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Abstract

1-Nitronaphthalene (1NN) was used as a model of nitro-PAHs to investigate photosensitized reactions in aqueous solution in the presence of oxygen and halides. Laser Flash Photolysis (LFP) was employed to investigate electron transfer between halide anions and the triplet state of 1NN, leading to the formation of dihalogen radical anions ($X_2^{\bullet-}$) in solution. The experiments were performed in the absence or presence of oxygen, showing a bimolecular quenching rate constant for the triplet state of 1NN (^{3}1NN) by oxygen of $(1.95 \pm 0.05) \times 10^9$ M^{-1} s^{-1}. The decay of ^{3}1NN was observed to strongly depend on the pH of the medium. At pH > 2, ^{3}1NN decayed with a pseudo-first order rate constant close to 6.0×10^5 s^{-1}. The rate constant was markedly enhanced at lower pHs, reaching 2.0×10^6 s^{-1} at pH ~ 0.1, which suggests formation of the protonated triplet state (^{3}1NNH$^+$) at low pHs. Furthermore, we showed that the photoreactions of ^{3}1NN in the presence of oxygen are potential sources of $HO_2^{\bullet}$, $^1O_2$ and possibly $^{\bullet}OH$ in aqueous media.

In Milli-Q water (pH ~ 6.5) and in the presence of halide anions the quenching rate constant of ^{3}1NN was evaluated to be $(2.9 \pm 0.4) \times 10^4$ M^{-1} s^{-1} for chloride, $(7.5 \pm 0.2) \times 10^8$ M^{-1} s^{-1} for bromide, and $(1.1 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1} for iodide. Also in this case a pH-dependent reactivity was evidenced, and the quenching rate constant was $(7.7 \pm 1.2) \times 10^5$ M^{-1} s^{-1} with chloride at pH 1.1.

Keywords
Atmospheric chemistry, nitro-PAH, dihalogen radical anions, electron transfer

Introduction

The development of models to describe the behaviour of the atmosphere requires a detailed knowledge of the atmospheric processes. Despite a satisfactory understanding of atmospheric gas-phase chemistry, several processes linked to the role of anthropic emissions and their photoreactivity in both atmospheric gas and aqueous phases (clouds) are still not well understood.

Each cloud droplet can be considered as a highly efficient chemical reactor, where new reactions could start via absorption of sunlight [1]. In particular, anthropic emissions may increase the concentration of organic and inorganic compounds in and on the surface of atmospheric water droplets. These compounds could be able to start photochemical and photosensitized reactions upon radiation absorption.

Polycyclic Aromatic Hydrocarbons (PAHs) constitute one of the most widespread classes of organic pollutants in water, soil and atmosphere [2-7], and received particular attention due to their mutagenic effects [8]. The PAH nitroderivatives also cause concern for their direct mutagenicity. In addition to direct emission [9-11], some nitro-PAHs are formed in the atmospheric liquid and gas phases via photochemical and dark nitration [12-14].

Concerning the inorganic composition of the atmospheric aqueous phase, halides (mainly chloride) are among the most abundant water-soluble anions. The concentration of halide anions is comparable with that of sulphate and nitrate in marine clouds [15]. Typical values are from just a few up to 300 µM for chloride, from 0.06 to a few tens of µM for bromide, and less than 0.5 µM for iodide [15-18]. The concentration of halide anions increases considerably in marine surface water, and the photoinduced formation of halogenated radicals via homogeneous and heterogeneous photoreaction with organic compounds has been investigated in this medium recently [19-21].

Radical species such as $NO_3^\bullet$, $^\bullet OH$ and $SO_4^{\bullet-}$ are also present in and on the surface of cloud droplets. They could react with halide anions yielding halogen radicals ($X^\bullet$) [1,22,23] and dihalogen radical anions ($X_2^{\bullet-}$) (R1). These radicals are known to be responsible for ozone depletion [24], and consequently they can alter the oxidant capacity of the atmospheric aqueous and gas phases. They react with organic compounds (R2 - R3) via electron transfer, addition to double bonds and H-abstraction [25].

$$X^\bullet + X^- \leftrightarrows X_2^{\bullet-} \qquad\qquad\qquad\qquad (R1)$$
$$X_2^{\bullet-} + organics \rightarrow products \qquad\qquad (R2)$$
$$X^\bullet + organics \rightarrow products \qquad\qquad\quad (R3)$$

Although the halogen radicals can initiate a set of catalytic cycles capable of destroying ozone [26] or of oxidizing organic compounds (R2 and R3), to our knowledge only a limited number

of studies have investigated their formation via photosensitized reactions of organic compounds in the atmospheric aqueous phase.

The interaction between the excited state of 1NN (^{3}1NN) and halides has previously been reported in ethanol-water solution [27]. The H-atom abstraction between ^{3}1NN and ethanol, reported by the cited authors as the main reaction, suggests that the interaction between 1NN and halides could be affected by a solvent-triplet state interaction.

The aim of the present work was to investigate the interaction of 1NN, used as model compound for nitro-PAHs in the atmospheric aqueous phase, in the presence of halide anions. In the first part of the work we assessed the photoreactivity of 1NN in aqueous solution in the presence of oxygen at various pH values. The second part focused on electron-transfer reactions between ^{3}1NN and halides, which is a possible source of dihalogen radical anions ($X_2^{\bullet-}$) in the atmosphere. Furthermore, we point out the formation of $^1O_2$, $HO_2^{\bullet}$ and possibly $^{\bullet}OH$ due to the reactivity of ^{3}1NN in aqueous solution.

The presence of hydroperoxy radicals (*i.e.* $O_2^{\bullet-}$ / $HO_2^{\bullet}$) and singlet oxygen in the atmospheric aqueous phase is well established, and *in-situ* formation and gas-to-drop partitioning have been identified as two major sources [28-30]. It is clear that knowledge of new possible sources of such reactive species and their precursors in the atmospheric aqueous phase is a key step to a better understanding of the oxidant capacity of the atmosphere.

The majority of the work was carried out using the Laser Flash Photolysis technique (LFP), which allows the pseudo-first and pseudo-second order reaction rate constants of ^{3}1NN to be determined and the transient intermediates generated to be identified.

Experimental section

Materials

1-nitronaphthalene (99%), NaOH, HClO$_4$, H$_2$SO$_4$, HCl, sodium chloride, bromide and iodide (all of analytical grade) were purchased from Sigma-Aldrich and were used without further purification.

