase (CAT) from bovine liver were purchased from Sigma Chem. Co. Furfuryl alcohol (FFA) was from Riedel de Haën. The solvents employed were deuterated water (D_2O , 99.9% D), monodeuterated methanol (MeOD) (both from Aldrich), methanol (MeOH) (from Sintorgan, Argentine) and triply distilled H_2O . Phosphate buffer was used to regulate pH. D_2O and MeOD were employed in the time-resolved determinations of $O_2(^1\Delta_g)$, in order to enlarge the lifetime of this species [26].

2.2. Methods

Ground state absorption spectra were registered in a Hewlett Packard 8452A diode array spectrophotometer. The overall quenching rate constant of $O_2(^1\Delta_g)$ by each pesticide, k_t , was determined using time resolved phosphorescence detection (TRPD) and methodology already described [27], with RB as a dye sensitizer. Continuous aerobic photolysis of aqueous solutions of PP with RB or Rf as sensitizers was carried out in a home-made photolyser with the filtered light (>350 nm, cut-off filter) from a 150-W quartz-halogen lamp. The rate constant k_r for the reaction of $O_2(^1\Delta_g)$ with each PP was determined by oxygen consumption upon photosen-



Scheme 1. Main processes in the visible-light photoirradiation of Rf in the presence of a phenolic pesticide (PP), under aerobic conditions, and influence of superoxide dismutase (SOD) and catalase (CAT) on the decay of $O_2^{\cdot-}$ and H_2O_2 , respectively. P(n): reaction product. $O_2(^3\Sigma_g^-)$: ground state oxygen. The overall quenching constant k_t is the sum of the rate constants k_q and k_r .

sitized irradiation, according to a described method [10] for which the knowledge of the reactive rate constant k_{rR} for the photooxidation of a reference compound R is required, using the expression $\text{slope}/\text{slope}_R = k_r [PP]/k_{rR} [R]$, where slope and slope_R are the respective slopes of the first-order plots of PP and R consumption. FFA ($k_{rR} = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [10] was employed as a reference. The rates of oxygen consumption were determined with the specific oxygen electrode Orion 97-08.

Fluorescence lifetimes were evaluated with a time-correlated single photon counting technique (SPC) on an Edinburgh FL-9000CD instrument provided with an nF900 nanosecond flash-lamp. Excitation and emission wavelengths for Rf were 445 and 515 nm, respectively. The quenching rate constant 1k_q of the interaction of the singlet excited state of Rf (${}^1\text{Rf}^*$) with each PP was calculated through a classical Stern–Volmer treatment.

The triplet excited state of Rf (${}^3\text{Rf}^*$) was generated by a 355-nm laser pulse, and the ${}^3\text{Rf}^*$ disappearance was monitored from the first-order decay of the absorbance at 670 nm. The rate constant 3k_q of the interaction of ${}^3\text{Rf}^*$ with each PP was evaluated through a Stern–Volmer treatment. The laser flash photolysis apparatus and the methodology employed for the generation and detection of transient species have been described [16].

Electrochemical measurements were performed in a two-compartment pyrex cell. The working electrode was a platinum wire, and the counter electrode was a platinum foil of approx. 2 cm^2 . The reference electrode was an aqueous saturated calomel electrode (SCE). All measurements were performed at $25 \pm 0.5^\circ \text{C}$ in 10 mM KOH aqueous solution. The convolution of Faraday current was calculated by applying the algorithm proposed by Oldham [28] to the background-corrected voltammograms. The measuring system for linear scan voltammetry (LSV) was constructed from an Autolab PGSTAT30 potentiostat.

3. Results

The results are interpreted and discussed following the self-explanatory processes shown in Scheme 1, with Rf as a sensitizer [4,29], in the presence and in the absence of an electron donor such as a PP.

