Oxidation of ophthalmic drugs photopromoted by inorganic radicals

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ABSTRACT

The rate constants of the reactions of the sulfate ($SO_4^{\bullet-}$) and hydrogen phosphate ($HPO_4^{\bullet-}$) radicals with the imidazoline derivatives naphazoline, tetrahydrozoline, oxymetazoline, xylometazoline, and the model compound 2-methyl-2-imidazoline (IZ), were measured by flash-photolysis. The experimental values of these rate constants are on the order of 10^8–10^9 M^{-1} s^{-1}. The reactions with the sulfate radicals proceed by an initial attack on the aromatic rings, which leads to the formation of N-centered radicals of naphazoline and to phenoxyl radicals of the other substrates. The experimental absorption spectra of the intermediates were compared to those obtained from theoretical time-dependent density functional calculations with explicit account for bulk solvent effects.

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1. Introduction

The primary mechanism of action of several imidazoline derivatives employed in formulations of topical ocular decongestants is the vasoconstriction, accomplished by direct stimulation of α-receptors on blood vessels [1]. The drugs naphazoline (NZ), tetrahydrozoline (TZ), oxymetazoline (OZ) and xylometazoline (XZ) belong to this family of compounds (Scheme 1). For instance, OZ is usually found as a decongestant in various pharmaceutical preparations used in the treatment of eye-irritation and nasal-congestion derived of cold, rhinosinusitis and/or allergic symptoms. XZ acts locally as a nasal decongestant. It is also indicated for the symptomatic relief of redness of the conjunctiva in ocular surface mild irritation, such as those due to smoke, dust, stale air and allergies [2–4].

The presence of pharmaceuticals belonging to the groups of emerging pollutants (EPs) in surface and groundwaters although at low concentration (typically µg L^{-1}), constitutes an important concern because of their potential effects on humans and natural ecosystems [5,6]. Thus, research is currently being developed on the chemical identification and quantification of EPs, elucidation of transformation pathways assessment of their potential biological effects; and development and application of advanced treatment processes for their removal and/or mineralization.

Pharmaceuticals are generally absorbed by humans or animals after intake and are then attacked by metabolic degradation processes. However, significant fractions of the original drugs often are excreted in unmetabolized form [7]. In addition to metabolic excretion, disposal by flushing of unused or expired medication and drug-containing waste from manufacturing facilities can also contribute to environmental contamination [8]. Besides, some pharmaceutical pollutants escape degradation in waste treatment plants and enter the environment [9,10].

Advanced oxidation/reduction processes (AO/RPs), based on the intermediacy of hydroxyl and other radicals were proposed for the degradation of various pharmaceuticals detected in ground and surface waters [11]. A new AO/RP radical concept involving the activation of added potassium persulfate ($K_2S_2O_8$) to generate the strongly oxidizing sulfate radicals ($SO_4^{\bullet-}$, E^0 = 2.43 V) [12] was recently proposed for treating pharmaceutical drugs [13].

The presence of inorganic components in the aqueous matrix is of importance to the chemistry related with these reactive species, i.e., as the HO$^\bullet$ and/or $SO_4^{\bullet-}$ radicals involved in AO/RPs. These 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, HO$^\bullet$ and $SO_4^{\bullet-}$ radicals oxidize phosphate ions to phosphate radicals [14] ($H_2PO_4^\bullet$, $HPO_4^{\bullet-}$, $PO_4^{\bullet2-}$).

One of the objectives of this study is to determine the absolute rate constants for the reactions of the following substrates (S): NZ, TZ, OZ, and XZ with the $SO_4^{\bullet-}$ and $HPO_4^{\bullet-}$ radicals (reactions (1) and (2), respectively). For comparative purposes 2-methyl-2-imidazoline (IZ, Scheme 1) was employed as a common chromophoric model compound.