The water used to prepare the solutions was purified with a Millipore water system (Millipore αQ, resistivity 18 MΩ cm, DOC < 0.1 mg L^{-1}). All solutions were stored in the dark at 4° C.

Before each experiment, solutions were made by mixing appropriate volumes of concentrated 1NN solution and scavengers (i.e. halide anions) in a volumetric flask, filling with water up to 50 mL.

Laser Flash Photolysis

For 355 nm excitation, experiments were carried out using the third harmonic (λ_{exc} = 355 nm) of a Quanta Ray GCR 130-01 Nd:YAG laser system instrument, used in a right-angle

geometry with respect to the monitoring light beam. The single pulses were ca. 9 ns in duration, with an energy of ~ 45 mJ/pulse. Individual cuvette samples (3 mL volume) were used for a maximum of four consecutive laser shots. The transient absorbance at the pre-selected wavelength was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator and a photomultiplier (1P28). A spectrometer control unit was used for synchronising the pulsed light source and programmable shutters with the laser output. The signal from the photomultiplier was digitised by a programmable digital oscilloscope (HP54522A). A 32 bits RISC-processor kinetic spectrometer workstation was used to analyse the digitised signal.

Stock solutions of quenchers (i.e. halides) were prepared in Milli-Q water and an appropriate volume was added to the 1NN solution just before each experiment, to obtain the desired concentration of all the species. To derive the second-order rate constant for the quenching of ^{3}1NN, plots were made of the first-order decay constant of ^{3}1NN, determined from the regression lines of the logarithmic decays of ^{3}1NN monitored at 620 nm, against the concentration of quencher. Each value reported in figure 2, 3 and 5 was the average of 4 laser shots, and the standard deviation (not reported in plots) was less then 5%.

All experiments were performed at ambient temperature (295 ± 2 K) and in aerated solution, unless otherwise stated. Oxygen concentration (reported in figure 3) was checked with a YSI 550A oximeter.

Quantification of singlet oxygen and 1NN photodegradation under polychromatic irradiation

To evaluate the photochemical production of $^1O_2$ by 1NN, furfuryl alcohol (FFA) was used as $^1O_2$ acceptor [31]. In our experiments, 1NN (5.5×10^{-5} M) in presence of FFA (1×10^{-4} M) in water was irradiated under polychromatic light within the wavelength range 300-370 nm, with an energy of 60 W m^{-2} (Xenon AMKO-light 1000W). At fixed time intervals during irradiation, a sample aliquot was analysed by HPLC-UV on a 4.6 x 150 mm C-18 column. Elution was carried out with H_2O (pH = 2.7 with H_3PO_4)/ CH_3CN (85/15) at a flow rate of 1 mL min^{-1}, and FFA was detected at 220 nm with a retention time of 6.2 min. The same set-up was also used to monitor the transformation of 1NN in acidic solution. Analysis was carried out with the same instrument and column, eluting with H_2O/CH_3CN 50/50 at a flow rate of 1 mL min^{-1}. 1NN was detected at 230 nm with a retention time of 8.1 min.

Results and discussion

Photoreactivity of 1NN. Figure 1 shows a set of transient absorption spectra (up to 18 µs) obtained after a 355 nm laser pulse in pure water (pH 6.5) at 295 ± 2 K, in aerated (A) and oxygen-free (B) aqueous solutions of 1.1×10^{-4} M 1NN. Three different transition peaks were clearly discerned: two very intense absorptions at 620 and 400 nm were assigned to the lowest triplet excited state of 1NN (^{3}1NN) [32]. The transient species ^{3}1NN decays uniformly on a submicron time scale, and no residual absorbance was observed after about 20 µs. The nature of the 1NN triplet state has been the subject of discussion: some authors suggested a $\pi - \pi^*$ state, others a $n - \pi^*$ state, while some even suggest that the lowest energy state is correlated with the increase in solvent polarity, switching from $n - \pi^*$ to $\pi - \pi^*$. Fournier and co-workers [27] demonstrated that in polar solvents (e.g. water) the dipolar $\pi - \pi^*$ should be more stable than $n - \pi^*$.

The third transient peak, with a maximum absorption at 380 nm, was observed after the rest of the absorption bands significantly decreased. Figure 2 shows transient absorption decays of 1NN (5.0×10^{-5} M) aqueous solution at 380 nm as a function of oxygen concentration, obtained after the 355 nm laser pulses. A good fit of absorbance decay at 380 nm was obtained with a double-exponential plot (see solid line in figure 2 for the argon-saturated solution), indicating the presence of two transient species. The first one was attributed to ^{3}1NN because its pseudo-first order rate constant was identical to the 620 nm transient (k_{decay} ~ 6.5×10^5 s^{-1} in aerated aqueous solution). The second species had a first-order decay of 2.3×10^4 s^{-1}, absorbing light between 350 and 420 nm as shown in figure 1. A similar transient absorption spectrum was observed by Martins et al. [33] and was attributed to the radical anion of 1NN (1NN$^{\bullet-}$), which is formed mainly in the absence of oxygen (in agreement with our results) and in water-ethanol solution. The cited authors suggested that 1NN$^{\bullet-}$ was produced upon H-atom abstraction by excited 1NN from the solvent (ethanol, in α-position), followed by deprotonation of the radical thus generated (1NNH$^{\bullet}$). It would also follow a one-electron transfer from the resulting 1-hydroxyethyl radical (CH$_3$C$^{\bullet}$HOH) to 1NN, leading the formation of a further 1NN$^{\bullet-}$ molecule.

An interesting novelty of the present work is represented by the detection of 1NN$^{\bullet-}$ in the absence of organic H-donors. In fact, our experimental results in pure aqueous solution suggest that the formation of 1NN$^{\bullet-}$ arises directly from oxidation of water by ^{3}1NN. The excited triplet state of 1NN may react with water via H-abstraction, yielding the hydroxyl radical ($^{\bullet}$OH) and 1NNH$^{\bullet}$, in equilibrium with the deprotonated form (1NN$^{\bullet-}$). Finally, such a process is a potential $^{\bullet}$OH source in aqueous solution, and is consistent with previous findings concerning the oxidation of OH$^-$ by ^{3}1NN in water/ethanol systems [33].

Further investigations showed that ^{3}1NN decay was independent of the initial concentration of 1NN between 1.4 and 14×10^{-4} M, suggesting that 1NN self-quenching should not occur in the concentration range adopted in this work.