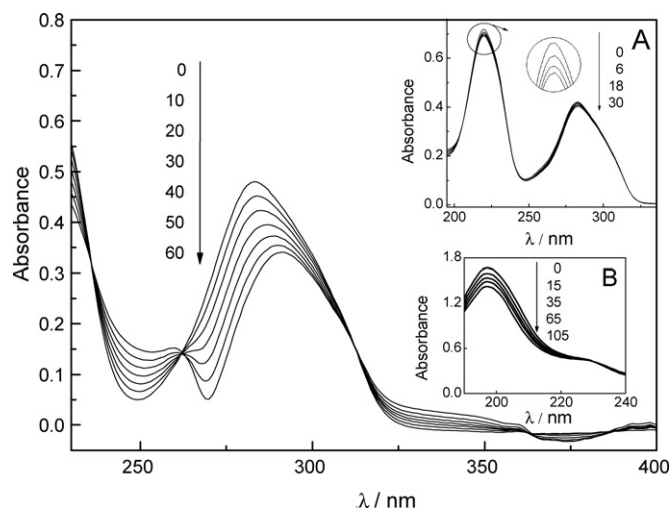


Fig. 1. Changes in the UV-vis absorption spectrum of a pH 7 aqueous solution of Rf (0.023 mM) plus BXN (0.47 mM), taken vs. Rf (0.023 mM) in the same solvent, upon photoirradiation (>400 nm) under air-saturated conditions. Numbers on the spectra represent irradiation times in minutes. Inset A: changes in the UV-vis absorption spectrum of a pH 7 aqueous solution of RB ($A_{549} = 0.41$) plus BXN (0.42 mM), taken vs. RB ($A_{549} = 0.41$) in the same solvent, upon photoirradiation under the same conditions. Numbers on the spectra represent irradiation times in minutes. Inset B: changes in the UV-vis absorption spectrum of a pH 12 aqueous solution of RB ($A_{549} = 0.38$) plus DCP (0.30 mM), taken vs. RB ($A_{549} = 0.38$), upon photoirradiation (>400 nm). Numbers on the spectra represent irradiation times in seconds.

3.1. Stationary photoirradiation

The photoirradiation of the mixture Rf (0.023 mM) plus BXN or DCP in the sub-mM range, in pH 7 water (>350 nm, cut off filter) produced spectral changes that can be attributed to transformations in both components of the mixtures (Fig. 1). In parallel, the photoirradiations gave rise to oxygen consumption. The rate of oxygen uptake at pH 7 of the system Rf (0.04 mM) plus BXN (0.5 mM) was ca. 1.5 times faster than the corresponding one of the system Rf (0.04 mM) plus DCP (0.5 mM) under identical experimental conditions (Table 1).

These results strongly suggest that either Rf electronically excited states or ROS produced through these states, or even both species operating simultaneously, are responsible for the photodegradation of each PP. It is well known that Rf is highly reactive when its water solutions are irradiated with visible light, due to the generation of ROS [4,17,29]. In the present case, the participation of ROS was evaluated through oxygen consumption experiments in the presence of specific ROS quenchers (Fig. 2). Thus, the presence of NaN_3 (10 mM) (not shown) or CAT (1 $\mu\text{g}/\text{mL}$) neatly decreased the rate of oxygen consumption, whereas the presence of the enzyme SOD (1 $\mu\text{g}/\text{mL}$) increased this rate. Similar experiments with these specific ROS quenchers have been formerly employed to confirm/discard the participation of $\text{O}_2(^1\Delta_g)$, H_2O_2 , and $\text{O}_2^{\bullet-}$, respectively, in a given oxidative event [4,30], because NaN_3 physically quenches $\text{O}_2(^1\Delta_g)$, SOD dismutates the species $\text{O}_2^{\bullet-}$ (process (15)), whereas CAT decomposes H_2O_2 (process (16)). The observed increase of oxygen consumption in the presence of SOD, and the decrease of this consumption in the presence of CAT, under identical experimental conditions, is a consequence of the different stoichiometry of the involved processes. Process (15) (with SOD) yields one oxygen molecule from one $\text{O}_2^{\bullet-}$ radical (generated from one oxygen molecule, process (5)) and H_2O_2 , and the latter oxidant, as well as the amount generated by process (8), can react with a PP (process (10)) without regenerating oxygen. On the other hand, process (16) (with CAT) regenerates oxygen from H_2O_2 , and the relative oxygen consumption must be lower.

