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# Photochemistry of 1-Nitronaphthalene: A Potential Source of Singlet Oxygen and Radical Species in Atmospheric Waters

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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 ( $^3\text{1NN}$ ) by oxygen of  $(1.95 \pm 0.05) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The decay of  $^3\text{1NN}$  was observed to strongly depend on the pH of the medium. At  $\text{pH} > 2$ ,  $^3\text{1NN}$  decayed with a pseudofirst order rate constant close to  $6.0 \times 10^5 \text{ s}^{-1}$ . The rate constant was markedly enhanced at lower pHs, reaching  $2.0 \times 10^6 \text{ s}^{-1}$  at  $\text{pH} \sim 0.1$ , which suggests formation of the protonated triplet state ( $^3\text{1NNH}^+$ ) at low pHs. Furthermore, we showed that the photoreactions of  $^3\text{1NN}$  in the presence of oxygen are potential sources of  $\text{HO}_2^\bullet$ ,  $^1\text{O}_2$ , and possibly  $^\bullet\text{OH}$  in aqueous media. In Milli-Q water ( $\text{pH} \sim 6.5$ ) and in the presence of halide anions, the quenching rate constant of  $^3\text{1NN}$  was evaluated to be  $(2.9 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for chloride,  $(7.5 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for bromide, and  $(1.1 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for iodide. Also in this case a pH-dependent reactivity was evidenced, and the quenching rate constant was  $(7.7 \pm 1.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  with chloride at  $\text{pH} 1.1$ .

## Introduction

The development of models to describe the behavior 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.<sup>1</sup> 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<sup>2–7</sup> and received particular attention due to their mutagenic effects.<sup>8</sup> The PAH nitroderivatives also cause concern for their direct mutagenicity. In addition to direct emission,<sup>9–11</sup> some nitro-PAHs are formed in the atmospheric liquid and gas phases via photochemical and dark nitration.<sup>12–14</sup>

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 sulfate and nitrate in marine

clouds.<sup>15</sup> Typical values are from just a few up to  $300 \mu\text{M}$  for chloride, from  $0.06$  to a few tens of micromolar for bromide, and less than  $0.5 \mu\text{M}$  for iodide.<sup>15–18</sup> 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.<sup>19–21</sup>

Radical species such as  $\text{NO}_3^\bullet$ ,  $^\bullet\text{OH}$ , and  $\text{SO}_4^{\bullet-}$  are also present in and on the surface of cloud droplets. They could react with halide anions yielding halogen radicals ( $X^\bullet$ ),<sup>22,23</sup> and dihalogen radical anions ( $X_2^{\bullet-}$ ) (R1). These radicals are known to be responsible for ozone depletion,<sup>24</sup> 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<sup>25</sup>



Although the halogen radicals can initiate a set of catalytic cycles capable of destroying ozone<sup>26</sup> 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 ( $^3\text{1NN}$ ) and halides has previously been reported in ethanol–water solution.<sup>27</sup>

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The H-atom abstraction between  $^3\text{1NN}$  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  $^3\text{1NN}$  and halides, which is a possible source of dihalogen radical anions ( $\text{X}_2^{\cdot-}$ ) in the atmosphere. Furthermore, we point out the formation of  $^1\text{O}_2$ ,  $\text{HO}_2^{\cdot}$ , and possibly  $^{\cdot}\text{OH}$  due to the reactivity of  $^3\text{1NN}$  in aqueous solution.

The presence of hydroperoxy radicals (i.e.,  $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$ ) 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.<sup>28–30</sup> 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 pseudofirst and pseudosecond order reaction rate constants of  $^3\text{1NN}$  to be determined and the transient intermediates generated to be identified.

## Experimental Section

**Materials.** 1-Nitronaphthalene (99%), NaOH,  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ , 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  $\alpha\text{Q}$ , resistivity  $18\text{ M}\Omega\text{ cm}$ ,  $\text{DOC} < 0.1\text{ mg L}^{-1}$ ). All solutions were stored in the dark at  $4^\circ\text{C}$ .

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 ( $\lambda_{\text{exc}} = 355\text{ nm}$ ) 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  $\sim 45\text{ mJ/pulse}$ . Individual cuvette samples (3 mL volume) were used for a maximum of four consecutive laser shots. The transient absorbance at the preselected 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 synchronizing the pulsed light source and programmable shutters with the laser output. The signal from the photomultiplier was digitized by a programmable digital oscilloscope (HP54522A). A 32 bits RISC-processor kinetic spectrometer workstation was used to analyze the digitized 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  $^3\text{1NN}$ , plots were made of the first-order decay constant of  $^3\text{1NN}$ , determined from the regression lines of the logarithmic decays of  $^3\text{1NN}$  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 than 5%.