Effect of oxygen. It is evident from Figure 1 that oxygen has no impact on the concentration of ^{3}1NN initially formed after the pulse, as can be seen from the initial absorbance. However, concentration of the 380 nm transient species (1NN$^{\bullet-}$) increased about two-fold in the absence of oxygen. To evaluate and understand the processes involving oxygen, the pseudo-first order decay rates of ^{3}1NN and 1NN$^{\bullet-}$ were monitored at 620 and 380 nm, respectively, in aerated, oxygen-saturated and deaerated solutions. From figure 3 it is clear that the first-order decay rates of ^{3}1NN and 1NN$^{\bullet-}$ increase with increasing oxygen concentration (from 8.0×10^4 to 2.0×10^6 s^{-1} and from 5.7×10^3 to 1.5×10^5 s^{-1}, respectively), showing a good linear dependence on [O$_2$]. The values of the bimolecular quenching rate constants with O$_2$ were determined as $(1.95 \pm 0.05) \times 10^9$ M^{-1} s^{-1} and $(1.51 \pm 0.25) \times 10^8$ M^{-1} s^{-1} for ^{3}1NN and 1NN$^{\bullet-}$, respectively. Our data are in agreement with a previous investigation by Wilkinson et al. [34], who reported a solvent-independent pseudo-second order decay constant for ^{3}1NN of 1.5×10^9 M^{-1} s^{-1}. In addition, we found that also 1NN$^{\bullet-}$ is able to react with oxygen. Some oxygen-mediated reactions (R4 – R6) are suggested to explain the experimental data reported above:

$$^3\text{1NN} + \text{O}_2 \rightarrow \text{1NN} + {}^1\text{O}_2 \qquad\qquad\qquad \text{(R4)}$$
$$\text{1NN}^{\bullet-} + \text{O}_2 \rightarrow \text{1NN} + \text{O}_2^{\bullet-} \qquad\qquad\qquad \text{(R5)}$$
$$\text{O}_2^{\bullet-} + \text{H}^+ \leftrightarrows \text{HO}_2^{\bullet} \qquad\qquad \text{pK}_a = 4.88 \qquad \text{(R6)}$$
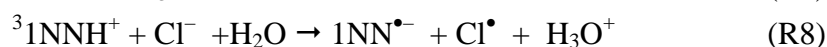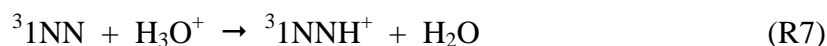
It is well known that most triplet states of organic compounds are efficiently quenched by oxygen through energy transfer. Taking into account the energy of ^{3}1NN (E$_T$ = 231 kJ mol^{-1}) [35] we can argue that, following reaction 4, interaction with molecular oxygen leads to the formation of both the first and the second electronically excited singlet states: O$_2$($^1\Delta_g$) (94 kJ mol^{-1}) and O$_2$($^1\Sigma_g^+$) (157 kJ mol^{-1}). Quantification of singlet oxygen photoformation via reaction R4 was possible by using FFA as a chemical probe, and we found a formation rate $R_{{}^1O_2} = 1.5 \pm 0.1 \times 10^{-8}$ M s^{-1}.

The reaction between 1NN$^{\bullet-}$ and oxygen (R5) resulting in superoxide was proposed by analogy with the corresponding processes that involve species produced upon reduction of the triplet states of aromatic carbonyls [36] and anthraquinones [37]. It is also consistent with the detection of H$_2$O$_2$ upon irradiation of 1NN in the presence of oxidisable organic substrates [38], where hydrogen peroxide would be formed upon dismutation of O$_2^{\bullet-}$/HO$_2^{\bullet}$.

Effect of acidity. Martins et al. [33] investigated the effect of pH on 1NN photoreactivity in aqueous-ethanol solution in the presence of salts (i.e. Cl$^-$ and Br$^-$). The authors showed that the pH plays a key role during electron transfer from halides to the excited state of 1NN, via formation of the protonated triplet state (^{3}1NNH$^+$) (pKa ~ 0.66) in ethanol-water solution.

We monitored the decay of ^{3}1NN at 620 nm both in pure water and in the presence of halide anions (i.e. Cl$^-$) at various pH values as reported in figure 4. The pH was adjusted upon addition of HClO$_4$. Interestingly, in the presence or absence of Cl$^-$, the pseudo-first order degradation rate constant of ^{3}1NN was close to 6.0×10^5 s^{-1} between pH 2.0 and 10.7. By decreasing the pH of the solutions down to ~ 0.1, the rate constant increased up to 2×10^6 s^{-1} and 1×10^7 s^{-1} in pure water and in the presence of 0.33 M NaCl, respectively. The results show that at very low pHs the medium has a strong effect on the triplet lifetime (τ), which is reduced from 1.8 to 0.1 µs in salted solution at pH ~ 0.1. Trotter and Testa [39] investigated the photochemical behaviour of 1NN in isopropanol–water medium with addition of HCl. The cited authors reported that protonation of the excited state to form ^{3}1NNH$^+$ (R7) is the cause of the fast disappearance of 1NN under acidic compared to circumneutral pH conditions. Our experimental data, obtained by use of water as a solvent, suggest that the protonated triplet state (^{3}1NNH$^+$) could react with chloride ions (R8), with possible formation of chlorine radicals (Cl$^\bullet$). This reaction could explain the faster quenching of the triplet state at very low pHs in the presence of chloride, and the occurrence of ^{3}1NNH$^+$ would also be consistent with the pH trend of triplet quenching without chloride.

The results displayed in figure 4 give clear evidence that the decay of ^{3}1NN monitored at 620 nm is higher at low pH and in the presence of chloride. At pH 6.5 in aerated solution the ^{3}1NN lifetime is about 1.8 µs, and it decreases to ~1.0 µs by acidifying the solution to pH 1.1. Moreover, in the presence of 0.33 M NaCl the triplet lifetime drops to 0.5 µs, most likely due to the reaction R8 that quenches the triplet state.

$$^3\text{1NN} + \text{H}_3\text{O}^+ \rightarrow {}^3\text{1NNH}^+ + \text{H}_2\text{O} \qquad\qquad\qquad (R7)$$
$$^3\text{1NNH}^+ + \text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{1NN}^{\bullet-} + \text{Cl}^\bullet + \text{H}_3\text{O}^+ \qquad\qquad (R8)$$

Flash photolysis of 1NN in the presence of chloride results in the formation of a transient species that absorbs in the wavelength range from 280 to 450 nm. The decay rate in aqueous solution and the spectrum of this new transient species (shown in Figure 5) are in agreement with those reported in the literature for Cl$_2^{\bullet-}$ [40]. According to R8, chlorine radicals (Cl$^\bullet$) would be produced directly upon electron transfer between chloride and ^{3}1NN. They would react rapidly with chloride ions to form Cl$_2^{\bullet-}$ (R1), with a second-order rate constant of 8.0×10^9 M^{-1} s^{-1} [40]. In the presence of an elevated chloride concentration as chosen in this work, the [Cl$_2^{\bullet-}$]/[Cl$^\bullet$] ratio is expected to be high and, consequently, the contribution of the chlorine radical to the observed absorption traces can be neglected [25].