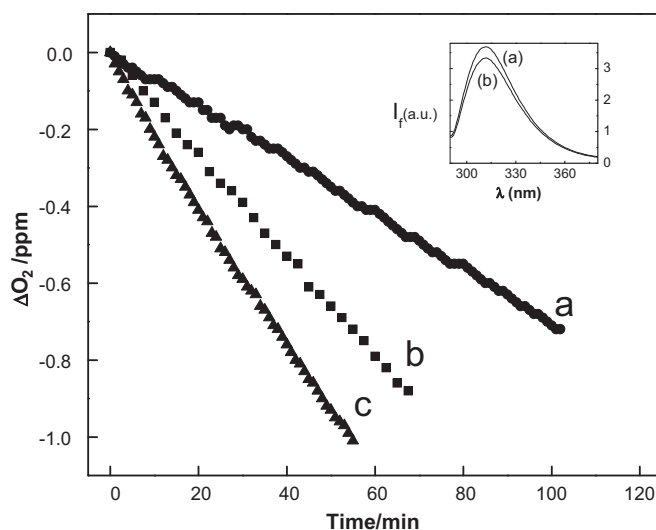


Fig. 2. Oxygen consumption vs. photoirradiation time in pH 7 aqueous solutions for the systems: (a) Rf ($A_{446} = 0.5$) plus BXN (0.5 mM) plus CAT (1 $\mu\text{g}/\text{mL}$); (b) Rf ($A_{446} = 0.5$) plus BXN (0.5 mM); (c) Rf ($A_{446} = 0.5$) plus BXN (0.5 mM) plus SOD (1 $\mu\text{g}/\text{mL}$). Inset: fluorescence spectra of (a) DCP (0.1 mM) in pH 7 aqueous solution, and (b) the same solution in the presence of H_2O_2 (0.05 mM).

The reaction between H_2O_2 and BXN or DCP (process (10)) was detected by the absorption or fluorescence changes, respectively, after the addition of H_2O_2 (0.05 mM) to solutions of each PP (0.12 mM) in pH 7 aqueous buffer at room temperature. In the case of DCP (Fig. 2, inset), the initially observed change indicated oxidation of the pesticide, and the modified spectrum did not change for at least the next 5 min. In the case of BXN, a non-fluorescent compound at pH 7 due to the total ionization of its OH group, a similar change was observed in the absorption spectrum (not shown).

3.2. Quenching of $^1\text{Rf}^*$ and $^3\text{Rf}^*$ by BXN and DCP

For these experiments, MeOH was chosen as a solvent in order to increase the PP solubility, especially in the case of the quenching of $^1\text{Rf}^*$, where a relatively high PP concentration was required. In air-equilibrated MeOH solution, Rf showed a fluorescence emission band centered at 520 nm. In the presence of ≥ 2 mM PP, the quenching of the fluorescence from $^1\text{Rf}^*$ was detectable as a decrease in the stationary emission intensity, but the shape of the emission spectrum did not change. The interaction $^1\text{Rf}^*\text{-PP}$ was quantified through time-resolved methods by monitoring the fluorescence lifetime of $^1\text{Rf}^*$ in the absence ($^1\tau_0$) and in the presence ($^1\tau$) of different PP concentrations. Through the classical Stern-Volmer treatment ($^1\tau_0/^1\tau = 1 + ^1k_q ^1\tau_0 [\text{PP}]$), the rate constant 1k_q (process (2), Scheme 1) was graphically determined (Fig. 3, Table 1). The fluorescence decay of $^1\text{Rf}^*$ in the absence and in the presence of PP was monoexponential, with $^1\tau_0 = 5.4$ ns, in agreement with previously reported data [31].

The decay of $^3\text{Rf}^*$ was measured at much lower Rf concentration, typically 0.02 mM, and at low enough laser energy in order to avoid self-quenching and triplet-triplet annihilation, respectively. The disappearance of $^3\text{Rf}^*$, generated by a 355 nm laser pulse, was monitored from the first-order decay of the absorbance at 670 nm, a wavelength where the interference from other possible species is negligible. The lifetime of $^3\text{Rf}^*$ appreciably decreased in the presence of a PP (process (4), Scheme 1). As before, a Stern-Volmer treatment of the triplet quenching, using the expression $^3\tau_0/^3\tau = 1 + ^3k_q ^3\tau_0 [\text{PP}]$ (where $^3\tau_0$ and $^3\tau$ are the experimentally determined lifetimes of $^3\text{Rf}^*$ in the absence and in the presence of a PP, respectively), yielded the bimolecular rate con-

Table 1

Rate constant values for the quenching of $^1\text{Rf}^*$ (1k_q) and $^3\text{Rf}^*$ (3k_q), overall (k_t) and reactive (k_r) quenching of $\text{O}_2(^1\Delta_g)$ by bromoxynil (BXN) and dichlorophen (DCP), and relative rates of oxygen consumption (ΔO_2) upon RB or Rf sensitization in air-equilibrated solutions. Reported data for phenol are included for comparison. Deuterated solvents were only employed in the determinations of k_t values.