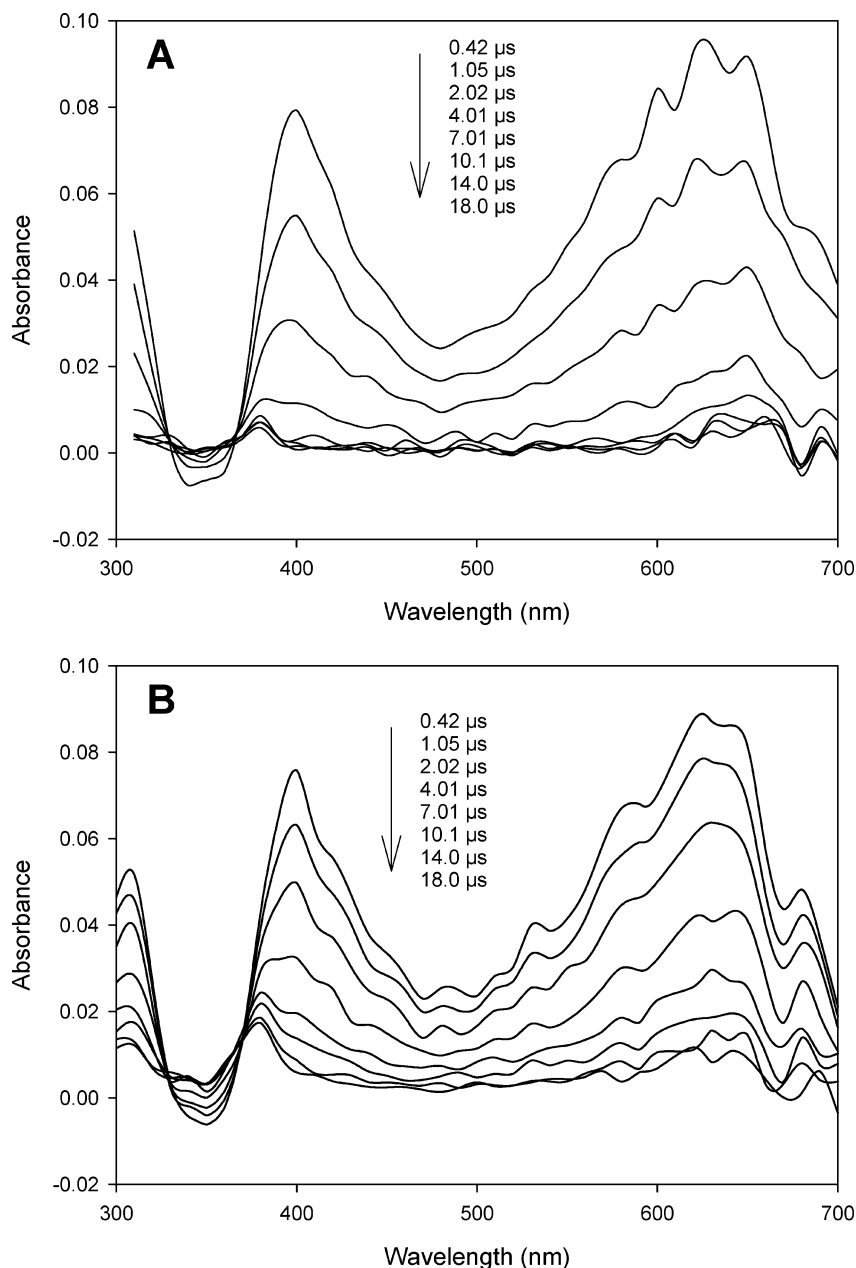
All experiments were performed at ambient temperature ( $295 \pm 2\text{ K}$ ) and in aerated solution, unless otherwise stated. Oxygen concentration (reported in figure 3) was checked with a YSI 550A oximeter.

**Quantification of Singlet Oxygen and 1NN Photodegradation under Polychromatic Irradiation.** To evaluate the photochemical production of  $^1\text{O}_2$  by 1NN, furfuryl alcohol (FFA) was used as  $^1\text{O}_2$  acceptor.<sup>31</sup> In our experiments, 1NN ( $5.5 \times 10^{-5}\text{ M}$ ) in presence of FFA ( $1 \times 10^{-4}\text{ M}$ ) in water was irradiated under polychromatic light within the wavelength range 300–370 nm, with an energy of  $60\text{ W m}^{-2}$  (Xenon AMKO-light 1000W). At fixed time intervals during irradiation, a sample aliquot was analyzed by HPLC-UV on a  $4.6 \times 150\text{ mm C-18}$  column. Elution was carried out with  $\text{H}_2\text{O}$  (pH = 2.7 with  $\text{H}_3\text{PO}_4$ )/ $\text{CH}_3\text{CN}$  (85/15) at a flow rate of  $1\text{ mL min}^{-1}$ , and FFA was detected at 220 nm with a retention time of 6.2 min. The same setup was also used to monitor the transformation of 1NN in acidic solution. Analysis was carried out with the same instrument and column, eluting with  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  50/50 at a flow rate of  $1\text{ mL min}^{-1}$ . 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  $18\text{ }\mu\text{s}$ ) obtained after a 355 nm laser pulse in pure water (pH 6.5) at  $295 \pm 2\text{ K}$  in aerated (A) and oxygen-free (B) aqueous solutions of  $1.1 \times 10^{-4}\text{ M}$  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 ( $^3\text{1NN}$ ).<sup>32</sup> The transient species  $^3\text{1NN}$  decays uniformly on a submicrometer time scale, and no residual absorbance was observed after about  $20\text{ }\mu\text{s}$ . 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<sup>27</sup> 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 ( $5.0 \times 10^{-5}\text{ M}$ ) 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  $^3\text{1NN}$  because its pseudofirst order rate constant was identical to the 620 nm transient ( $k_{\text{decay}} \sim 6.5 \times 10^5\text{ s}^{-1}$  in aerated aqueous solution). The second species had a first-order decay of  $2.3 \times 10^4\text{ s}^{-1}$ , absorbing light between 350 and 420 nm as shown in Figure 1. A similar transient absorption spectrum was observed by Martins et al.<sup>33</sup> and was attributed to the radical anion of 1NN ( $\text{1NN}^{\cdot-}$ ), which is formed mainly in the absence of oxygen (in agreement with our results) and in water–ethanol solution. The cited authors suggested that  $\text{1NN}^{\cdot-}$  was produced upon H-atom abstraction by excited 1NN from the solvent (ethanol, in  $\alpha$ -position), followed by deprotonation of the radical thus generated ( $\text{1NNH}^{\cdot}$ ).  $\text{1NN}^{\cdot-}$  generation was also attributed to