Steady-state irradiation of 0.1 mM 1NN, using $HClO_4$, HCl or H_2SO_4 to fix the pH at 1, showed that the decay rate of 1NN in acidified aerated solution was lowest using HCl. This result would seem to contrast with the data reported in figure 4 and with R7 and R8 that suggest a fast degradation of the 1NN triplet state in acidified media containing chloride. However, it should be remembered that the reaction R8 between ^{3}1NNH$^+$ and Cl$^-$ would yield the radical anion (1NN$^{\bullet-}$) and the chlorine radical (Cl$^{\bullet}$). Furthermore, 1NN$^{\bullet-}$ would react with oxygen to yield back 1NN (following a catalytic-type reaction) and $O_2^{\bullet-}$ (reaction R5). The whole process would be a null cycle as far as 1NN is concerned, with no net degradation. For this reason, despite R8, chloride is expected to inhibit rather than enhance the photodegradation of 1NN.

Reactions with halide anions.

The quenching rate constant and the photoinduced formation of dihalogen radical anions via electron transfer between halides and the excited state of 1NN (^{3}1NN) were investigated for the three main halide ions present in the atmospheric aqueous phase, *i.e.* chlorine, bromine and iodine.

Figure 6 reports the rate constants for the pseudo-first order decay of ^{3}1NN as a function of chloride concentration, at pH 6.5 and 1.1. In both cases the rate constant increased with increasing chloride, which is consistent with a reaction between the triplet state(s) of 1NN and the chloride anion. As reported before, the data allow for the determination of the second-order rate constants for the quenching of the triplet state by chloride. The calculated value was quite low at pH 6.5 ((2.9 ± 0.4) $\times 10^4$ M^{-1} s^{-1}) compared with pH 1.1 ((7.7 ± 1.2) $\times 10^5$ M^{-1} s^{-1}). This finding suggests that two different species are involved in the reaction with chloride: they could be ^{3}1NN and its protonated form ^{3}1NNH$^+$, with ^{3}1NNH$^+$ being more reactive than ^{3}1NN. The dichlorine radical anion (Cl$_2^{\bullet-}$) was identified upon LFP of 1NN + Cl$^-$ at both circumneutral and acidic pH, which further supports the hypothesis that both ^{3}1NNH$^+$ and ^{3}1NN can oxidise chloride to Cl$^{\bullet}$, and that the latter reacts with chloride to yield Cl$_2^{\bullet-}$. The growth and decay of Cl$_2^{\bullet-}$ were monitored at 340 nm, which is the absorption maximum for this transient species [41].

Bromide is present in the atmospheric aqueous phase at typical concentrations ranging from tens nM to a few tens μM [17]. LFP experiments with 1.1×10^{-4} M 1NN in the presence of 500 μM bromide showed the formation of a new long-lived transient species that absorbs from 300 to 420 nm. This transient species, with a maximum absorption at 360 nm, has previously been identified as the dibromine radical anion (Br$_2^{\bullet-}$) [40].

The presence and quantification of iodide anions in atmospheric waters has been reported by Neal and co-workers [18]. They reported iodide concentrations ranging from about 0.01 to 0.52 μM, and suggested both anthropic and marine contributions. In the present work, the presence of 50 μM iodide was sufficient to quantitatively quench the triplet state (^{3}1NN), generated by

LFP (355 nm, 40 mJ) of 1.1×10^{-4} M 1NN at pH 6.5. Triplet lifetime was decreased from 1.8 µs (in the absence of iodide) to 1 µs. The formation of a new transient species with an absorption maximum at 385 nm was attributed to the diiodine radical anion ($I_2^{\bullet-}$), by comparison with literature data [42].

Table 1 reports the bimolecular quenching constants of ^{3}1NN in aerated solution, with different halides and at different pH values. The quenching rate constant increased with decreasing the standard oxidation potential, $E°(X^-/X^\bullet)$, of the respective quenchers (Cl^-, Br^- and I^-)[43]. These results are in agreement with the above-reported mechanism that involves oxidation of the halide via electron transfer to ^{3}1NN. They are also in agreement with the results of Reeser and co-workers [20], concerning the photooxidation of halides by chlorophyll via heterogeneous reactions at the air-water interface.

Although bromide and iodide are present at lower concentration than chloride in cloud water, their higher reactivity toward ^{3}1NN might be an additional source of dihalogen radical anions in the atmospheric aqueous phase. Furthermore, Matthew and co-workers [44] have shown that the reaction in aqueous solution of $Br_2^{\bullet-}$ with $HO_2^\bullet$ may play a key role in the formation of gaseous and aqueous molecular bromine (Br_2).

Considering the second-order reaction rate constants reported in Table 1 and referred to circumneutral conditions, chloride at a concentration of 300 µM would scavenge as much ^{3}1NN as 0.01 µM bromide and 0.001 µM iodide. From the typical concentration values of the halogenide anions in the atmospheric aqueous phase [15-18], it could be inferred that the irradiation of 1NN could sensitise the formation of $Br_2^{\bullet-}$ and $I_2^{\bullet-}$ to a higher extent than for $Cl_2^{\bullet-}$.

Figure 7 reports the percentage of triplet quenching by 300 µM O_2 (which yields $^1O_2$), 300 µM chloride (to give $Cl_2^{\bullet-}$), and 0.5 µM iodide (to give $I_2^{\bullet-}$), as a function of the concentration of bromide up to 20 µM (which yields $Br_2^{\bullet-}$). Based on data of this work we can argue that most ^{3}1NN would be scavenged by oxygen to give $^1O_2$. Moreover, negligible production of $Cl_2^{\bullet-}$ and non-negligible generation of $Br_2^{\bullet-}$ and $I_2^{\bullet-}$ are expected. Also note that the concentration of the halide anions in the aqueous film surrounding the airborne particles of marine origin could even be higher (up to 8 mM Br^- and 6 M Cl^-) [45] than in seawater, where in turn the halides are much more concentrated than in cloud water. Therefore, in the surface aqueous film of marine aerosols, the production of dihalogen radicals could be considerably increased at the expense of $^1O_2$.