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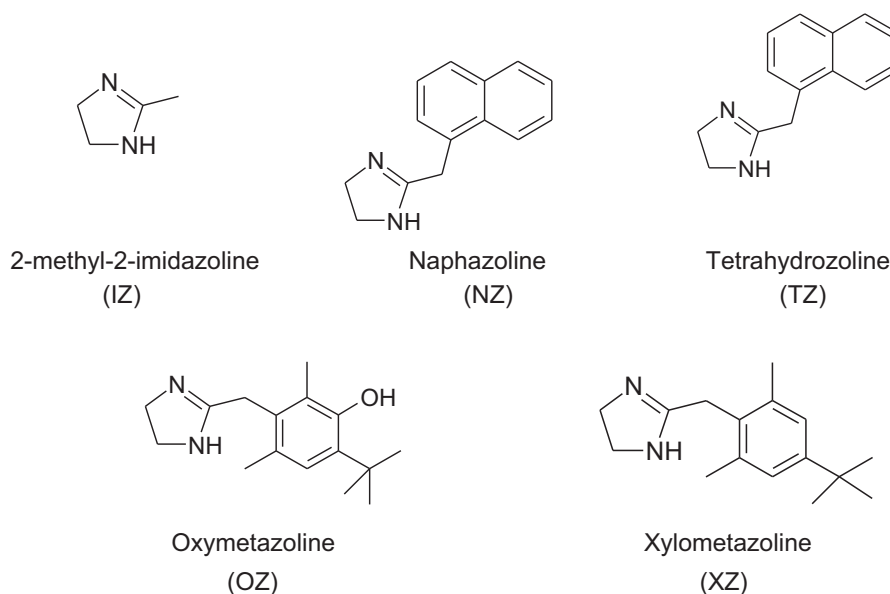
Scheme 1. Chemical structures of naphazoline (NZ), tetrahydrozoline (TZ), oxymetazoline (OZ), xylometazoline (XZ) and 2-methyl-2-imidazoline (IZ).

$$SO_4^{\bullet -} + S \rightarrow \text{organic radical} \qquad (1)$$

$$HPO_4^{\bullet -} + S \rightarrow \text{organic radical} \qquad (2)$$

The second objective is to obtain mechanistic information of reaction (1). For this purpose, the absorption spectra of the intermediates were obtained by means of flash-photolysis and some of them were compared to those obtained from theoretical time-dependent density functional calculations with explicit account for bulk solvent effects.

2. Experimental

2.1. Materials

Oxymetazoline (OZ), 3-(4,5-dihydro-1H-imidazol-2-ylmethyl)-2,4-dimethyl-6-tert-butyl-phenol, xylometazoline (XZ), 2-[(2,6-dimethyl-4-tert-butyl-phenyl)methyl]-4,5-dihydro-1H-imidazole, naphazoline (NZ) 2-(naphthalen-4-ylmethyl-4,5-dihydro-1H-imidazole, tetrahydrozoline (TZ), 2-tetralin-1-yl-4,5-dihydro-1H-imidazole, 2-methyl-2-imidazoline (IZ) were purchased from Sigma Chem. Co.; $Na_2S_2O_8$ (PS) was from Riedel de Haën. KH_2PO_4, K_2HPO_4 and NaOH (99%) were all from Merck. Potassium peroxodiphosphate (PP) was obtained from the electrolysis of alkaline solutions of KH_2PO_4 in the presence of KF and K_2CrO_4, as described in the literature [15].

2.2. Methods

2.2.1. Flash-photolysis

All the experiments were carried out at $25 \pm 1\,^\circ C$.

The equipment employed for the conventional flash-photolysis experiments was already described [16].

The method used to generate sulfate radical ions was the photolysis of PS solutions with $\lambda_{exc} < 300$ nm [17,18]. Phosphate radicals, were generated by photolysis ($\lambda_{exc} < 300$ nm) of PP aqueous solutions (pH 7.1 ± 0.1, adjusted with a KH_2PO_4/K_2HPO_4 buffer) [16].