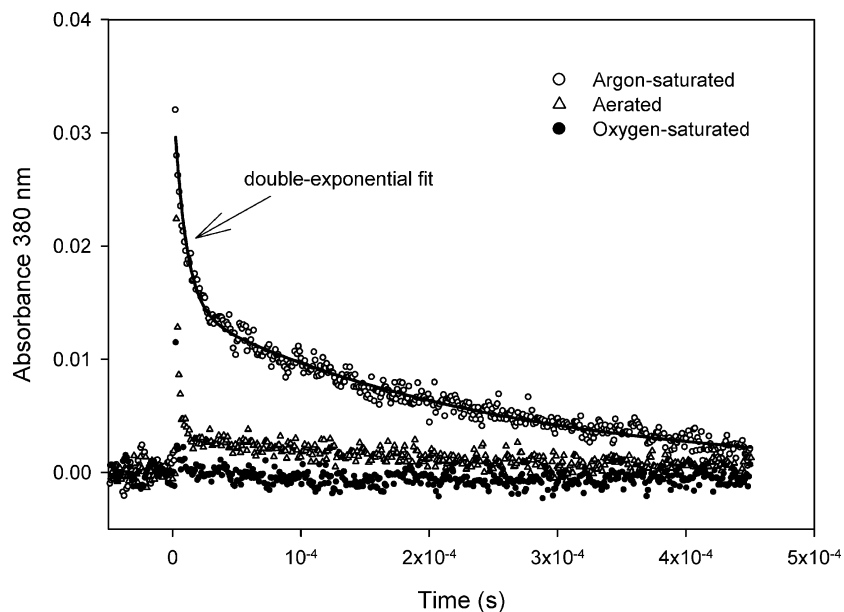
**Figure 1.** Transient absorption spectra produced upon LFP (355 nm, 45 mJ) of 1NN ( $1.1 \times 10^{-4}$  M) in aerated (A) and oxygen-free (B) aqueous solutions (pH 6.5) at ambient temperature ( $295 \pm 2$  K).

the reaction of 1-hydroxyethyl radical (generated by reaction of  $^3\text{1NN}$  with ethanol) with 1NN leading, via electron transfer, a new molecule of  $1\text{NN}^{\bullet-}$ .

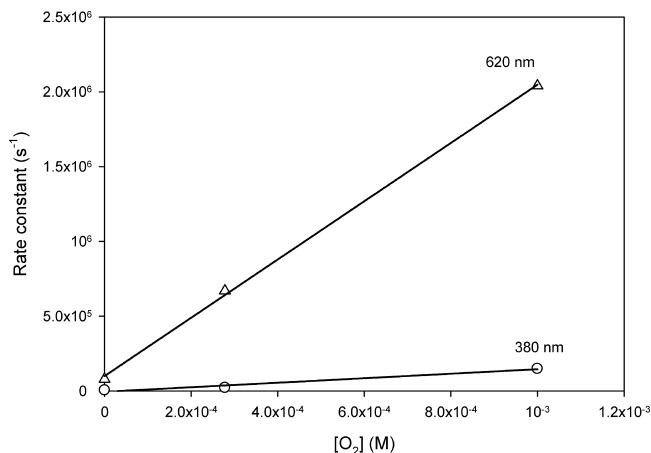
An interesting novelty of the present work is represented by the detection of  $1\text{NN}^{\bullet-}$  in the absence of organic H-donors. In fact, our experimental results in pure aqueous solution suggest that the formation of  $1\text{NN}^{\bullet-}$  arises directly from oxidation of water by  $^3\text{1NN}$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

Further investigations showed that  $^3\text{1NN}$  decay was independent of the initial concentration of 1NN between  $1.4$  and  $14 \times 10^{-4}$  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  $^3\text{1NN}$  initially formed after the pulse, as can be seen from the initial absorbance. However, concentration of the 380 nm transient species ( $1\text{NN}^{\bullet-}$ ) increased about 2-fold in the absence of oxygen. To evaluate and understand the processes involving oxygen, the pseudofirst order decay rates of  $^3\text{1NN}$  and  $1\text{NN}^{\bullet-}$  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  $^3\text{1NN}$  and  $1\text{NN}^{\bullet-}$  increase with increasing oxygen concentration (from  $8.0 \times 10^4$  to  $2.0 \times 10^6$   $\text{s}^{-1}$  and from  $5.7 \times 10^3$  to  $1.5 \times 10^5$   $\text{s}^{-1}$ , respectively), showing a good linear dependence on  $[\text{O}_2]$ . The values of the bimolecular quenching rate constants with  $\text{O}_2$  were determined as  $(1.95 \pm 0.05) \times 10^9$   $\text{M}^{-1} \text{s}^{-1}$  and  $(1.51 \pm 0.25) \times 10^8$   $\text{M}^{-1} \text{s}^{-1}$  for  $^3\text{1NN}$  and  $1\text{NN}^{\bullet-}$ , respectively. Our data are in agreement with a previous investigation by Wilkinson et al.,<sup>34</sup> who reported a



**Figure 2.** Decay at 380 nm as a function of oxygen concentration. Transient were obtained upon LFP (355 nm) of 1NN ( $5.0 \times 10^{-5}$  M) as function of oxygen concentration: after 20 min of argon saturation ( $\circ$ ) in aerated solution ( $\Delta$ ) and after 20 min of oxygen saturation ( $\bullet$ ).