Compd.	Solvent	1k_q ($\times 10^9$)	3k_q ($\times 10^9$)	k_t ($\times 10^8$)	k_r ($\times 10^8$)	k_r/k_t	ΔO_2 (RB) (relative)	ΔO_2 (Rf) (relative)
BXN	H ₂ O pH 7 or D ₂ O pD 7			0.24 ± 0.04	0.16 ± 0.005	0.66	0.18	1.00
	D ₂ O pD 12			0.25 ± 0.03				
DCP	MeOH or MeOD	2.6 ± 0.1	2.0 ± 0.08	0.04 ± 0.002	0.02 ± 0.002	0.50	1.00	0.66
	H ₂ O pH 7 or D ₂ O pD 7			2.70 ± 0.05	0.87 ± 0.04	0.32		
	D ₂ O pD 12			7.00 ± 0.08				
Phenol	MeOH or MeOD	4.7 ± 0.1	2.1 ± 0.1	0.08 ± 0.001	0.02 ± 0.002	0.25		
	H ₂ O pH 8			0.01 ^a	<0.01 ^a			
	MeOH	4.1 ^b	0.5 ^b					

^a From Ref. [36].

^b From Ref. [16].

starts 3k_q (Table 1). The determined values of 1k_q and 3k_q for each PP are similar to those reported for phenol [16].

In the absence of a PP, a spectrum similar to the expected one for $^3\text{Rf}^*$ was observed after the laser pulse (Fig. 3, inset) [15,32,33], while in the presence of a PP (0.6 mM, ca. 95% $^3\text{Rf}^*$ quenched by the PP) the shape of the long-lived absorption is in good agreement with that reported for the semiquinone radical RfH^* , formed from the radical anion $\text{Rf}^{\bullet-}$ (process (6)) [20,34]. Both $\text{Rf}^{\bullet-}$ and RfH^* have been formerly generated by electron transfer processes to $^3\text{Rf}^*$ from several hydroxyaromatic substrates of environmental and biological importance [33,35].

3.3. Quenching of $\text{O}_2(^1\Delta_g)$ by BXN or DCP

When solutions of the well-known exclusive $\text{O}_2(^1\Delta_g)$ generator RB were irradiated in pH 7 aqueous solution with visible light in the presence of a PP, oxygen consumption was observed, as well as small changes in the PP spectral component (Fig. 1, inset A). The spectral changes were more pronounced when the photoirradiation was performed under identical conditions but in pH 12 aqueous solution, as shown in Fig. 1, inset B, for the representative case of DCP.

The rate of oxygen uptake in the system RB ($A_{530} = 0.5$) plus DCP (0.5 mM) was ca. 5.5 times faster than in the system RB ($A_{530} = 0.5$) plus BXN (0.5 mM), measured under identical experimental con-

ditions (Table 1). As a comparison, the system RB ($A_{530} = 0.5$) plus phenol (0.5 mM) practically did not consume oxygen at all, within the same temporal window employed for the PPs. These results strongly suggest some degree of interaction of $\text{O}_2(^1\Delta_g)$ with the PP. RB was chosen as a sensitizer in order to focalize on the potential reaction of each PP with $\text{O}_2(^1\Delta_g)$, avoiding possible interferences due to interactions of the substrates with Rf electronically excited states.

The decay kinetics of $\text{O}_2(^1\Delta_g)$ phosphorescence was first order, and the lifetime agreed well with literature data [26]. The addition of a PP as a quencher lead to a decrease of the $\text{O}_2(^1\Delta_g)$ lifetime, unambiguously confirming the interaction of the pesticides with this oxidative species. The k_t values (Table 1) were graphically obtained in D₂O at pD 7 or pD 12 and in MeOD through the expression $\tau_{\Delta 0}/\tau_{\Delta} = 1 + k_t\tau_{\Delta 0}[\text{PP}]$, where τ_{Δ} and $\tau_{\Delta 0}$ are the $\text{O}_2(^1\Delta_g)$ lifetimes in the presence and in the absence of a PP, respectively (see representative plots in Fig. 4). Highly alkaline medium and methanol were employed as solvents in order to evaluate possible effects of pH and solvent polarity on the rate constants of the interaction $\text{O}_2(^1\Delta_g)$ –PP (Table 1). Both k_t and k_r values for PP are significantly higher than those described for phenol [36]. Furthermore, according to the data, the interaction $\text{O}_2(^1\Delta_g)$ –phenol appears as almost totally physical in nature (Table 1). Other authors [37] have also reported the absence of observable effective $\text{O}_2(^1\Delta_g)$ -mediated phenol oxidation in H₂O.

