Enhancement by anthraquinone-2-sulphonate of the photonitration of phenol by nitrite: Implication for the photoproduction of nitrogen dioxide by coloured dissolved organic matter in surface waters

Pratap Reddy Maddigapu [a], Claudio Minero [a], Valter Maurino [a], Davide Vione [a,b,*], Marcello Brigante [c,**], Gilles Mailhot [c]

[a] Dipartimento di Chimica Analitica, Università di Torino, Via P. Giuria 5, 10125 Torino, Italy[1]
[b] Centro Interdipartimentale NatRisk, Università degli Studi di Torino, Via Leonardo da Vinci 44, 10095 Grugliasco (TO), Italy
[c] Laboratoire de Photochimie Moléculaire et Macromoléculaire (LPMM), Université Blaise Pascal, UMR CNRS 6505, F-63177, Aubière Cedex, France

ABSTRACT

Anthraquinone-2-sulphonate (AQ2S) under UVA irradiation is able to oxidise nitrite to $\cdot NO_2$ and to induce the nitration of phenol. The process involves the very fast reactions of the excited triplet state $^3AQ2S^*$ and its 520-nm absorbing exciplex with water, at different time scales (ns and μs, respectively). Quinones are ubiquitous components of coloured dissolved organic matter (CDOM) in surface waters and AQ2S was adopted here as a proxy of CDOM. Using a recently developed model of surface-water photochemistry, we found that the oxidation of nitrite to $\cdot NO_2$ by $^3CDOM^*$ could be an important $\cdot NO_2$ source in water bodies with high $[NO_2^-]$ to $[NO_3^-]$ ratio, for elevated values of column depth and NPOC.

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1. Introduction

Nitrophenols are environmentally harmful nitroaromatic compounds, with a potential to act as uncoupling agents in oxidative phosphorylation (Shea et al., 1983) and to cause oxidative damage to DNA (Chiron et al., 2007a). Nitrophenols occur in surface waters because of several pathways: atmospheric deposition, hydrolysis of parathion and similar products (Agarwal et al., 1994), and photonitration of the corresponding phenols (Chiron et al., 2007b). The latter may be environmental transformation intermediates of phenolic herbicides (Chiron et al., 2009). Exposure to nitrophenols can cause harmful effects to algae (Umamaheswari and Venkateswarlu, 2004) and aquatic organisms (Howe et al., 1994).

The photonitration of aromatic compounds is started by the production of $\cdot NO_2$ upon photolysis of nitrate and nitrite (Machado and Boule, 1995; Dzengel et al., 1999; Vione et al., 2002). Another potentially important source of $\cdot NO_2$ in the aqueous solution is the photooxidation of nitrite, in the presence of $\cdot OH$ or of irradiated metal oxides (Chiron et al., 2007b).

The excited triplet states of coloured dissolved organic matter ($^3CDOM^*$) are important reactive transients in surface waters (Canonica et al., 2005; Halladja et al., 2007). The species $^3CDOM^*$ are often able to abstract electrons or hydrogen atoms from other dissolved molecules, as well as to transform ground-state O_2 into $^1O_2$. $^3CDOM^*$ is for instance involved to a very significant extent into the transformation of phenylurea herbicides (Canonica et al., 2006). The excited triplet states of quinones are representative of the coloured moieties of natural dissolved organic matter (Cory and McKnight, 2005). They have often very high reduction potentials (Wardman, 1989) and could oxidise nitrite to $\cdot NO_2$ ($E^{\circ}_{NO_2/NO_2^-} \approx 1$ V). However, no data are available on the process of $\cdot NO_2$ production by nitrite and $^3CDOM^*$, nor on the potential of such a reaction to induce aromatic nitration.

We chose anthraquinone-2-sulphonate (AQ2S) as model photoactive organic compound. The photochemistry and photophysics of AQ2S are rather well known (Loeff et al., 1983; Maurino et al., 2008). Interestingly, the excited triplet state of AQ2S ($^3AQ2S^*$) does not react with O_2 to yield $^1O_2$ (Maddigapu et al., 2010). With AQ2S it is thus possible to study the triplet-state reactivity, without the additional complication of the reactions of $^1O_2$.

