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The photochemistry of anthraquinone-2-sulphonate (AQ2S) was studied as a function of pH, combining laser flash photolysis and steady-state irradiation experiments, with the additional help of a computational study of energy levels. Two out of the three transient species produced upon 10 irradiation of AQ2S can be involved into the degradation of dissolved molecules, and also AQ2S in its ground state is degraded. The reactive transients are less stable but often more reactive under acidic conditions, which modulates the pH trend of the photodegradation of the adopted organic substrates (furfuryl alcohol, benzene, nitrobenzene). The ability of the excited states of irradiated AQ2S to simulate the reactivity of singlet oxygen upon degradation of furfuryl alcohol, and that of 15 the hydroxyl radical by producing phenol from benzene, can have important consequences. Furfuryl alcohol and benzene are widely adopted probe molecules for the respective quantification of singlet oxygen and the hydroxyl radical in many systems, among which are the natural waters under irradiation. This study shows that the interference of AQ2S on singlet oxygen determination would be higher in acidic or basic than in circumneutral conditions, while in the case of the 20 hydroxyl radical the interference would increase with pH. Processes analogous to the studied ones could account for the interference of coloured dissolved organic matter on the quantification of singlet oxygen, observed in previous studies.

Introduction

Photochemical reactions are important pathways for the 25 transformation of naturally occurring compounds as well as of man-made xenobiotics in surface and atmospheric waters. The photoinduced transformation of a dissolved molecule can be induced by the direct photolysis, which occurs if the absorption of sunlight causes a chemical bond to break. 30 However, also the dissolved compounds that do not absorb radiation can be transformed upon reaction with transient species, which are produced upon irradiation of the so-called photosensitisers or photoinducers. The latter (mainly coloured dissolved organic matter (CDOM), nitrate, nitrite, hydrogen 35 peroxide, and Fe species) absorb sunlight and produce as a consequence reactive transients that can be involved into the degradation of the dissolved molecules.[1-6] The transients can be for instance the hydroxyl ($^\bullet OH$) and the carbonate ($CO_3^{-\bullet}$) radicals, singlet oxygen ($^1O_2$), and the excited triplet states of 40 CDOM (CDOM T_1).[7,8]

In surface waters CDOM is probably the most important photosensitiser: it is for instance a major source of $^\bullet OH$, and as a consequence of $CO_3^{-\bullet}$ that is produced by $^\bullet OH + CO_3^{2-}$ or HCO_3^-.[7,8] Light-excited CDOM can also produce $CO_3^{-\bullet}$ via a 45 minor pathway, upon direct oxidation of the carbonate anion, and it is practically the only source of $^1O_2$ and obviously of CDOM T_1.[9] Although the chemical structure of dissolved organic matter is still poorly understood, it is thought that aromatic carbonyls [10] and quinones [1] would account for an 50 important part of CDOM photochemistry. Quinones are in fact remarkably photoactive compounds that are able to absorb UV and visible radiation. Sunlight absorption causes promotion of electrons from the ground state to the first excited singlet state, from which an inter-system crossing could occur to 55 yield the first excited triplet state. The latter process is particularly favoured in the case of the anthraquinones. Their excited triplet states are relatively strong oxidants, and can extract electrons or hydrogen atoms from other dissolved molecules or transfer them energy.[11-14] These processes, along 60 with the occurrence of anthraquinones in surface and atmospheric waters and on atmospheric airborne particles,[15,16] make these compounds a potentially important class of photosensitisers in the environment.