**Figure 3.** Dependence on the oxygen concentration of the pseudofirst order decay of 1-nitronaphthalene triplet state ( $^3\text{1NN}$ ) and 1-nitronaphthalene radical anion ( $\text{1NN}^{\bullet-}$ ) 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 min of bubbling with Argon or pure oxygen, respectively.

solvent-independent pseudosecond order decay constant for  $^3\text{1NN}$  of  $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . In addition, we found that also  $\text{1NN}^{\bullet-}$  is able to react with oxygen. Some oxygen-mediated reactions (R4–R6) are suggested to explain the experimental data reported above



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  $^3\text{1NN}$  ( $E_T = 231 \text{ kJ mol}^{-1}$ )<sup>35</sup> we can argue that, following reaction 4, interaction with

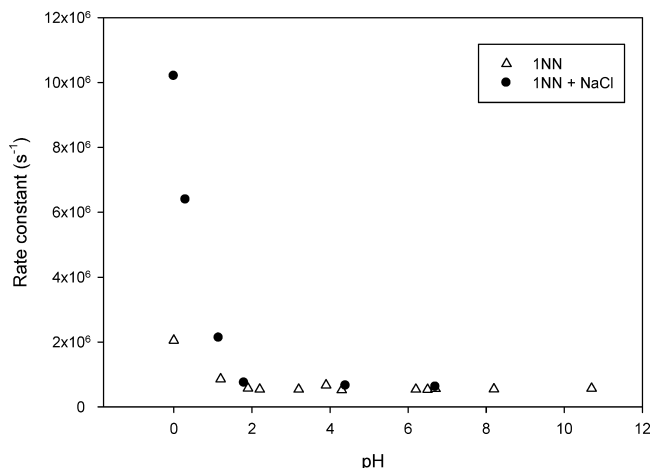
molecular oxygen leads to the formation of both the first and the second electronically excited singlet states,  $\text{O}_2({}^1\Delta_g)$  ( $94 \text{ kJ mol}^{-1}$ ) and  $\text{O}_2({}^1\Sigma_g^+)$  ( $157 \text{ kJ mol}^{-1}$ ). Quantification of singlet oxygen photoformation via reaction R4 was possible by using FFA as a chemical probe, and we found a formation rate  $R_1\text{O}_2 = 1.5 \pm 0.1 \times 10^{-8} \text{ M s}^{-1}$ .

The reaction between  $\text{1NN}^{\bullet-}$  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<sup>36</sup> and anthraquinones.<sup>37</sup> It is also consistent with the detection of  $\text{H}_2\text{O}_2$  upon irradiation of 1NN in the presence of oxidizable organic substrates,<sup>38</sup> where hydrogen peroxide would be formed upon dismutation of  $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ .

**Effect of Acidity.** Martins et al.<sup>33</sup> investigated the effect of pH on 1NN photoreactivity in aqueous-ethanol solution in the presence of salts (i.e.,  $\text{Cl}^-$  and  $\text{Br}^-$ ). 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 ( $^3\text{1NNH}^+$ ) ( $\text{pK}_a \sim 0.66$ ) in ethanol–water solution.

We monitored the decay of  $^3\text{1NN}$  at 620 nm both in pure water and in the presence of halide anions (i.e.,  $\text{Cl}^-$ ) at various pH values as reported in Figure 4. The pH was adjusted upon addition of  $\text{HClO}_4$ . Interestingly, in the presence or absence of  $\text{Cl}^-$ , the pseudofirst order degradation rate constant of  $^3\text{1NN}$  was close to  $6.0 \times 10^5 \text{ s}^{-1}$  between pH 2.0 and 10.7. By decreasing the pH of the solutions down to  $\sim 0.1$ , the rate constant increased up to  $2 \times 10^6$  and  $1 \times 10^7 \text{ s}^{-1}$  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 ( $\tau$ ), which is reduced from 1.8 to 0.1  $\mu\text{s}$  in salted solution at pH  $\sim 0.1$ . Trotter and Testa<sup>39</sup> investigated the photochemical behavior of 1NN in isopropanol–water medium with addition of HCl. The cited authors reported that protonation of the excited state to form  $^3\text{1NNH}^+$  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 ( $^3\text{1NNH}^+$ ) could react with chloride ions R8, with possible formation of chlorine radicals ( $\text{Cl}^\bullet$ ). This reaction could explain

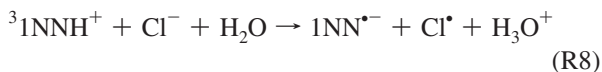




**Figure 4.** Pseudofirst order decay of  $^3\text{1NN}$  (monitored at 620 nm) as a function of pH. Open triangles using a solution of  $1.1 \times 10^{-4}$  M 1NN in Milli-Q water and full circle with addition of 0.33 M NaCl.