In order to avoid thermal reactions of substrates (S) with the oxidants, the solutions containing PS or PP and S were prepared a few minutes before their irradiation. Accumulation of reaction products was precluded by doing single-shot experiments.

For the determination of the bimolecular rate constants of the reactions of the inorganic radicals with S, lower S concentrations (0–8.0 μM) than those used for the characterization of the organic radicals were employed. Photolysis experiments performed with solutions containing S in the absence of PS or PP did not yield detectable formation of transients, which guarantee that the organic radicals were formed by reaction of $SO_4^{\bullet -}$ or $HPO_4^{\bullet -}$ with S.

2.2.2. Computational details

The geometrical structures of the ground state intermediates were fully optimized by using the three-parameter hybrid functional O3LYP [19] combined with the 6-311++G(d,p) split valence basis set. This approach takes implicitly into account that the exchange (O) and the correlation (LYP) functionals are non-separable. Bulk solvent effects were accounted for with the conductor-like polarizable continuum model, CPCM [20] with a dielectric constant for water of 78.3553. For all cases, positive harmonic vibrational frequencies were obtained assuring that computed structures correspond to stable structures. Afterwards, the time-dependent density functional theory was employed to estimate the absorption spectra of the possible radical and radical cation transients [21–23]. To characterize the position and the intensity of the bands, the energies of the first twenty doublet–doublet electronic transitions and their associated oscillator strengths were calculated at the CPCM-TD-O3LYP/6-311++G(d,p) level of theory [24–27]. For all quantum-chemical calculations the Gaussian 09 package was employed [28]. To compare with the experiments, the simulated spectra were obtained by representing each electronic transition with Gaussian shape functions centered at the calculated band maxima. Finally, each whole spectrum was obtained by summing over all computed transitions [29]. As a previous work from this laboratory [25] a Gaussian band-width of $0.2\,\text{eV}\,(1613\,\text{cm}^{-1})$ was used to interpret the experimental spectra.

3. Results

Sulfate radicals were generated by irradiation of pH 4.4 $Na_2S_2O_8$ solutions containing the substrates in the concentration range from 0 to 8.0 μM. The apparent first order rate constants for the decay
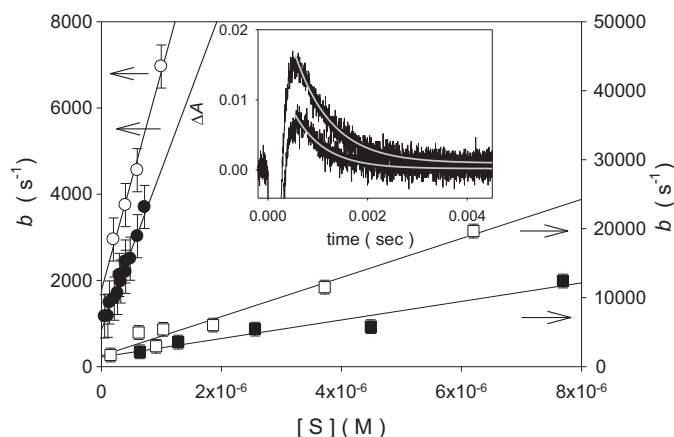
Fig. 1. Apparent rate constant b obtained for $SO_4^{\bullet-}$ radicals *vs.* [S] for (○) tetrahydrozoline, (●) oxymetazoline, (□) naphazoline and (■) xylometazoline. Inset: absorbance change obtained at 450 nm for solutions containing 5.0 mM of PS in the absence (upper trace) and in the presence (lower curve) of oxymetazoline 2.7×10^{-4} mM. Solid lines indicate fitting functions.

of $SO_4^{\bullet-}$ measured at 450 nm, b, linearly increases with [S] (Fig. 1). The slopes of the experimental linear plots yield the bimolecular rate constants k_1 shown in Table 1.