The water-soluble anthraquinone-2-sulphonate (AQ2S) is an 65 important model compound for the reactivity of the quinones in the aqueous solution. Accordingly, a number of studies have been dedicated to its photophysics and photochemistry. A remarkable feature of AQ2S is that its excited triplet state has an hydroxylating power, which was initially attributed to 70 the photogeneration of $^\bullet OH$ upon oxidation of water. There ensued a long-lasting controversy about the possibility for excited AQ2S to actually form the hydroxyl radical in the aqueous solution,[17,18] but recent evidence seriously questioned the possibility that free $^\bullet OH$ is being formed in the system in 75 significant amount.[19] However, irradiated AQ2S is able to simulate the formation of $^\bullet OH$ in the presence of probe molecules for the hydroxyl radical (benzene, nitrobenzene, benzoic acid).[20] Therefore, it could be a major interferent for the determination of $^\bullet OH$. A better understanding of the 80 photochemistry of AQ2S would help the comprehension of the possible role of the excited states of CDOM as interfering agents in the quantification of $^\bullet OH$. Moreover, considering that irradiated CDOM is able to interfere with the

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measurement of $^1O_2$,[21] it is also of interest to study the reactivity of AQ2S excited states with furfuryl alcohol (FFA), a widely used probe molecule for singlet oxygen.[22,23]

The purpose of the present paper is to study the photophysics and photochemistry of AQ2S as a function of pH, with a particular interest in the pH-dependent lifetime of the excited states, and their ability to induce the degradation of some probe molecules. The latter were chosen for their peculiar reactivity with the excited states of AQ2S and/or for their use to measure the occurrence of definite transients in illuminated natural waters. A possible application concerns the recent finding that the formation rate of $^\bullet OH$ upon irradiation of lakewater (measured by the hydroxylation of benzene) is considerably higher under acidic compared with neutral conditions, and that the photochemistry of CDOM would play a major role in the phenomenon.[24] The present study aims at elucidating the photochemical behaviour, as a function of pH, of a molecule that has an analogy with the photoactive moieties of CDOM. It would also help assessing the potential for CDOM excited states to interfere with the determination of reactive transients such as the hydroxyl radical and singlet oxygen, and the effect of pH on such a process.

Experimental

All the adopted reagents were of analytical grade and were used as received, without further purification. Water was of Milli-Q quality. pH was measured with a Metrohm combined glass electrode, connected to a Metrohm 713 pH-meter.

Laser flash photolysis experiments (LFP)

Transient absorption experiments were carried out on a nanosecond flash photolysis spectrometer from Applied Photophysics. The third harmonic (355 nm, 30mJ) of a pulsed Nd:YAG laser (Quanta Ray GCR 130-1, flash time of 9 ns) was used as the excitation light source in a right-angle geometry with respect to the monitoring light beam. The laser irradiated a quartz cell of internal dimension 10 mm × 10 mm × 35 mm (length × width × height). Transient species produced by the pulsed laser beam were monitored by means of time-resolved absorption spectroscopy, using a 100 W Xenon arc lamp as the light source, and a LKS 60 detection system from Applied Photophysics. A spectrometer control unit was used for synchronising the pulsed light source and programmable shutters with the laser output. This also housed the high-voltage power supply for the photomultiplier. 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.

The stock solutions of AQ2S with or without addition of quencher were prepared just prior to the LFP experiments and were stored in the dark. All experiments were performed at room temperature in the range 293-298 K and, unless otherwise stated, in aerated solutions.

The transients species were identified on the basis of their different degradation time scales, and monitored at the wavelength of maximum absorption or at the wavelength where the interference of other species was minimal.

The pseudo-first order degradation rate constant k_i of a certain species i at a given wavelength was derived by fitting the absorbance vs. time data with $A_t = A_o \, exp(-k_i \, t)$, where A_t is the absorbance at the time t and A_o the initial absorbance. Because of the elevated number of data points, the error derived from the scattering of the experimental data around the fitting curve was very low (σ = 0.1-1%). The reproducibility of repeated runs was within 5-15%. To derive the second-order reaction rate constant $k_{i,x}$ of the transient species i with the quencher x, it was plotted k_i vs. $[x]$ and the value of $k_{i,x}$ was determined as the line slope $k_{i,x} = k_i \, [x]^{-1}$ (with error $\pm\sigma$, obtained from the scattering of the experimental data around the fitting line).