The nitration of phenol was studied upon irradiation of AQ2S and nitrite, to get insight into the ability of the process to yield

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harmful nitroaromatic compounds. Moreover, the transformation of phenol into nitrophenols is a suitable probe reaction for the assessment of ·NO$_2$ generation (Chiron et al., 2007b). The potential importance of the production of ·NO$_2$ by triplet-state reactivity under environmental conditions was assessed by means of a combination of experimental results and modelling of surface-water photochemistry.

2. Experimental

All reagents were of analytical grade and were used as received, without further purification. Water used was of Milli-Q quality.

2.1. Irradiation experiments

The aqueous solutions to be irradiated (5 mL total volume) were placed into cylindrical Pyrex glass cells (4.0 cm diameter, 2.3 cm height, lateral inlet with screw-cap closure). Irradiation with magnetic stirring took place under a 40 W Philips TL K05 UVA lamp. The incident photon flux in solution, actinometrically determined with the ferrioxalate method (Kuhn et al., 2004) was 2.1×10^{-5} Einstein L^{-1} s^{-1} and corresponded to a UV irradiance (290–400 nm) of 28 W m^{-2}, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter. Fig. 1 reports the emission spectrum of the adopted lamp, measured with an Ocean Optics SD 2000 CCD spectrophotometer and normalised to the actinometry results, taking into account the transmittance of the Pyrex glass window of the irradiation cells. The figure also reports the absorption spectra of AQ2S and nitrite, taken with a Varian Cary 100 Scan UV–Vis spectrophotometer.

2.2. Analytical determinations

After irradiation the solutions were allowed to cool for 10–15 min under refrigeration, and then analysed by High Performance Liquid Chromatography coupled with UV–Vis detection (HPLC–UV). The adopted Merck–Hitachi instrument was equipped with AS2000A autosampler (100 μL sample volume), L-6200 and L-6000 pumps for high-pressure gradients, Merck LiChrocart RP-C18 column packed with LiChrospher 100 RP-18 (125 mm × 4.6 mm × 5 μm), and L-4200 UV–Vis detector (detection wavelength 210 nm). The isocratic elution was carried out with a 50:50 mixture of methanol: aqueous H$_3$PO$_4$ (pH 2.8). With an eluent flow rate of 1.0 mL min^{-1} the retention times were (min): phenol (2.55), 4-nitrophenol (3.20), 2-nitrophenol (5.15). The column dead time was 0.90 min.
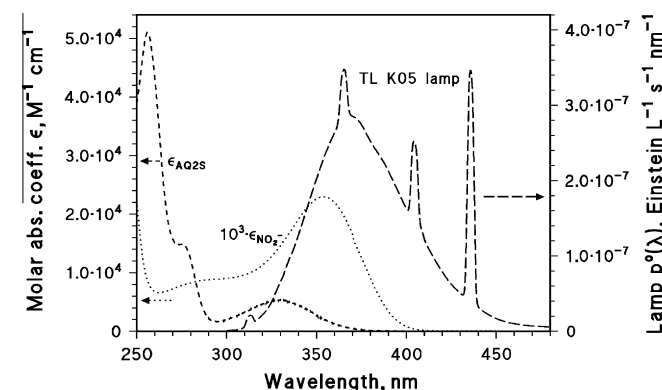

Fig. 1. Molar absorption coefficients of AQ2S and nitrite (the latter multiplied by 10^3). Emission spectrum of the adopted UVA lamp.