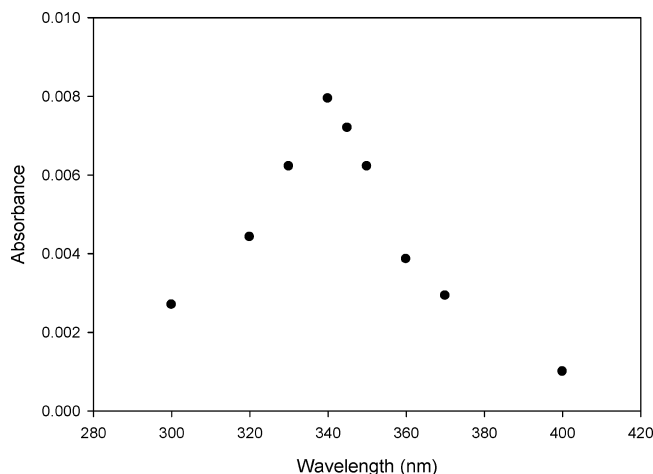
the faster quenching of the triplet state at very low pHs in the presence of chloride, and the occurrence of  $^3\text{1NNH}^+$  would also be consistent with the pH trend of triplet quenching without chloride.

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

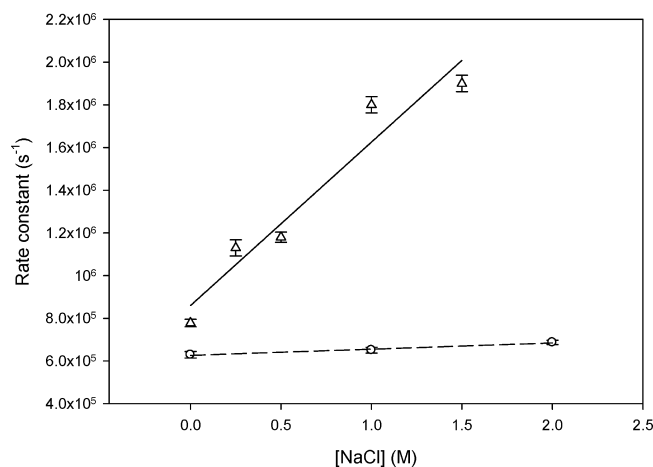


Flash photolysis of 1NN in the presence of chloride results in the formation of a transient species that absorbs in the wavelength range from 280 to 450 nm. The decay rate in aqueous solution and the spectrum of this new transient species (shown in Figure 5) are in agreement with those reported in the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

Steady-state irradiation of 0.1 mM 1NN, using  $\text{HClO}_4$ , HCl or  $\text{H}_2\text{SO}_4$  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  $^3\text{1NNH}^+$  and  $\text{Cl}^-$  would yield the radical anion ( $\text{1NN}^{\bullet-}$ ) and the chlorine radical ( $\text{Cl}^\bullet$ ). Furthermore,  $\text{1NN}^{\bullet-}$  would react with oxygen to yield back 1NN (following a catalytic-type reaction) and  $\text{O}_2^{\bullet-}$  (reaction R5). The whole process would be a null cycle as far as 1NN is concerned, with no net degradation. For this reason,



**Figure 5.** Transient absorption spectrum produced after 355 nm excitation of  $1.1 \times 10^{-4}$  M 1NN at pH 1.0 in presence of 0.5 M NaCl.



**Figure 6.** Pseudofirst order decay of  $^3\text{1NN}$  in the presence of different chloride anions concentration at two different pHs: 6.5 (open circles) and 1.1 (open triangles). The experiments were carried out in aerated solution at  $295 \pm 2$  K. The pH of the  $1.1 \times 10^{-4}$  M 1NN solution was adjusted using  $\text{HClO}_4$ . The experimental data were obtained from the average of 3 separate runs, and the error bars derived at the  $1\sigma$  level simply from the scattering of the experimental data.

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 ( $^3\text{1NN}$ ) 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 pseudofirst order decay of  $^3\text{1NN}$  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 ( $(2.9 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) compared with pH 1.1 ( $(7.7 \pm 1.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ). This finding suggests that two different species are involved in the reaction with chloride; they could be  $^3\text{1NN}$  and its protonated form  $^3\text{1NNH}^+$ , with  $^3\text{1NNH}^+$  being more reactive than  $^3\text{1NN}$ . The dichlorine radical anion ( $\text{Cl}_2^{\bullet-}$ ) was identified upon LFP of  $\text{1NN} + \text{Cl}^-$  at both circumneutral and acidic pH,

**TABLE 1: Second-Order Rate Constants for the Quenching of the Triplet State of 1-Nitronaphthalene ( $^3\text{INN}$ ) in Aqueous Solution, and Comparison with Literature Data<sup>a</sup>**

anion	$E^\circ(\text{X}^-/\text{X}^\bullet)$ (V)	conditions	$k$ ( $\text{M}^{-1} \text{s}^{-1}$ )
$\text{Cl}^-$	1.36	pH1.1 <sup>b</sup>	$(7.7 \pm 1.2) \times 10^5$
		pH6.5 <sup>b</sup>	$(2.9 \pm 0.4) \times 10^4$
		pH7.7 <sup>c</sup>	$(5.4 \pm 1.0) \times 10^4$
$\text{Br}^-$	1.09	pH6.5 <sup>b</sup>	$(7.5 \pm 0.2) \times 10^8$
		pH7.7 <sup>c</sup>	$(6.0 \pm 0.2) \times 10^8$
$\text{I}^-$	0.54	pH6.5 <sup>b</sup>	$(1.1 \pm 0.1) \times 10^{10}$
		pH7.7 <sup>c</sup>	$(5.4 \pm 0.5) \times 10^9$