Steady-state irradiation experiments

Irradiation was carried out in Pyrex glass cells (4.0 cm diameter, 2.3 cm height), containing 5 mL of magnetically stirred solution. The adopted irradiation device was a set of 5 Philips TL K05 UVA lamps (emission maximum at 365 nm). The UV irradiance that reached the top of the solutions was 60 W m^{-2}, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter and corresponding to 4.5×10^{-5} einstein L^{-1} s^{-1}. Figure 1 shows the emission spectrum of the lamps, measured with an Ocean Optics SD 2000 CCD spectrophotometer, and the absorption spectra (molar absorption coefficients) of AQ2S at different pH values, taken with a Varian Cary 100 Scan UV-Vis spectrophotometer. It is apparent that the absorption spectrum of the compound does not change with pH, coherently with the absence of acid-base equilibria within the studied pH range.
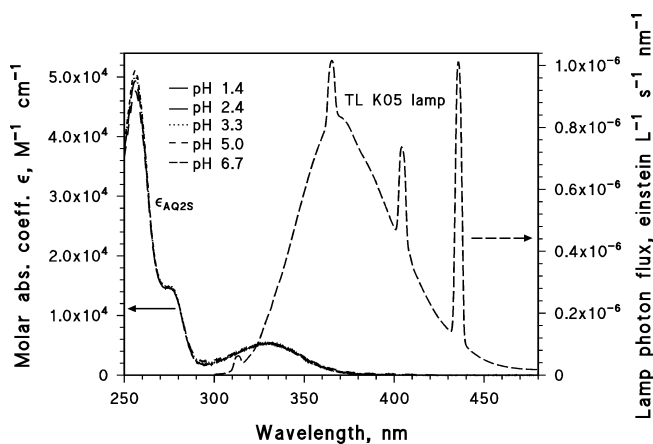
Figure 1. Molar absorption coefficients of AQ2S as a function of pH, natural or adjusted by addition of HClO$_4$. Emission spectrum of the adopted UVA lamp (emission maximum at 365 nm).

After irradiation, the solutions were analysed by High Performance Liquid Chromatography coupled with UV detection (HPLC-UV), adopting a Merck-Hitachi chromatograph equipped with autosampler (model AS2000), two pumps (model L6000 and L6200) for high-pressure gradients and a UV detector (model L4200). The column used was a RP-C18 LichroCART (Merck, length 125 mm, diameter 4 mm), packed with LiChrospher 100 RP-18 (5 μm diameter). Elution was carried out with a mixture of acetonitrile and TBA/H$_3$PO$_4$ in water (5 mM TBA = tetrabutylammonium

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bromide, pH 2.8), at a flow rate of 1.0 mL min^{-1}. Under these conditions the column dead time was 0.90 min. Different elution conditions were adopted for different systems. In the case of AQ2S + benzene, it was adopted a 30:70 mixture of CH$_3$CN:(TBA+H$_3$PO$_4$), with detection at 210 nm. Under these conditions the retention times were (min): phenol (3.7), AQ2S (12.4), benzene (15.4). In the case of AQ2S + FFA, it was adopted the following gradient of CH$_3$CN:(TBA+H$_3$PO$_4$): 10:90 for 4 min, then 40:60 up to 12.5 min, and back to the initial conditions for 9 min. The detection wavelength was 220 nm, the retention times (min): FFA (3.3), AQ2S (11.6). For AQ2S + nitrobenzene it was used the following gradient of CH$_3$CN:(TBA+H$_3$PO$_4$): 15:85 for 8 min, then 30:70 for 17 min, and back to the initial conditions for 5 min. The detection wavelength was 264 nm, the retention times (min): nitrobenzene (19.7), AQ2S (23.8).