Conclusions

The present work shows that 1NN can be excited by UVA radiation to yield the triplet state, which can react with oxygen, the halide anions (X^-) and possibly water. Therefore, the photochemistry of 1NN yields reactive species ($^1O_2$, $X_2^{\bullet-}$, possibly $^\bullet OH$) that play an important role in the chemistry and photochemistry of the aqueous phase in the atmosphere. The present work also shows that these processes can take place in aqueous solution which, despite the presence of H-donors in the atmospheric aqueous phase, is much more representative of the environmental conditions than water-ethanol mixtures, where the H-donor concentration is much higher than in atmospheric waters.

The different reactions of the 1NN triplet state are in competition with one another, and the reaction with O_2 to yield $^1O_2$ is likely to prevail in cloud water. Figure 2, which reports the pseudo-first order decay constant of the triplet state vs. $[O_2]$, suggests an upper limit for the reaction rate between ^{3}1NN and water that corresponds to the behaviour of the deoxygenated solution. In the most favourable hypothesis, the possible production of $^\bullet OH$ from ^{3}1NN under atmospherically significant conditions would represent only a small fraction of that of $^1O_2$.

The pH trend of the decay of the triplet state suggests that two forms may be present, ^{3}1NN and ^{3}1NNH$^+$. The reactivity of the protonated form would be considerably higher than that of the neutral one. The reaction rate constants between ^{3}1NN and the halide anions come in the order iodide > bromide > chloride, which is reasonable considering that the process involves a one-electron transfer and given the reduction potential of the halogen radicals thus generated. The reaction rate constants are in reverse order than the typical concentration values of the anions in the atmospheric aqueous phase, but the reaction between ^{3}1NN and chloride is too slow to yield $Cl_2^{\bullet-}$ in significant amount. The reaction with iodide would be limited by the low concentration of the anion in atmospheric waters. In contrast, the production of $Br_2^{\bullet-}$ could be significant in bromine-rich aerosols, where bromide concentration is enhanced at the solution/vapour interface compared to chloride [46]. This is potentially very significant because bromine radicals take part to ozone depletion processes [24,47] and are very effective brominating agents in aqueous solution [48,49], which could lead to the formation of environmentally persistent brominated secondary pollutants.

Certainly, the real impact of 1NN depends on its concentration and on the inorganic composition of the media, but nevertheless we have demonstrated that the reaction of nitro-PAHs with inorganic compounds (i.e. halide anions) may be extremely important for assessing the radical formation in the atmospheric aqueous phase.

Finally, in order to mimic the aqueous-phase interaction between nitro-PAHs and organic H-donors, future works will be focused on the effect of phenol (as model H-donor in atmospheric water) on the 1NN photochemistry, with particular attention to the photoreaction products (i.e. halogenated and hydroxylated species).

Table 1

Second-order rate constants for the quenching of the triplet state of 1-nitronaphthalene (^{3}1NN) in aqueous solution, and comparison with literature data. The differences between the literature rate constants and those found in the present work at comparable pH are most likely accounted for by the different solvent adopted (ethanol-water [33] vs. water in the present work).

Anion	E°(X⁻/X•) (V)	conditions	k (M⁻¹ s⁻¹)
Cl⁻	1.36	pH 1.1 [a]	$(7.7 \pm 1.2) \times 10^5$
		pH 6.5 [a]	$(2.9 \pm 0.4) \times 10^4$
		pH 7.7 [b]	$(5.4 \pm 1.0) \times 10^4$
Br⁻	1.09	pH 6.5 [a]	$(7.5 \pm 0.2) \times 10^8$
		pH 7.7 [b]	$(6.0 \pm 0.2) \times 10^8$
I⁻	0.54	pH 6.5 [a]	$(1.1 \pm 0.1) \times 10^{10}$
		pH 7.7 [b]	$(5.4 \pm 0.5) \times 10^9$