<sup>a</sup> 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<sup>33</sup> vs water in the present work). <sup>b</sup> This work. <sup>c</sup> From literature data in buffered solution, 25% (v/v) ethanol–water.<sup>33</sup>

which further supports the hypothesis that both  $^3\text{INN}^\bullet$  and  $^3\text{INN}$  can oxidize chloride to  $\text{Cl}^\bullet$ , and that the latter reacts with chloride to yield  $\text{Cl}_2^{\bullet-}$ . The growth and decay of  $\text{Cl}_2^{\bullet-}$  were monitored at 340 nm, which is the absorption maximum for this transient species.<sup>41</sup>

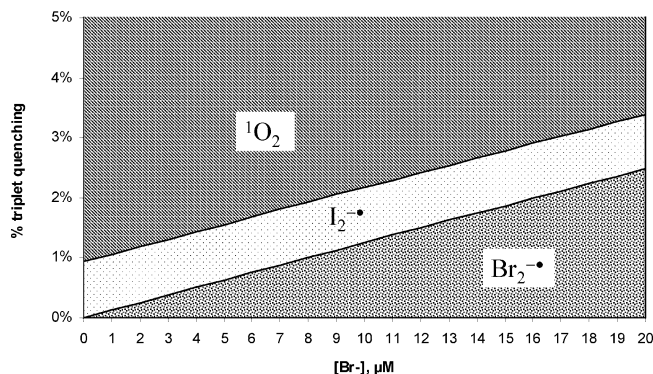
Bromide is present in the atmospheric aqueous phase at typical concentrations ranging from tens nanomolar to a few tens micromolar.<sup>17</sup> LFP experiments with  $1.1 \times 10^{-4}$  M INN in the presence of 500  $\mu\text{M}$  bromide showed the formation of a new long-lived transient species 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 ( $\text{Br}_2^{\bullet-}$ ).<sup>40</sup>

The presence and quantification of iodide anions in atmospheric waters has been reported by Neal and co-workers.<sup>18</sup> They reported iodide concentrations ranging from about 0.01 to 0.52  $\mu\text{M}$  and suggested both anthropic and marine contributions. In the present work, the presence of 50  $\mu\text{M}$  iodide was sufficient to quantitatively quench the triplet state ( $^3\text{INN}$ ), generated by LFP (355 nm, 40 mJ) of  $1.1 \times 10^{-4}$  M INN at pH 6.5. Triplet lifetime was decreased from 1.8  $\mu\text{s}$  (in the absence of iodide) to 1  $\mu\text{s}$ . The formation of a new transient species with an absorption maximum at 385 nm was attributed to the diiodine radical anion ( $\text{I}_2^{\bullet-}$ ), by comparison with literature data.<sup>42</sup>

Table 1 reports the bimolecular quenching constants of  $^3\text{INN}$  in aerated solution with different halides and at different pH values. The quenching rate constant increased with decreasing the standard oxidation potential,  $E^\circ(\text{X}^-/\text{X}^\bullet)$ , of the respective quenchers ( $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ).<sup>43</sup> These results are in agreement with the above-reported mechanism that involves oxidation of the halide via electron transfer to  $^3\text{INN}$ . They are also in agreement with the results of Reeser and co-workers,<sup>20</sup> 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 cloudwater, their higher reactivity toward  $^3\text{INN}$  might be an additional source of dihalogen radical anions in the atmospheric aqueous phase. Furthermore, Matthew and co-workers<sup>44</sup> have shown that the reaction in aqueous solution of  $\text{Br}_2^{\bullet-}$  with  $\text{HO}_2^\bullet$  may play a key role in the formation of gaseous and aqueous molecular bromine ( $\text{Br}_2$ ).

Considering the second-order reaction rate constants reported in Table 1 and referred to circumneutral conditions, chloride at a concentration of 300  $\mu\text{M}$  would scavenge as much  $^3\text{INN}$  as 0.01  $\mu\text{M}$  bromide and 0.001  $\mu\text{M}$  iodide. From the typical concentration values of the halogenide anions in the atmospheric aqueous phase,<sup>15–18</sup> it could be inferred that the irradiation of



**Figure 7.** Percentages of  $^3\text{INN}$  scavenging carried out by 0.3 mM  $\text{O}_2$ , 0.5  $\mu\text{M}$   $\text{I}^-$ , and  $\text{Br}^-$  up to 20  $\mu\text{M}$  at pH 6.5. Note that 0.3 mM  $\text{Cl}^-$  would scavenge  $^3\text{INN}$  to a negligible extent, and that most of the scavenging of  $^3\text{INN}$  would be carried out by oxygen.

INN could sensitize the formation of  $\text{Br}_2^{\bullet-}$  and  $\text{I}_2^{\bullet-}$  to a higher extent than for  $\text{Cl}_2^{\bullet-}$ .