The time trend of the degradation of AQ2S, FFA and nitrobenzene was fitted with equations of the form $C_t = C_o \ exp(-k\ t)$, where C_t is substrate concentration at the time t, C_o the initial concentration, and k the pseudo-first order degradation rate constant. The initial degradation rate is $R = k\ C_o$. The time evolution of phenol formation from benzene was fitted with $C'_t = C'_o\ [1-exp(-k'\ t)]$, where C'_t is phenol concentration at the time t, C'_o the initial concentration of benzene, and k' the pseudo-first order formation rate constant of phenol. The initial rate of phenol formation is expressed by $R' = k'\ C'_o$. The reported errors on the rates ($\pm\sigma$) represent the scattering of the experimental data around the fitting curve (intra-series variability). The reproducibility of repeated runs (inter-series variability) was around 10%. No reaction was detected between AQ2S and the substrates in the dark, and negligible transformation of the substrates was observed without AQ2S at the adopted irradiation time scales.

The average quantum yields of phototransformation or photoformation were calculated by dividing the corresponding reaction rates for the photon flux absorbed by AQ2S, P_a^{AQ2S}. The latter was calculated as $P_a^{AQ2S} = \int_\lambda p°(\lambda)\cdot[1-10^{-\varepsilon_{AQ2S}(\lambda)\cdot b\cdot[AQ2S]}]d\lambda$,[19] where $p°(\lambda)$ is the incident spectral photon flux density (lamp emission spectrum, see Figure 1), $\varepsilon_{AQ2S}(\lambda)$ the molar absorption coefficient of AQ2S (Figure 1), b = 0.4 cm the optical path length inside the cylindrical Pyrex cells used for the irradiation experiments (thickness of the irradiated solution), and [AQ2S] = 1×10^{-3} M.

Computational methods

A computational study was carried out for the possible reaction between radiation-excited AQ2S and water to yield the hydroxyl radical. Geometry optimisations in the ground state (S$_0$) of AQ2S and of all the species involved in the relevant reaction were performed in the gas phase, and confirmed by analytical calculation of the vibrational frequencies.[25] For AQ2S, also an optimisation of its lowest-energy triplet state (T$_1$) was carried out. For each molecular species, the gas-phase optimised structures were determined by gradient procedures [26-30] within the Density Functional Theory (DFT) [31] and the B3LYP hybrid functional.[32] The

polarized 6-311G(d,p) basis set was used in all the calculations.[32-34] Finally, the energy values obtained in the gas-phase calculations have been refined taking into account the solvent effect through single-point calculations at the SCIPCM (Self-Consistent Isodensity Polarised Continuum Method) level.[35] For the gas-phase simulation, zero-point energy corrections to the electronic energy values were derived from the thermochemical section of a frequency calculation output. Such values and corrections were employed to compute the thermodynamic properties of some reactions involving AQ2S in its triplet state. For the liquid-phase simulation, only the electronic energy was used because only single-point calculations were carried out. All the molecular calculations were performed with the GAUSSIAN 03W programs suite.[36]

## Results and discussion

Reactivity of the excited states

The excitation of AQ2S with a 355 nm laser pulse yields three different transient species (A, B and C).[17] The species A has an absorption band in the 350-500 nm range, with a maximum at 380 nm; it is formed just after the pulse and undergoes decay within some hundreds ns. The species B and C are formed while A disappears, consistently with their formation from A. B absorbs at 400-550 nm and at around 600 nm, decaying within some tens µs. C absorbs at 600 nm, and its decay time scale is within some hundreds ns like that of A. The relevant absorption spectra under different time scales are reported in the Supplementary Information (Figures ESI1-ESI4). To maximise selectivity, the monitoring of A, B and C was carried out at 380, 520 and 600 nm, respectively.