Hydrogen phosphate radicals were generated by irradiation of buffered (pH 7.1) PP solutions containing the substrates in the concentration range from 0 to 8.0 μM. The slopes of the linear plots of the apparent first order rate constants for the decay of $HPO_4^{\bullet-}$ measured at 500 nm *vs.* [S] (results not shown) yield the bimolecular rate constants k_2 shown in Table 1.

In order to characterize the organic radicals formed after reaction (1), air-saturated PS solutions with [S] higher than those employed for the determination of k_1 were used. Under these conditions the $SO_4^{\bullet-}$ radicals lifetime is <2 μs, and the absorption spectra of the intermediates obtained at 1 ms after the flash of light (see Figs. 2–4) are assigned to the organic radicals formed after reaction (1).

The organic transients observed for S in air-saturated solution decay by second-order kinetics, which indicates that the bimolecular decay with oxygen is not a competitive pathway for these radicals. Table 2 shows the values of $2k/\varepsilon$ at the maxima of absorption for all the substrates.

4. Discussion

Sortino and Scaiano [30] studied the reaction of the $SO_4^{\bullet-}$ radicals with NZ and reported a rate constant very similar to that measured here. As shown in Table 1, the values of k_1 for S are on the same order than the rate constants for the reactions of $SO_4^{\bullet-}$ radicals with substituted benzenes [31] ($1–5 \times 10^9$ M^{-1} s^{-1}) and with naphthalene [32] (2.8×10^9 M^{-1} s^{-1}). Based on the value of k_1 for IZ, which is one order of magnitude lower than for the other
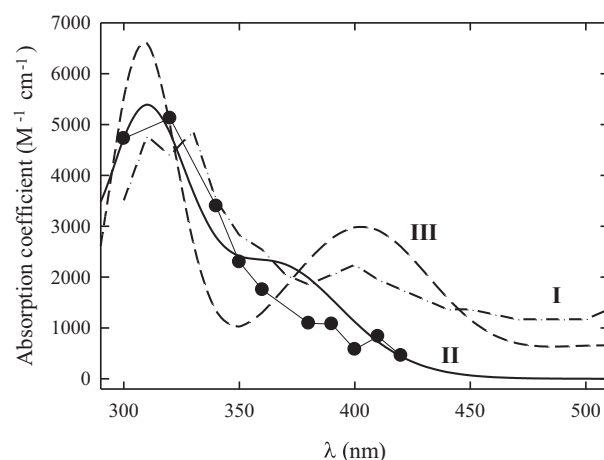
Fig. 2. Transient absorption spectra obtained 1 ms after the flash of light from irradiation of 25.0 mM PS solutions containing 5.0×10^{-2} mM naphazoline (●). (I) Literature absorption spectrum of the N-centered radical (product of reaction (4)) measured by Sortino and Scaiano [30]; (II) calculated absorption spectrum of N-centered radical cation; (III) calculated absorption spectrum of α-aminoalkyl radical. The absorption coefficients correspond to the theoretical spectra. The experimental data from this work and Ref. [24] were normalized.
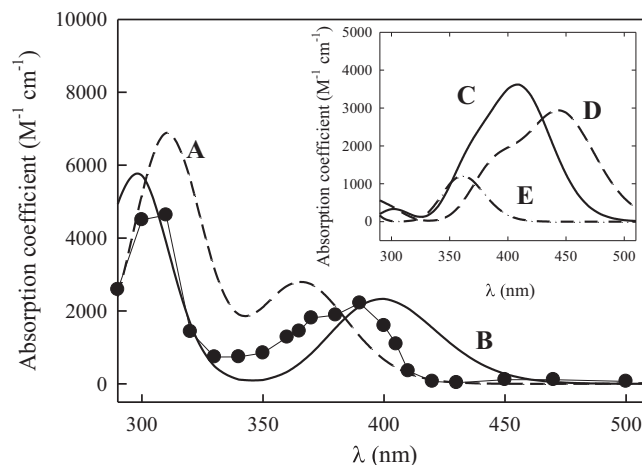
Fig. 3. Transient absorption spectra obtained 1 ms after the flash of light from irradiation of 25.0 mM PS solutions containing 1.1×10^{-2} mM oxymetazoline (●). Theoretical spectra for: (A) phenoxyl radical of OZ (reaction (3)); (B) phenoxyl radical of OZ (reaction (4)); (C) N-centered radical cation (reaction (5)); (D) C-centered radical (reaction (6)); (E) N-centered radical (reaction (7)). The absorption coefficients correspond to the theoretical spectra. The experimental data from this work were normalized.