The rate constant k_r (process (14)) was determined by the above mentioned actinometric method, monitoring oxygen photoconsumption (Fig. 4, inset). The $\text{O}_2(^1\Delta_g)$ -mediated photooxidation

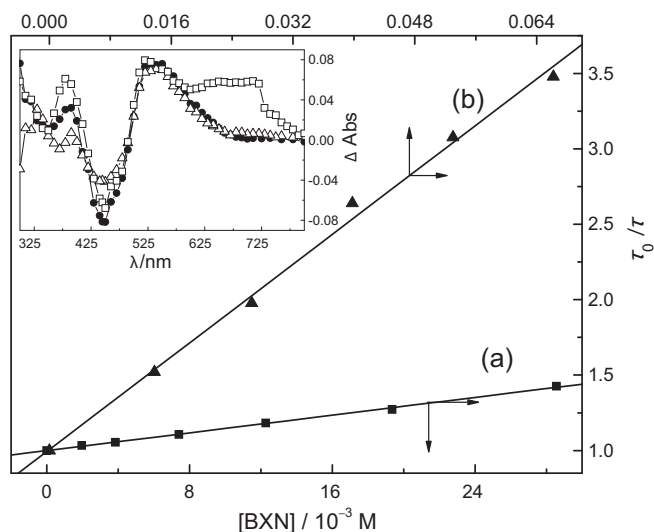


Fig. 3. Stern–Volmer plots for the quenching of $^1\text{Rf}^*$ (a) and $^3\text{Rf}^*$ (b) by BXN in MeOH. τ_0 and τ refer to $^1\text{Rf}^*$ or $^3\text{Rf}^*$ lifetimes in the absence and in the presence of BXN, respectively. Inset: transient absorption spectra of Rf (0.05 mM) in argon-saturated MeOH in the absence (■) (1 μs after the laser pulse) and in the presence of DCP (●) or BXN (Δ) (both 5 μs after the laser pulse).

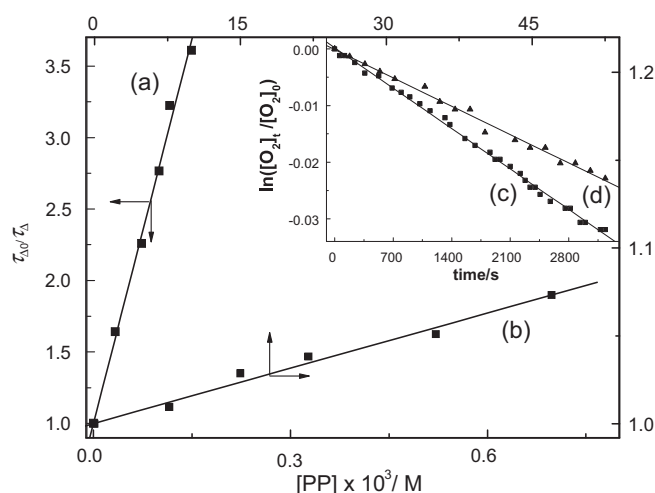


Fig. 4. Stern–Volmer plots for the quenching of $\text{O}_2(^1\Delta_g)$ phosphorescence by DCP in pH 12 D₂O solution (a), and in MeOD solution (b). Inset: first order plots for oxygen uptake in pH 7 H₂O by DCP (d), and FFA (c). RB as a sensitizer ($A_{548} = 0.5$).

quantum efficiency Φ_r ($\Phi_r = k_r [PP]/(k_d + k_t [PP])$) [11] is not easy to evaluate, particularly in natural environments, because its determination includes the knowledge of the actual concentration of the photooxidizable substrates, represented by the PP in this case. A simpler and useful approach is the evaluation of the k_r/k_t ratio (Table 1), which indicates the fraction of overall quenching of $O_2(^1\Delta_g)$ by the substrate that effectively leads to a chemical transformation.