We could confirm previous results [17] that the pseudo-first order decay rate constants k_A, k_B and k_C are unaffected by O$_2$ (they do no vary within oxygen-free, normally aerated and oxygen-saturated solutions). The rate constants show some pH trend: k_A and k_C decrease with increasing pH, k_B increases with pH (see Supplementary Information, Figure ESI5). The study of the evolution of k_C at low pH was made difficult by fast disappearance. Another difficulty that is connected with the study of C at acidic pH is that A disappears more rapidly under those conditions, possibly because of an additional transformation pathway that would be in competition with the formation of C.

The pH trend of B has been attributed to a fast reaction with OH$^-$.[17] In a similar way, A and C could react with H$^+$. It has been reported that k_C increases with [AQ2S],[17] and in fact we observed a linear increase of k_C from 2×10^6 to 3×10^6 s^{-1} while [AQ2S] varied from 0.1 to 0.3 mM. The constant k_C then reached a plateau for higher [AQ2S] (see Supplementary Information, Figure ESI6). The linear increase can be attributed to a reaction between C and ground-state AQ2S.[17] Within such a scenario, our data allow the calculation of a second-order rate constant of (4.35±0.20)×10^9 M^{-1} s^{-1} between C and AQ2S. There is also no indication of a significant effect of pH on that reaction. Accordingly, the faster disappearance of C under acidic conditions cannot be accounted for by a faster reaction with ground-state AQ2S.

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The results reported so far have been rationalised under the hypothesis that A is the first triplet state of AQ2S (AQ2S T_1), while B and C would be two different exciplexes between the triplet state and H_2O.[17] The apparent lack of reactivity of A toward O_2 or AQ2S could be accounted for by the presence of a faster reaction between A and water to yield B and C. This hypothesis is consistent with our data and will be retained as the basis for further discussion.