2.3. Kinetic treatment of the data

The time evolution data of phenol were fitted with pseudo-first order equations of the form $C_t = C_o \exp(-k_d^{Ph} \cdot t)$, where C_t is the concentration of phenol at the time t, C_o its initial concentration, and k_d^{Ph} the pseudo-first order degradation rate constant. The initial transformation rate of phenol is Rate$_{Ph} = k_d^{Ph} \cdot C_o$. The time evolution of 2- and 4-nitrophenol was fitted with $C_t' = k_f^{NP} \cdot C_o \cdot (k_d^{NP} - k_d^{Ph})^{-1} \cdot \left[\exp(-k_d^{Ph} \cdot t) - \exp(-k_d^{NP} \cdot t) \right]$, where C_t' is the concentration of each nitrophenol at the time t and k_f^{NP} and k_d^{NP} are the pseudo-first order formation and transformation rate constants of each nitrophenol. C_o and k_d^{Ph} have the same meaning as before. The nitrophenol initial formation rate is Rate$_{NP} = k_f^{NP} \cdot C_o$. The reported errors on the rates were derived at the σ level from the fit of the experimental data (intra-series variability). The reproducibility of repeated runs (inter-series variability) was in the range of 10–15%.

2.4. Radiation absorption calculations

To calculate the photon flux absorbed by AQ2S (P_a^{AQ2S}) in the presence of nitrite, one should consider that nitrite and AQ2S compete for the lamp irradiance (see Fig. 1). The absorbance of a species S does not vary if S is alone in solution or if it is in mixture with other radiation-absorbing compounds, but the photon flux absorbed by S is lower in the mixture. Interestingly, in a solution containing S and R as radiation-absorbing species, at a given wavelength λ the ratio of the respective absorbances would be equal to the ratio of the absorbed spectral photon flux densities: $A_S(\lambda)$ $[A_R(\lambda)]^{-1} = p_{a,S}(\lambda) [p_{a,R}(\lambda)]^{-1}$ (Braslavsky, 2007). It is also $A_S(\lambda)$ $[A_{tot}(\lambda)]^{-1} = p_{a,S}(\lambda) [p_{a,tot}(\lambda)]^{-1}$, where $A_{tot}(\lambda) = A_S(\lambda) + A_R(\lambda)$. Given these premises, the photon flux absorbed by AQ2S in the presence of nitrite (P_a^{AQ2S}) can be obtained as follows:

$$A_{tot}(\lambda) = b \cdot \{\varepsilon_{AQ2S}(\lambda) \cdot [AQ2S] + \varepsilon_{NO_2^-}(\lambda) \cdot [NO_2^-]\} \tag{1}$$

$$p_{a,tot}(\lambda) = p^\circ(\lambda) \cdot [1 - 10^{-A_{tot}(\lambda)}] \tag{2}$$

$$p_{a,AQ2S}(\lambda) = p_{a,tot}(\lambda) \cdot \varepsilon_{AQ2S}(\lambda) \cdot [AQ2S] \cdot \{\varepsilon_{AQ2S}(\lambda) \cdot [AQ2S] + \varepsilon_{NO_2^-}(\lambda) \cdot [NO_2^-]\}^{-1} \tag{3}$$

$$P_a^{AQ2S} = \int_\lambda p_{a,AQ2S}(\lambda) \, d\lambda \tag{4}$$

where $p^\circ(\lambda)$ is the lamp photon flux reaching the solution, ε_{AQ2S} and ε_{NO2-} the molar absorption coefficients of AQ2S and nitrite, respectively, and $b = 0.4$ cm the optical path length of the irradiated solution. P_a^{AQ2S} decreases with increasing nitrite concentration (see Fig. A-SM in the Supplementary material, hereafter SM). In the case of 0.1 mM AQ2S one gets the following linear trend: P_a^{AQ2S} [Einstein L^{-1} s^{-1}] = $(2.01 \pm 0.01) \cdot 10^{-6} - (1.62 \pm 0.04) \cdot 10^{-5}$ [NO$_2^-$].

2.5. Laser flash photolysis experiments

Laser flash photolysis (LFP) experiments were performed by using the third harmonic ($\lambda_{exc} = 355$ 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 65 mJ/pulse. Individual cuvette samples (3 mL volume) were used for a maximum of two consecutive laser shots. The transient absorbance at the pre-selected wavelength (λ_{det}) 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