3.4. Determination of half-wave potentials

The possible participation of charge transfer-type components in the photopromoted Rf–PP interactions was studied by determining the oxidation potentials of each PP. Linear scan voltammograms for the electro-oxidation of BXN and DCP, registered at a scan rate (ν) of 0.05 V s^{-1} , showed a well defined anodic oxidation peak in the potential region around 0.30 V vs. ECS. Linear voltammograms, after background current subtraction, were convoluted [38]. The convoluted current $I(t)$ for each PP reached a maximum value, I_L , which is characteristic of a purely diffusion-controlled process. If the reaction is Nernstian, the dependence of the potential, E , with $I(t)$ is expressed by $E = E_{1/2} - (RT/nF) \ln[(I_L - I(t))/I(t)]$ [38], where $E_{1/2}$ is the half-wave potential, n is the number of electrons exchanged per molecule of oxidized compound, and the other terms have their usual meaning. Linear plots were obtained from post-convolution analysis of E vs. $\ln(I_L - I(t))$ in the 90% of the curve for both BXN and DCP. The $E_{1/2}$ values, deduced from experimental plots with regression parameters better than 0.9992, were 0.71 V for BXN and 0.62 V for DCP. The $E_{1/2}$ value reported for the parent compound phenol is 0.63 [39].

4. Discussion

The above described results and the data in Table 1 allow the proposal of a plausible photochemical mechanism for the Rf-sensitized photodegradation of the studied pesticides, where Type I (radical reactions) and Type II ($O_2(^1\Delta_g)$ reactions) participate, as follows:

- The spectral changes observed upon aerobic photosensitization clearly show the occurrence of chemical transformations in both PP. With RB-sensitization, a pure $O_2(^1\Delta_g)$ -mediated process seems to operate. With Rf-sensitization, the different trend of the relative rates of oxygen uptake (Table 1), as compared to those obtained under RB-sensitization, suggests the operation of a more complex mechanism, at least different from a simple $O_2(^1\Delta_g)$ -mediated one.
- The quenching ability of each PP towards $O_2(^1\Delta_g)$ is moderate-to-high, according to the respective k_t and k_r values. For phenols and polyhydroxybenzenes [11,40], the accepted mechanism of the quenching is the initial formation of an encounter complex [$O_2(^1\Delta_g)$ -substrate] with partial charge-transfer character, from which an irreversible electron transfer process would yield the photooxidation products. The formation of this complex depends on the electron-donor ability of the substrate, and is favored in polar solvents. In phenols, the corresponding OH-ionized forms are the most photooxidizable species. In BXN, the electron withdrawing groups in the benzene ring decrease the pK_a value, selectively favoring the photooxidation (reaction (14)). In DCP, the presence of two phenol groups in the molecule gives rise to a relatively high value of the rate constant k_t . In spite of this, the observed k_r/k_t ratio in this pesticide indicates less efficient oxidation than in the case of BXN. This result can be a consequence of the partially ionized and non-ionized forms of the respective OH groups in the DCP molecule at pH 7. The for-

mation of the encounter-complex intermediate in both PPs is supported by the dependence of the kinetic data on both the pH of the medium and the solvent polarity. The rate constant k_t for BXN in pD 12 solution is the same as that in pD 7, because in both media the phenol group is totally ionized, whereas in DCP a substantial k_t increase is observed at higher pD value. In DCP at pD 12, both OH groups are almost totally ionized, whereas at pH 7 only one of the OH groups is partially ionized. In MeOD solution, both k_t and k_r values dramatically decrease in both PPs (Table 1). This dependence is interpreted as a solvent polarity effect on the charge-transfer mediated encounter complex.