We have found that sodium azide and Fe^{2+} undergo selective reaction with A, showing second-order rate constants of 4.4×10^9 M^{-1} s^{-1} at pH 6.2 and of 2.2×10^9 M^{-1} s^{-1} at pH 3.5, respectively (see Supplementary Information, Figure ESI7). In contrast, no reaction with B or C could be detected. Furfuryl alcohol (FFA) is able to react with both A and C. In the case of A the second-order rate constant with FFA is in the range of $(4.0-5.7) \times 10^9$ M^{-1} s^{-1}, depending on pH (see Figure 2), while for C it varies from 3.4×10^8 M^{-1} s^{-1} at pH 6.2 to 1.3×10^9 M^{-1} s^{-1} at pH 4.0 (Figure 3).
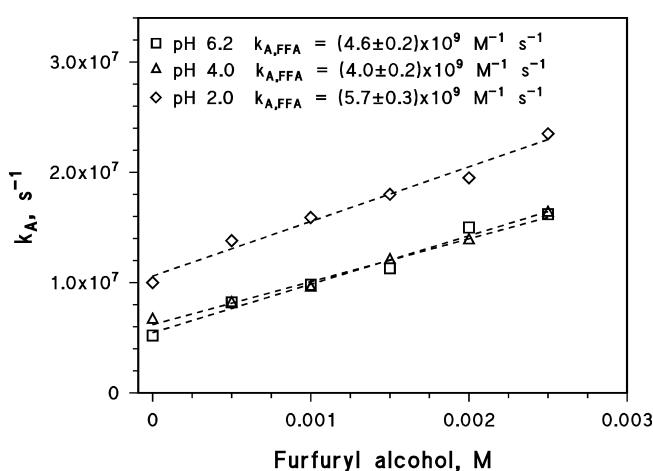
Figure 2. Pseudo-first order degradation rate constant of the transient species A, produced upon irradiation of 0.1 mM AQ2S, as a function of the concentration of added FFA. The pH was adjusted by addition of $HClO_4$. The reported values of $k_{A,FFA}$ are derived from the slopes of the relevant lines ($k_{A,FFA} = k_A [FFA]^{-1}$). Laser pulse: 30 mJ, 355 nm.
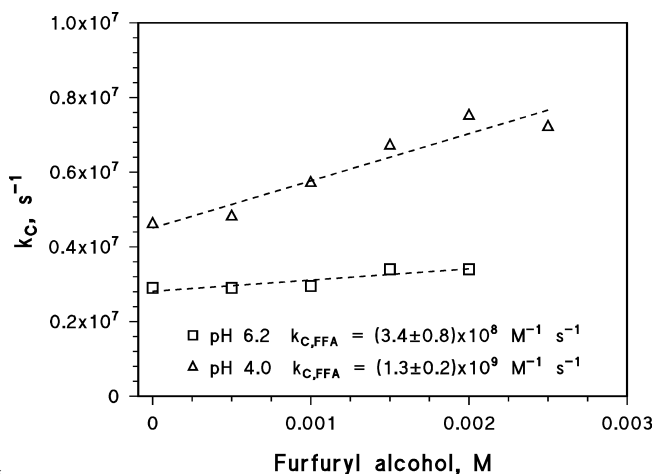
Figure 3. Pseudo-first order degradation rate constant of the transient species C, produced upon irradiation of 0.1 mM AQ2S, as a function of the concentration of added FFA. The pH was adjusted by addition of $HClO_4$. The reported values of $k_{C,FFA}$ are derived from the slopes of the relevant lines ($k_{C,FFA} = k_C [FFA]^{-1}$). Laser pulse: 30 mJ, 355 nm.
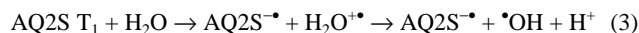
It is quite interesting that some transient species of the excited AQ2S are able to directly react with molecules (FFA, sodium azide) that are usually adopted as probes or scavengers of $^1O_2$. Such a behaviour provides potential for interference: the lack of reactivity of either A, B or C with oxygen makes the production of $^1O_2$ from AQ2S under irradiation very unlikely. A similar study as for FFA was also carried out in the presence of nitrobenzene and benzene (see Figures ESI8-ESI11, which report k_A and k_C as a function of the concentration of the two substrates at different pH values). The results show that both nitrobenzene (NBz) and benzene react with A, and that the second-order rate constants $k_{A,Benzene}$ and $k_{A,NBz}$ are higher at low pH. It is also $k_{A,NBz} < k_{A,Benzene} < k_{A,FFA}$ at all the studied pH values. Benzene and NBz do not appear to react with C at neutral or slightly acidic pH, while some evidence of reactivity could be obtained at pH 2. Interestingly, the excited states of AQ2S (mainly A in this case) are able to react with molecules (benzene and NBz) that are currently adopted for the determination of $^\bullet OH$, which leads to potential interferences.

Computational study of the reaction between excited AQ2S and water

The available literature data indicate that the radical $^\bullet OH$ is not the main reactive species that takes part to the processes involving AQ2S as a photosensitiser.[18,19] However, it would still be possible that the hydroxyl radical is produced in small amount, and partially contributes to the observed behaviour of the $^\bullet OH$ probe molecules in the presence of AQ2S under irradiation. To further understand the reactivity of the AQ2S molecule in its first excited triplet (T_1) state, it was carried out a simple energy evaluation of the active species that are supposed to be generated in the oxidising photochemical processes. The approach consisted in computing the difference between the sum of the energies of the products and that of the reagents. These calculations do not allow the estimation of energetic reaction barriers, but they permit the determination of the most likely fate of the substrate that reacts with AQ2S T_1. In particular, we are interested in studying the ability of AQ2S T_1 to form $^\bullet OH$ from water. The thermodynamic of the relevant reaction (1) was evaluated by analysing the two possible pathways of hydrogen abstraction (H_{abs}) and single electron transfer (SET), respectively reactions (2) and (3).