substrates, we propose that for NZ, TZ, OZ and XZ the attack of the $SO_4^{\bullet-}$ radicals takes place on the aromatic moiety of the substrates.

Thus, we propose an initial attack of the $SO_4^{\bullet-}$ radicals to the naphthalene moiety of NZ to yield a radical cation of the molecule. Because the imidazoline ring acts as an efficient intramolecular

Table 1
Bimolecular rate constants k_1 and k_2 for the reactions of S with $SO_4^{\bullet-}$ and $HPO_4^{\bullet-}$ radicals, respectively.

|	k_1 (M^{-1} s^{-1})	k_2 (M^{-1} s^{-1})
Naphazoline	$(2.8 \pm 0.2) \times 10^9$[a]	$(4.1 \pm 0.4) \times 10^8$
Tetrahydrozoline	$(5.1 \pm 0.3) \times 10^9$	$(7.4 \pm 0.4) \times 10^8$
Oxymetazoline	$(3.7 \pm 0.3) \times 10^9$	$(9.8 \pm 0.5) \times 10^8$
Xylometazoline	$(1.3 \pm 0.2) \times 10^9$	$(1.4 \pm 0.2) \times 10^8$
2-Methyl-2-imidazoline	$(0.50 \pm 0.07) \times 10^9$	ND[b]

[a] The value reported in Ref. [24] is 4.0×10^9.
[b] Not determined.

Table 2
Values of λ_{max} and $2k/\varepsilon$ (λ_{max}) obtained for the organic radicals.

|	λ_{max} (nm)	$2k/\varepsilon$ (λ_{max}) $\times 10^{-5}$ (cm s^{-1})
Naphazoline	320	39 ± 1 (air)
Tetrahydrozoline	295	11.1 ± 0.6 (air)
Oxymetazoline	300	4.6 ± 0.3 (Ar)
		5.1 ± 0.3 (air)
		3.6 ± 0.2 (O_2)
Xylometazoline	305	16.4 ± 0.3 (air)
2-Methyl-2-imidazoline	290	0.32 ± 0.02 (air)
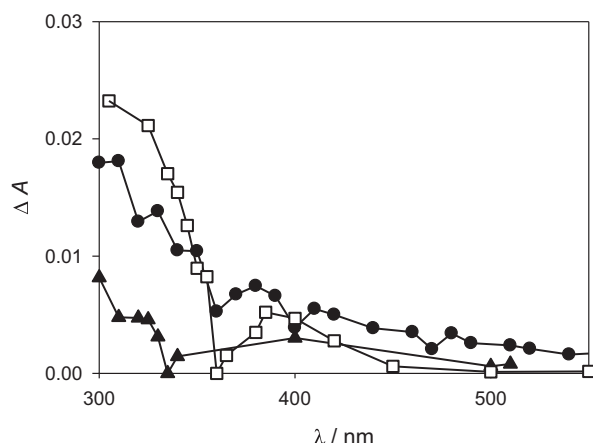
Fig. 4. Transient absorption spectra obtained 1 ms after the flash of light from irradiation of 25.0 mM PS solutions containing 0.12 mM 2-methyl-2-imidazoline (●), 7.6×10^{-3} mM tetrahydrozoline (▲), and 1.1×10^{-2} mM xylometazoline (□).