- Both excited species $^1Rf^*$ and $^3Rf^*$ are quenched by each PP with rate constant values 1k_q and 3k_q , respectively, close to the diffusion limit. Nevertheless, under the experimental conditions used, the $^1Rf^*$ quenching process (process (2)) is undetectable, because for this quenching to be important, and considering the short lifetime of $^1Rf^*$ [41], a much higher PP concentration would be used in the photoirradiation experiments. The species $Rf^{\bullet-}$ is formed through electron transfer from ground state PP to $^3Rf^*$ (process (4)). Then, $Rf^{\bullet-}$ can transfer an electron to $O_2(^3\Sigma_g^-)$ yielding $O_2^{\bullet-}$ and regenerating ground state Rf (process (5)), or can undergo a fast protonation to RfH^{\bullet} (process (6)) [34,42,43]. Consequently, both $O_2^{\bullet-}$ and H_2O_2 can be generated in the medium. The species $PP^{\bullet+}$, formed in reaction (4), can decay or regenerate PP through ulterior radical recombination reactions. The alternative generation of $O_2^{\bullet-}$ by direct interaction of $^3Rf^*$ with $O_2(^3\Sigma_g^-)$ has not been taken into account in the present discussion because of the very low quantum yield of process (3) [9].
- The quenching of $^3Rf^*$ by electron-donating compounds such as phenols and polyhydroxybenzenes occurs through an electron transfer process (process (4)), with high values of the respective rate constant values 3k_q , close to $10^9 \text{ M}^{-1} \text{ s}^{-1}$ [16]. The thermodynamic feasibility of the process can be evaluated by means of the Gibbs free energy for electron transfer, $\Delta_{ET}G_0 = E_{0(PP/PP^+)} - E_{0(Rf/Rf^{\bullet-})} - E_{Rf^{\bullet-}} + C$, where $E_{0(Rf/Rf^{\bullet-})}$ is the standard electrode potential of the acceptor Rf (-0.80 V), $E_{Rf^{\bullet-}}$ is the $^3Rf^*$ energy (2.17 eV), C is the coulombic energy term (-0.06 V) [44] and $E_{0(PP/PP^+)}$ is the standard electrode potential of each pesticide. We employed the experimentally determined $E_{1/2}$ values (0.71 V for BXN and 0.62 V for DCP) as the respective $E_{0(PP/PP^+)}$ values [38]. The so-calculated $\Delta_{ET}G_0$ values, lower than -0.71 eV for both PPs, indicates that process (4) may be operative and, consequently, that the species RfH^{\bullet} could be spontaneously formed (process (6)). Under aerobic conditions, a cascade of processes can occur after process (4) (Scheme 1), some of them generating ROS. Thus, the species RfH^{\bullet} can undergo a bimolecular disproportionation reaction yielding fully reduced Rf (RfH_2) and Rf (process (7)). In the presence of $O_2(^3\Sigma_g^-)$, RfH_2 can be reoxidized, giving rise to $RfH_2^{\bullet+}$ and $O_2^{\bullet-}$ and, finally, to Rf and H_2O_2 (process (8)). Both oxidative species $O_2^{\bullet-}$ and H_2O_2 may react with the PP in the medium.

The prevalence of either the electron transfer process from a PP (Type I reaction) or the energy transfer process from $^3Rf^*$ to $O_2(^3\Sigma_g^-)$ (Type II reaction) (process (4) vs. process (11), respectively) can be discussed in kinetic terms. Considering the described k_{ET} value of process (11) in H_2O ($7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, i.e. 1/9 of the diffusional value) [45], and a 3k_q value for both PPs of $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Table 1), it can be deduced that, for the same concentrations of PP and dissolved $O_2(^3\Sigma_g^-)$, the rate for the radical-mediated pathway (process (4)) is ca. three times higher than the $O_2(^1\Delta_g)$ -generation process (11). In practical terms this indicates the operation of both processes (4) and (11).

The decrease in the rate of oxygen uptake in the presence of CAT (reaction (16)) confirms that in situ generated H_2O_2 participates in

the oxidation of each PP. Moreover, the viability of this reaction was independently checked in the absence of light (Fig. 2, inset). On the other hand, the increase of the oxidation rate (measured as increase of oxygen uptake) in the presence of SOD (Fig. 3) points to the involvement of H_2O_2 in the process, as formerly observed in other hydroxyaromatic compounds [46]. This is a consequence of the consumption of the species $\text{O}_2^{\bullet-}$, thus promoting the subsequent formation of H_2O_2 (reaction (15)), which is concomitantly consumed in reaction (10).

5. Conclusions

The Rf-photosensitized oxidation of BXN and DCP occurs through a mechanism mediated by H_2O_2 and $\text{O}_2(^1\Delta_g)$. Both pesticides are more easily degraded through the $\text{O}_2(^1\Delta_g)$ -mediated process (Type II reaction) than phenol – a compound hardly degradable by photooxidation – as a consequence of the much lower pK_a values of the phenol groups in these compounds. This conclusion constitutes an open possibility for the design of photodegradation-time-tunable phenolic pesticides by the adequate substitution pattern in the phenol molecule, in order to achieve an enough low pK_a value of the OH group.

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