$$AQ2S\ T_1 + H_2O \rightarrow AQ2S_{red} + P \qquad (1)$$

In reaction (1), $AQ2S_{red}$ identifies a reduced AQ2S species such as $AQ2SH^\bullet$ (hydrogenated on one of the two oxygen atoms of the carbonyl groups) or $AQ2S^{-\bullet}$ (radical anion):

$$AQ2S\ T_1 + H_2O \rightarrow AQ2SH^\bullet + {^\bullet OH} \qquad (2)$$

$$AQ2S\ T_1 + H_2O \rightarrow AQ2S^{-\bullet} + H_2O^{+\bullet} \rightarrow AQ2S^{-\bullet} + {^\bullet OH} + H^+ \quad (3)$$

Results point out that both reactions are endothermic: for H_{abs} (reaction 2) values are $\Delta E = 11.87$ kcal mol^{-1} and $\Delta E = 9.48$ kcal mol^{-1}, respectively for gas and liquid phase. About SET (reaction 3), energy values are even more endothermic ($\Delta E = 179.65$ kcal mol^{-1} and $\Delta E = 72.56$ kcal mol^{-1}, respectively for gas and liquid phase), despite the strong stabilisation of the

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charged species in the dielectric represented by the aqueous solution. The elevated values of ΔE, even in the most favourable case of reaction (2) in solution, suggest that the photogeneration of $^{\bullet}OH$ from AQ2S T_1 and water could not occur to a significant extent. The present data are compatible with the results of previous experiments, according to which the degradation of phenol upon irradiation of AQ2S does not involve $^{\bullet}OH$.[19] It can therefore be excluded that the decay of B and C (possible exciplexes between AQ2S T_1 and H_2O, which could be intermediates of reactions 2 and 3) takes place through the formation of $^{\bullet}OH$.

By comparison of reactions (2) and (3), it is noticeable that AQ2S$^{-\bullet}$ is the conjugate base of AQ2SH$^{\bullet}$. Assume the deprotonation of AQ2SH$^{\bullet}$ into AQ2S$^{-\bullet}$:

$$AQ2SH^{\bullet} + H_2O \rightarrow AQ2S^{-\bullet} + H_3O^+ \qquad (4)$$
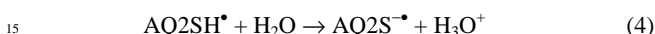
Calculation results indicate that reaction (4) in the aqueous solution has ΔE = 41.64 kcal mol^{-1}, which suggests that the reactants are more stable than the products. It is, therefore, very likely that AQ2SH$^{\bullet}$ behaves as a very weak acid.

Results of steady-state irradiation

The degradation of AQ2S when it is irradiated alone [18] is consistent with the reaction between ground-state AQ2S and one of the transient species produced upon AQ2S irradiation (in particular, that indicated as C in this work). Figure 4 shows the pH trend of the degradation rate of 1 mM AQ2S. With the exception of pH >10, the rate is about constant over a very wide interval (down to pH 4), and decreases considerably at pH < 4. The Figure also reports the quantum yield $\Phi_{AQ2S} = Rate_{AQ2S} (P_a^{AQ2S})^{-1}$, where $P_a^{AQ2S} = 2.6 \times 10^{-5}$ Einstein L^{-1} s^{-1}.
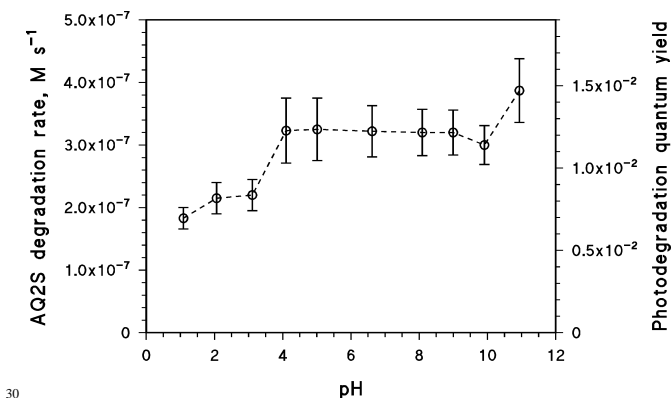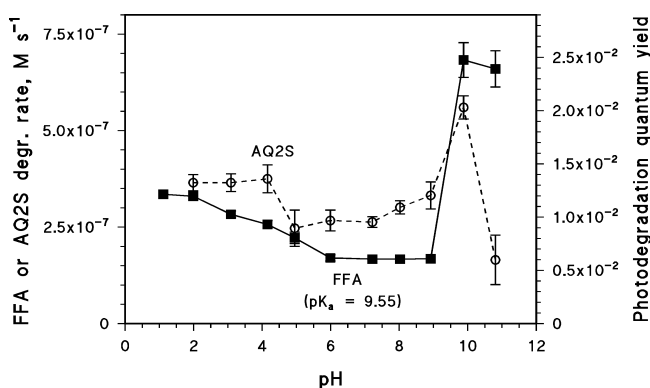