quencher in reducing the radical cation centered on the naphthalene moiety, we propose the formation of an N-centered radical cation (reaction (3)). Similar arguments were used by Sortino and Scaiano [30] to account for the formation of the N-centered radical cation after absorption of light by the naphthalene chromophore of NZ. This is in line with reported theoretical calculations, which show that in acidic or neutral solutions the oxidation occurs most readily at the naphthalene subunit of NZ [33]. The absorption spectrum of the N-centered radical cation was calculated here and is shown in Fig. 2 (spectrum II). Sortino and Scaiano [30] assigned the absorption spectrum of the organic intermediate to the deprotonated N-centered radical formed after reaction (4) (see spectrum I in Fig. 2). There is a good agreement between our flash-photolysis spectrum and that measured by Sortino and Scaiano [30], which is also similar to that calculated for the N-centered radical cation (spectrum II, Fig. 2). Thus, we assign our experimental spectrum to an N-centered radical.


(3)

(4)
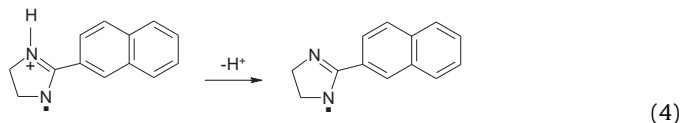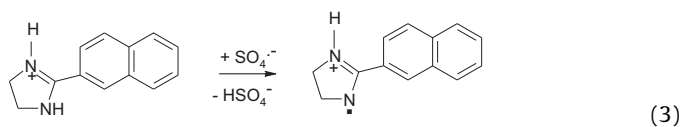
Due to the protonation of the imidazoline ring (pKa *ca.* 10), NZ is present in its cationic form under our experimental conditions [34].

The radical cations of N-containing heterocycles were reported to suffer H$^+$ elimination to yield α-aminoalkyl radicals [35,36], as shown in reaction (5) for NZ. For this reason, to evaluate if the intermediate generated after reaction of NZ with the sulfate radical could have any contribution of the α-aminoalkyl radical, the absorption spectrum of this radical was also calculated and is shown in Fig. 2. Because the calculations predict an absorption maximum in the region of 400 nm, which is not observed in the flash-photolysis experiments, the contribution of the α-aminoalkyl radical is expected to be negligible.

(5)
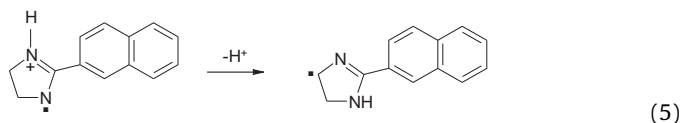
Phenoxyl radicals of substituted benzenes show two characteristic absorption maxima: one of them at around 300 nm and the other of lower intensity at 400 nm, and their bimolecular decay is independent of molecular oxygen [37]. Because of the shape of the absorption spectrum of the intermediate obtained for the reaction of the sulfate radicals with OZ (Fig. 3), the oxygen independence of its decay, and the expected reactivity of both N-centered and α-aminoalkyl radicals with molecular oxygen [35], we suspect that phenoxyl radicals are formed as reaction intermediates. Two different phenoxyl radicals A and B can be generated by H-abstraction (reaction (6)) or by an addition/elimination route (reaction (7)), respectively [37].

(6)