[a] this work; [b] from literature data in buffered solution, 25% (v/v) ethanol-water [33].
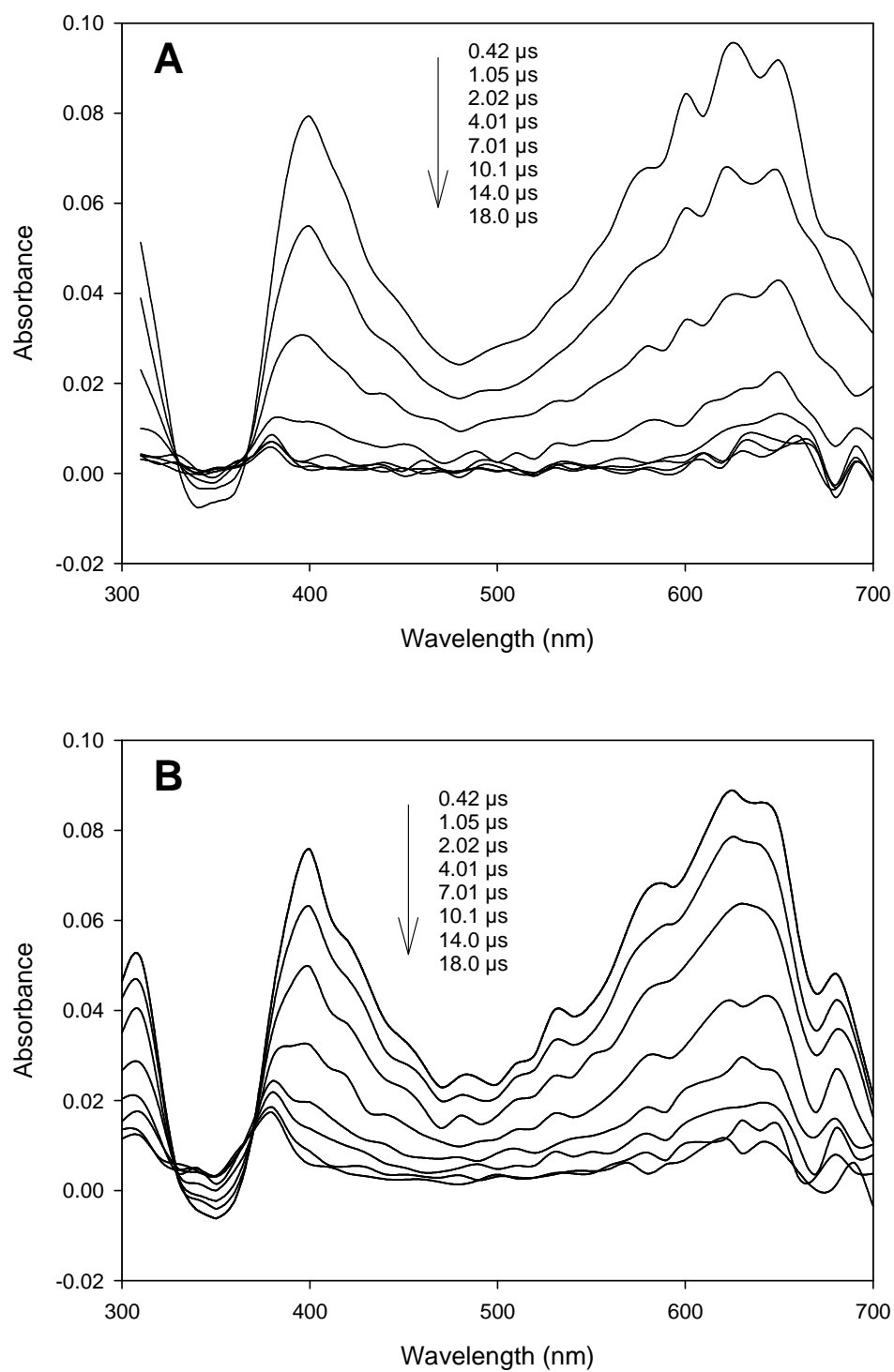
Figure 1. Transient absorption spectra produced upon LFP (355 nm, 45 mJ) of 1NN (1.1 × 10^{-4} M) in aerated (**A**) and oxygen-free (**B**) aqueous solutions (pH 6.5) at ambient temperature (295 ± 2 K).
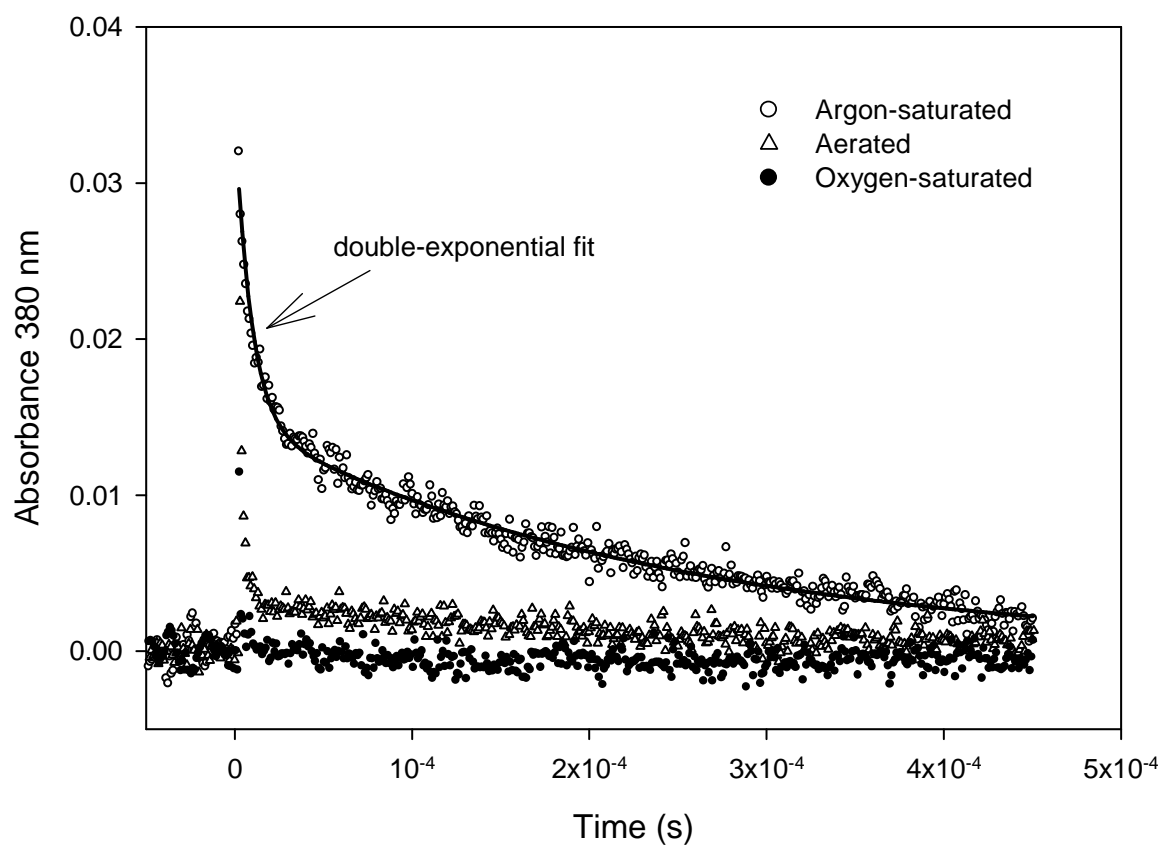
Figure 2. Decay at 380 nm as a function of oxygen concentration. Transient were obtained upon LFP (355 nm) of 1NN (5.0×10^{-5} M) as function of oxygen concentration: after 20 min of argon saturation (o) in aerated solution (Δ) and after 20 minutes of oxygen saturation ($\bullet$).
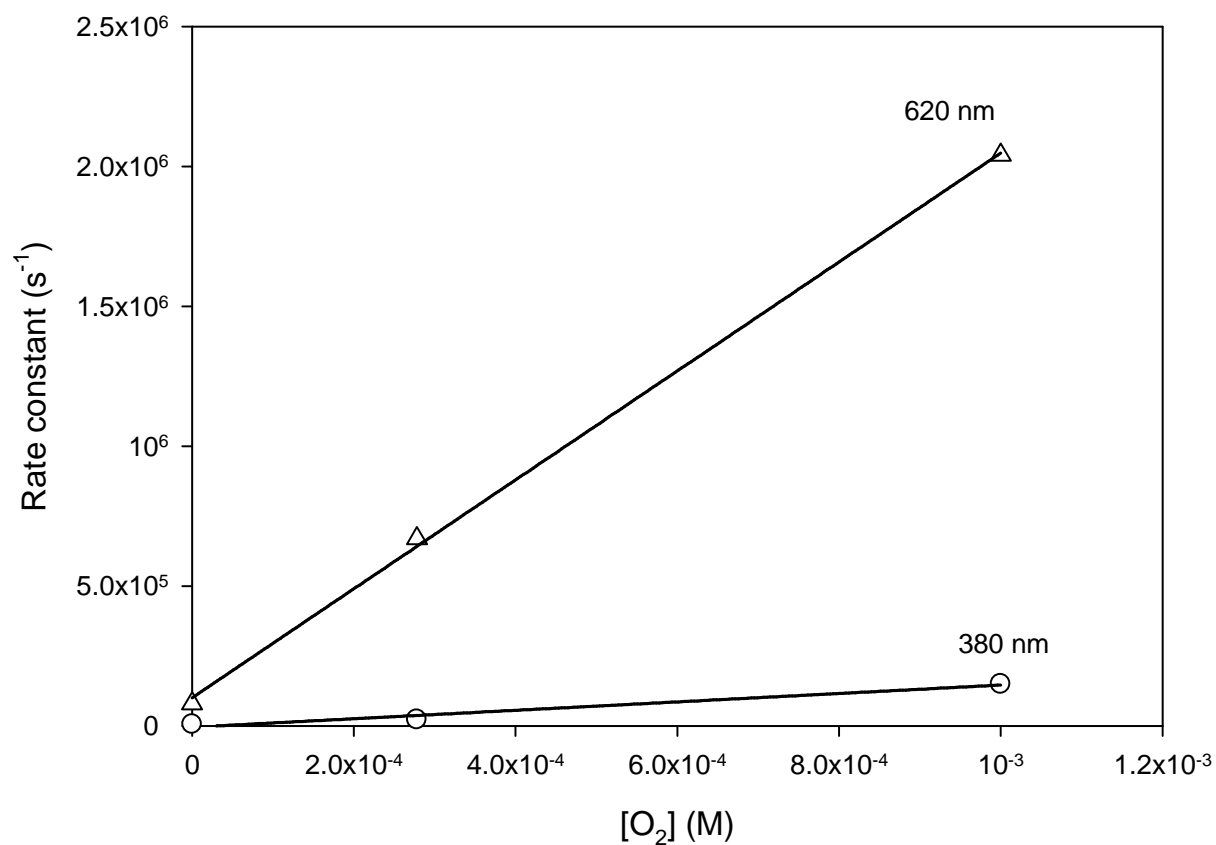