Figure 7 reports the percentage of triplet quenching by 300  $\mu\text{M}$   $\text{O}_2$  (which yields  $^1\text{O}_2$ ), 300  $\mu\text{M}$  chloride (to give  $\text{Cl}_2^{\bullet-}$ ), and 0.5  $\mu\text{M}$  iodide (to give  $\text{I}_2^{\bullet-}$ ), as a function of the concentration of bromide up to 20  $\mu\text{M}$  (which yields  $\text{Br}_2^{\bullet-}$ ). On the basis of data of this work we can argue that most  $^3\text{INN}$  would be scavenged by oxygen to give  $^1\text{O}_2$ . Moreover, negligible production of  $\text{Cl}_2^{\bullet-}$  and non-negligible generation of  $\text{Br}_2^{\bullet-}$  and  $\text{I}_2^{\bullet-}$  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  $\text{Br}^-$  and 6 M  $\text{Cl}^-$ )<sup>45</sup> than in seawater, where in turn the halides are much more concentrated than in cloudwater. Therefore, in the surface aqueous film of marine aerosols, the production of dihalogen radicals could be considerably increased at the expense of  $^1\text{O}_2$ .

## Conclusions

The present work shows that INN can be excited by UVA radiation to yield the triplet state, which can react with oxygen, the halide anions ( $\text{X}^-$ ) and possibly water. Therefore, the photochemistry of INN yields reactive species ( $^1\text{O}_2$ ,  $\text{X}_2^{\bullet-}$ , possibly  $^\bullet\text{OH}$ ) 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 INN triplet state are in competition with one another, and the reaction with  $\text{O}_2$  to yield  $^1\text{O}_2$  is likely to prevail in cloudwater. Figure 2, which reports the pseudofirst order decay constant of the triplet state vs  $[\text{O}_2]$ , suggests an upper limit for the reaction rate between  $^3\text{INN}$  and water that corresponds to the behavior of the deoxygenated solution. In the most favorable hypothesis, the possible production of  $^\bullet\text{OH}$  from  $^3\text{INN}$  under atmospherically significant conditions would represent only a small fraction of that of  $^1\text{O}_2$ .

The pH trend of the decay of the triplet state suggests that two forms may be present,  $^3\text{INN}$  and  $^3\text{INN}^\bullet$ . The reactivity of the protonated form would be considerably higher than that of the neutral one. The reaction rate constants between  $^3\text{INN}$  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  $^3\text{INN}$  and chloride is too slow to yield  $\text{Cl}_2^{\cdot-}$  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  $\text{Br}_2^{\cdot-}$  could be significant in bromine-rich aerosols, where bromide concentration is enhanced at the solution/vapor interface compared to chloride.<sup>46</sup> This is potentially very significant because bromine radicals take part to ozone depletion processes<sup>24,47</sup> and are very effective brominating agents in aqueous solution,<sup>48,49</sup> which could lead to the formation of environmentally persistent brominated secondary pollutants.

Certainly, the real impact of INN 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, 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 INN photochemistry with particular attention to the photoreaction products (i.e., halogenated and hydroxylated species).

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## References and Notes

- (1) Herrmann, H. *Chem. Rev.* **2003**, *103*, 4691.
- (2) Bjorseth, A.; Randahl, T. *CRC Press* 1985.
- (3) Nizzetto, L.; Lohmann, R.; Gioia, R.; Jahnke, A.; Temme, C.; Dachs, J.; Herckes, P.; Guardo, A. D.; Jones, K. C. *Environ. Sci. Technol.* **2008**, *42*, 1580.
- (4) Possanzini, M.; Di Palo, V.; Gigliucci, P.; Scianò, M. C. T.; Cecinato, A. *Atmos. Environ.* **2004**, *38*, 1727.
- (5) Wilcke, W.; Krauss, M.; Safronov, G.; Fokin, A. D.; Kaupenjohann, M. *J. Environ. Qual.* **2005**, *34*, 1581.
- (6) Dale, M. J.; Downs, O. H. J.; Costello, K. F.; Wright, S. J.; Langridge-Smith, P. R. R.; Cape, J. N. *Environ. Pollut.* **1995**, *89*, 123.
- (7) Raja, S.; Valsaraj, K. T. *Environ. Sci. Technol.* **2003**, *38*, 763.
- (8) Durant, J. L.; Busby, W. F.; Lafleur, A. L.; Penman, B. W.; Crespi, C. L. *Mutat. Res., Genet. Toxicol. Environ. Mutagen.* **1996**, *371*, 123.
- (9) Robbat, A.; Corso, N. P.; Doherty, P. J.; Wolf, M. H. *Anal. Chem.* **2002**, *58*, 2078.
- (10) Albinet, A.; Leoz-Garziandia, E.; Budzinski, H.; Villenave, E. *Atmos. Environ.* **2007**, *41*, 4988.
- (11) Kim Oanh, N. T.; Nghiem, L. H.; Phyu, Y. L. *Environ. Sci. Technol.* **2002**, *36*, 833.
- (12) Arey, J.; Zielinska, B.; Atkinson, R.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1989**, *21* (9), 775.
- (13) Gross, S.; Bertram, A. K. *J. Phys. Chem. A* **2008**, *112* (14), 3104.
- (14) Vione, D.; Maurino, V.; Minero, C.; Pelizzetti, E. *Environ. Sci. Technol.* **2005**, *39*, 1101.