(7)
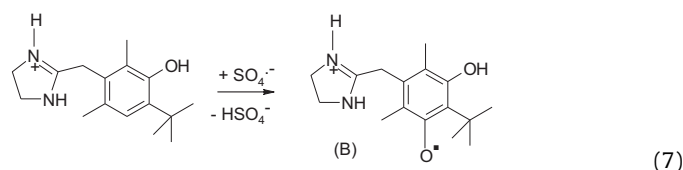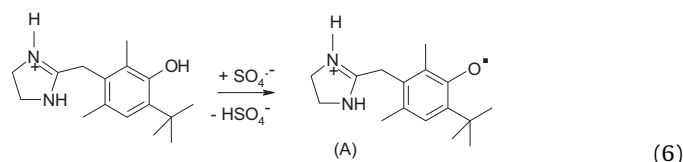
The absorption spectrum of radical A and even more that of radical B calculated here (Fig. 3) show a good agreement with the experimental traces, which supports the assignment to a phenoxyl radical. From the TD-DFT calculated molar absorption coefficient of the phenoxyl radical at 300 nm (5700 M^{-1} cm^{-1}) and the value of $2k/\varepsilon$ shown in Table 2, $2k = 2.6 \times 10^9$ M^{-1} s^{-1} is obtained in good agreement with the reported recombination rate constants of other phenoxyl radicals [16,38]. As can be seen from the inset Fig. 3 the N-centered radicals C and D, and the α-aminoalkyl radical E, which could be formed through reactions (8)–(10), similar to those proposed for NZ (see above) do not seem to contribute to the absorption spectra of the intermediate.

(8)

(9)

(10)
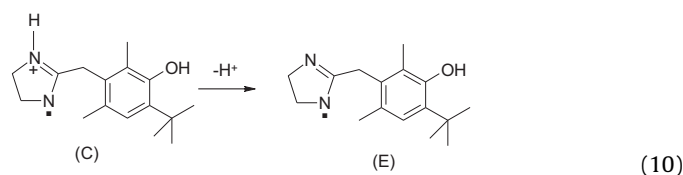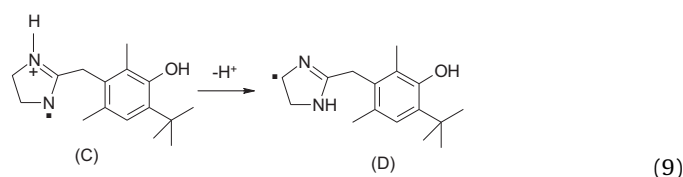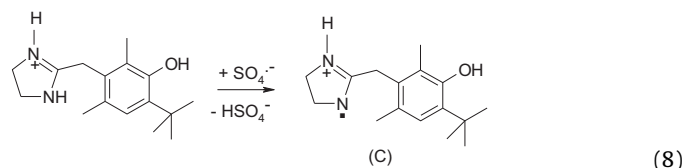
For the substrates TZ, OZ, and XZ, based on the measured values of k_1 compared to those obtained for IZ (see Table 2), we also propose an initial attack of the sulfate radicals on the aromatic ring. The similarity of the transient species observed for TZ, OZ, and XZ

also suggests the contribution of phenoxyl radicals to the measured absorption spectra.

The good agreement between the experimental transient spectra and that calculated for the phenoxyl radical B (reaction (4)) of OZ supports the assignment to this radical, although the contribution of species A (reaction (3)) cannot be neglected. Furthermore, both calculated spectra of the radical cation and the α-aminoalkyl radical of OZ show absorption above 400 nm, not observed in the experimental trace.

5. Conclusions

The ophthalmic drugs naphazoline, tetrahydrozoline, oxymetazoline and xylometazoline react with sulfate and hydrogen phosphate radicals with rate constants on the order of 10^8–10^9 M^{-1} s^{-1}.

The experimental spectra of the intermediate species formed after reaction of the sulfate radicals with the ophthalmic drugs were compared to those obtained from time-dependent density functional theory (TD-DFT) calculations. From this comparison, these reactions were shown to proceed by an initial attack of the inorganic radical on the aromatic rings, which leads to the formation of N-centered radicals of naphazoline and to phenoxyl radicals of the other substrates.

The presence of pharmaceuticals in surface and groundwaters although at low concentration, constitutes an important concern because of their potential effects on humans and natural ecosystems. Thus, the rate constants measured here and the information on the intermediate species of the reaction between the ophthalmic drugs and the sulfate and hydrogen phosphate radicals should be useful to understand possible alternative photodegradation routes of these pollutants in the presence of dissolved inorganic matter.

Acknowledgements

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