Figure 3. Dependence on the oxygen concentration of the pseudo-first order decay of 1-nitronaphthalene triplet state (^{3}1NN) and 1-nitronaphthalene radical anion (1NN$^{\bullet-}$) in Milli-Q water (pH 6.5) at ambient temperature. The two transient species were monitored at 620 and 380 nm, respectively. Deaerated and oxygen-saturated solutions were used after 20 minutes of bubbling with Argon or pure oxygen, respectively.
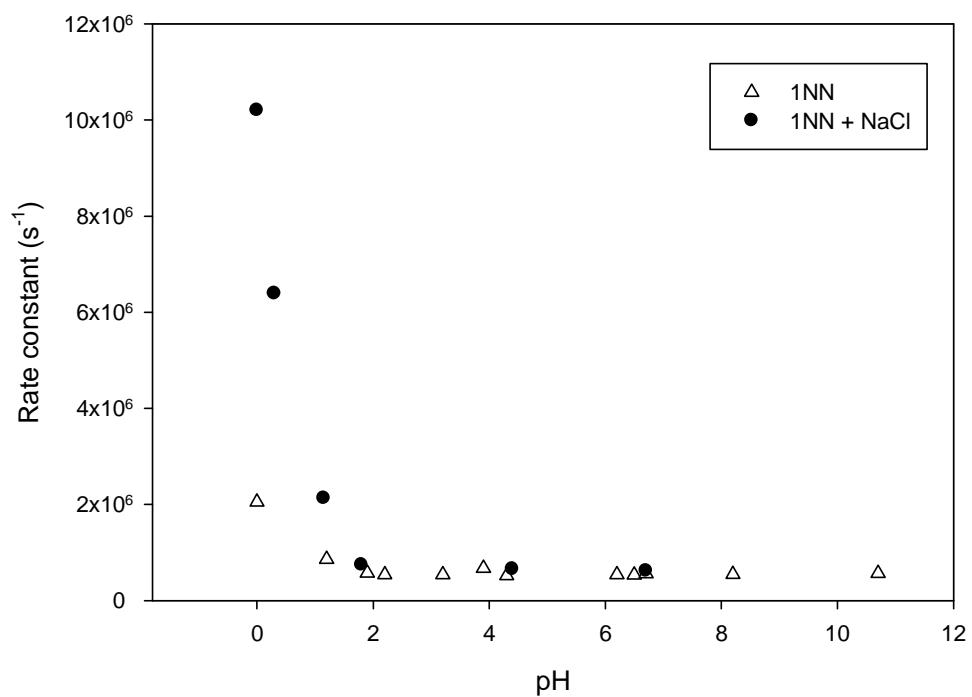
Figure 4. Pseudo-first order decay of ^{3}1NN (monitored at 620 nm) as a function of pH. Open triangles using a solution of 1.1×10^{-4} M 1NN in Milli-Q water and full circle with addition of 0.33 M NaCl.
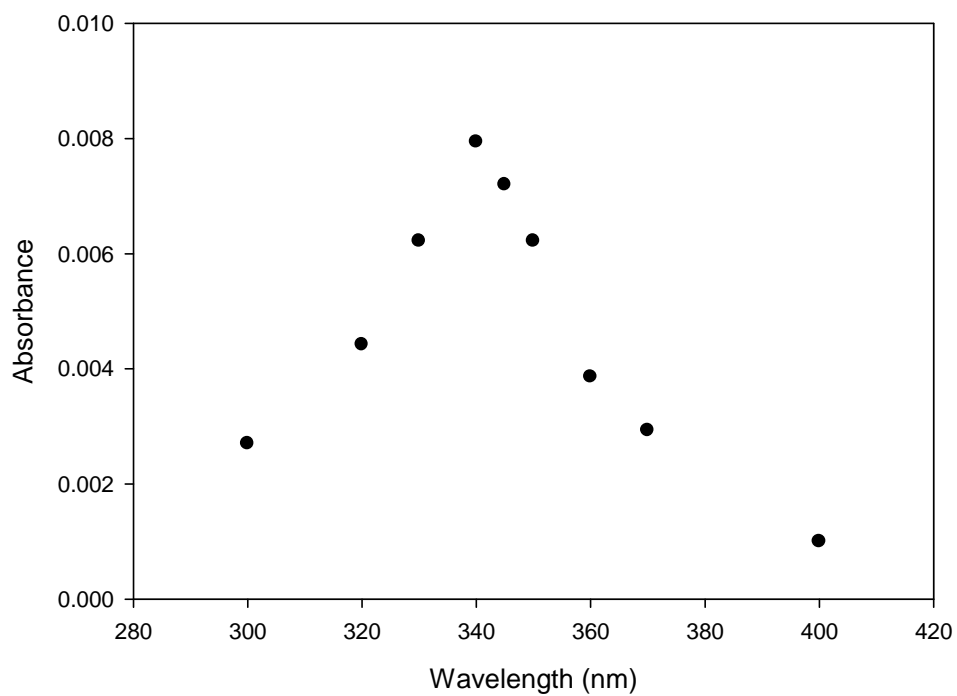
Figure 5. Transient absorption spectrum produced after 355 nm excitation of 1.1×10^{-4} M 1NN at pH 1.0 in presence of 0.5 M NaCl.
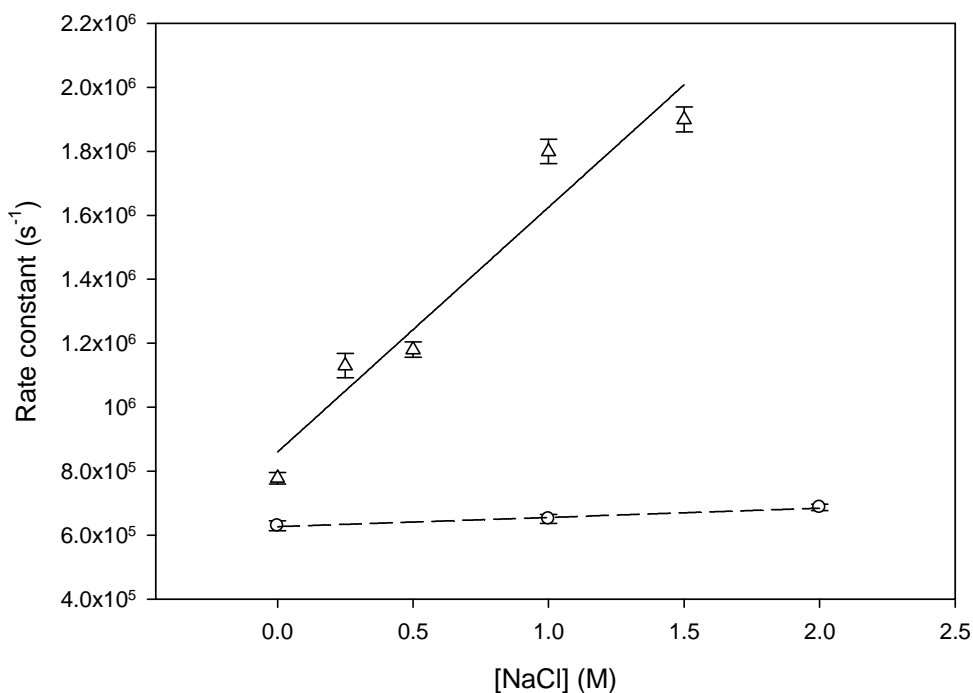