- (15) Neal, M.; Neal, C.; Wickham, H.; Harman, S. *Hydrol. Earth Syst. Sci.* **2007**, *11*, 294.
- (16) <http://www.obs.univ-bpclermont.fr/SO/beam/index.php>.
- (17) Neal, C.; Neal, M.; Hughes, S.; Wickham, H.; Hill, L.; Harman, S. *Hydrol. Earth Syst. Sci.* **2007**, *11*, 301.
- (18) Neal, C.; Neal, M.; Wickham, H.; Hill, L.; Harman, S. *Hydrol. Earth Syst. Sci.* **2007**, *11*, 283.
- (19) Jammoul, A.; Dumas, S.; D'Anna, B.; George, C. *Atmos. Chem. Phys.* **2009**, *9*, 4229.
- (20) Reeser, D. I.; George, C.; Donaldson, D. J. *J. Phys. Chem. A* **2009**, *113*, 8591.
- (21) Reeser, D. I.; Jammoul, A.; Clifford, D.; Brigante, M.; D'Anna, B.; George, C.; Donaldson, D. J. *J. Phys. Chem. C* **2008**, *113*, 2071.
- (22) Exner, M.; Herrmann, H.; Zellner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 470.
- (23) Finlayson-Pitts, B. J.; Pitts, J. J. N. *Chemistry of the Upper and Low Atmosphere*; Academic Press: San Diego, CA, 2000.
- (24) Simpson, W. R.; von Glasow, R.; Riedel, K.; Anderson, P.; Ariya, P.; Bottenheim, J.; Burrows, J.; Carpenter, L. J.; Friesse, U.; Goodsite, M. E.; Heard, D.; Hutterli, M.; Jacobi, H. W.; Kaleschke, L.; Neff, B.; Plane, J.; Platt, U.; Richter, A.; Roscoe, H.; Sander, R.; Shepson, P.; Sodeau, J.; Steffen, A.; Wagner, T.; Wolff, E. *Atmos. Chem. Phys.* **2007**, *7*, 4375.
- (25) Alegre, M. L.; Gerones, M.; Rosso, J. A.; Bertolotti, S. G.; Braun, A. M.; Martire, D. O.; Gonzalez, M. C. *J. Phys. Chem. A* **2000**, *104*, 3117.
- (26) Thomas, J. L.; Jimenez-Aranda, A.; Finlayson-Pitts, B. J.; Dabdub, D. *J. Phys. Chem. A* **2006**, *110*, 1859.
- (27) Fournier, T.; Tavender, S. M.; Parker, A. W.; Scholes, G. D.; Phillips, D. *J. Phys. Chem. A* **1997**, *101*, 5320.
- (28) Anastasio, C.; McGregor, K. G. *Atmos. Environ.* **2001**, *35*, 1079.
- (29) Chameides, W. L.; Davis, D. D. *J. Geophys. Res.* **1982**, *87*, 4863.
- (30) Creasey, D. J.; Heard, D. E.; Lee, J. D. *Atmos. Environ.* **2001**, *35*, 4713.
- (31) Haag, W. R.; Hoigne, J. R.; Gassman, E.; Braun, A. M. *Chemosphere* **1984**, *13*, 631.
- (32) Capellos, C.; Porter, G. *J. Chem. Soc., Faraday Trans.* **1974**, *70*, 1159.
- (33) Martins, L. J. A.; Fernandes, M. M. M.; Kemp, T. J.; Formosinho, S. J.; Branco, J. S. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3617.
- (34) Wilkinson, F.; McGarvey, D. J.; Olea, A. F. *J. Phys. Chem.* **1994**, *98*, 3762.
- (35) Rusakowicz, B.; Testa, A. C. *Spectrochim. Acta, Part A* **1971**, *27*, 787.
- (36) Anastasio, C.; Faust, B. C.; Rao, C. J. *Environ. Sci. Technol.* **1996**, *31*, 218.
- (37) Maurino, V.; Borghesi, D.; Vione, D.; Minero, C. *Photochem. Photobiol. Sci.* **2008**, *7*, 321.
- (38) Görner, H. *J. Photochem. Photobiol., A* **2008**, *195*, 235.
- (39) Trotter, W.; Testa, A. C. *J. Phys. Chem.* **1970**, *74*, 845.
- (40) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330.
- (41) Hug, G. L. *Optical spectra of nonmetallic inorganic transient species in aqueous solution*; U.S. Government Printing Office: Washington, DC, 1981.
- (42) Elliot, A. J.; Sopchysyn, F. C. *Int. J. Chem. Kinet.* **1984**, *16*, 1247.
- (43) Wiberg, N.; Holleman, A.; Wiberg, E. *Inorganic Chemistry*; Academic Press: New York, 2001.
- (44) Matthew, B. M.; George, I.; Anastasio, C. *Geophys. Res. Lett.* **2003**, *30*, 2297.
- (45) George, I. J.; Anastasio, C. *Atmos. Environ.* **2007**, *41*, 543.
- (46) Ghosal, S.; Brown, M. A.; Bluhm, H.; Krisch, M. J.; Salmeron, M.; Jungwirth, P.; Hemminger, J. C. *J. Phys. Chem. A* **2008**, *112*, 12378.
- (47) Monks, P. S. *Chem. Soc. Rev.* **2005**, *34*, 376.
- (48) Minero, C.; Pellizzari, P.; Maurino, V.; Pelizzetti, E.; Vione, D. *Appl. Catal., B* **2008**, *77*, 308.
- (49) Vione, D.; Maurino, V.; Man, S. C.; Khanra, S.; Arsene, C.; Olariu, R.-I.; Minero, C. *ChemSusChem* **2008**, *1*, 197.

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