Figure 6. Pseudo-first order decay of ^{3}1NN in presence of different chlorine anions concentration at two different pHs: 6.5 (open circles) and 1.1 (open triangles). The experiments were carried out in aerated solution at 295 ± 2 K. The pH of the 1.1×10^{-4} M 1NN solution was adjusted using $HClO_4$. The experimental data were obtained from the average of 3 separate runs, and the error bars derived at the 1σ level simply from the scattering of the experimental data.
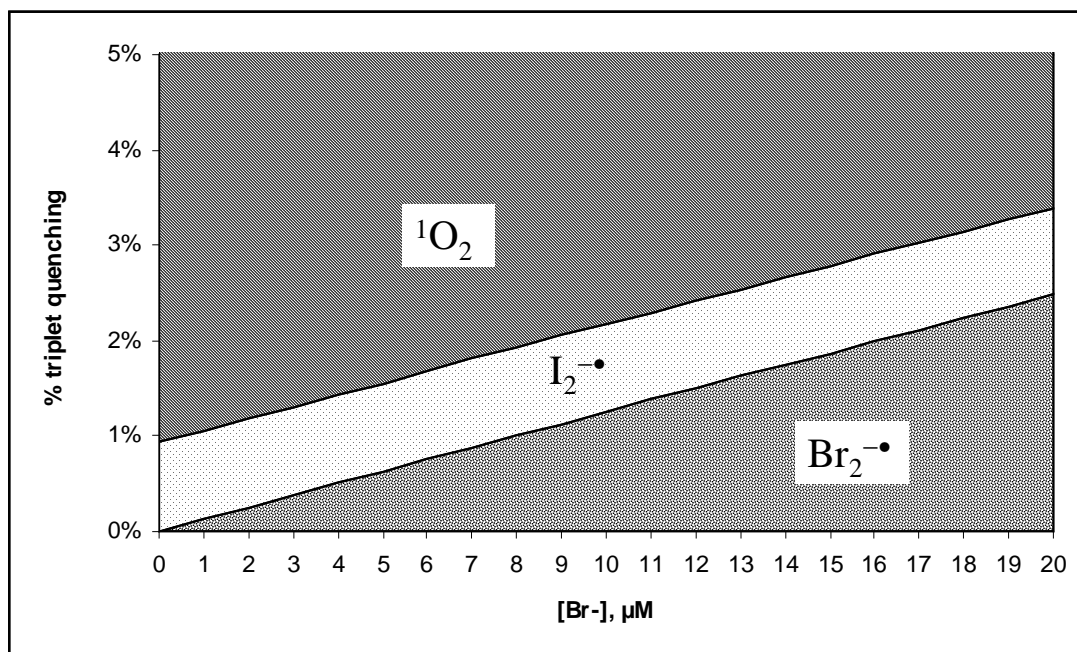
Figure 7. Percentages of ^{3}1NN scavenging carried out by 0.3 mM O_2, 0.5 µM I^-, and Br^- up to 20 µM at pH 6.5. Note that 0.3 mM Cl^- would scavenge ^{3}1NN to a negligible extent, and that most of the scavenging of ^{3}1NN would be carried out by oxygen.

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