Figure 4. Initial degradation rate of 1 mM AQ2S upon UVA irradiation, as a function of pH adjusted upon addition of HClO$_4$ or NaOH. Irradiation time was up to 1 h. The right Y axis reports the average photodegradation quantum yield of AQ2S, calculated as $\Phi_{AQ2S} = Rate_{AQ2S} (P_a^{AQ2S})^{-1}$.

The quantum yield values thus calculated are one order of magnitude or more lower than the quantum yield of formation of AQ2S T_1 upon irradiation of AQ2S.[18,19] The most likely explanation is that only a fraction of the photogenerated reactive species would be involved into the transformation processes under the adopted experimental conditions: the conversion of A into C is not quantitative, and the reaction between C and AQ2S would be in competition with other processes of C transformation.

The laser flash photolysis (LFP) results suggest that C should be the reactive species responsible for the degradation of AQ2S, thus the pH trend of Figure 4 could reflect the reactivity of C. The decrease of the AQ2S degradation rate below pH 4 could be the consequence of the very fast decay of C under those pH conditions (see Figure ESI5). If, at acidic pH, C were consumed by a pathway such as the reaction with H$^+$, there could be less C available for the degradation of AQ2S. The LFP data also suggest that the reaction rate constant between C and AQ2S does not vary significantly with pH, and the predicted outcome is, therefore, a decrease of the AQ2S degradation rate with decreasing pH. The LFP results are thus in agreement with the steady irradiation experiments.

Figure 5 shows the transformation rates of 0.1 mM furfuryl alcohol (FFA) and of 1 mM AQ2S, upon UVA irradiation. It should be noted that FFA has pK$_a$ = 9.55,[37] thus the FFA rates at pH 10-11 are referred to the furfurylate that is probably more labile.

Figure 5. Initial degradation rate of 0.1 mM FFA and of 1 mM AQ2S upon UVA irradiation, as a function of pH adjusted upon addition of HClO$_4$ or NaOH. Irradiation time was up to 1 h. The right Y axis reports the average photodegradation quantum yields, calculated as $\Phi_i = Rate_i (P_a^{AQ2S})^{-1}$ (i = AQ2S or FFA).

The LFP data suggest that FFA can react with both A and C. Under the adopted steady irradiation conditions, the degradation rate of FFA is higher under acidic compared with circumneutral pH. For instance, the degradation rate of FFA increases from 1.5×10^{-7} M s^{-1} at pH 6 to 2.5×10^{-7} M s^{-1} at pH 4, to 3.3×10^{-7} M s^{-1} at pH 2 (Figure 5). Interestingly, the reaction rate constant between FFA and C as determined by LFP also increases considerably between pH 6 and 4 (around 3.8 times, see Figure 3). Note that both ground-state AQ2S and H$^+$ would compete with FFA for the reaction with C. However, the LFP data indicate that the reaction rate constant between AQ2S and C would not vary significantly in the relevant pH interval. Moreover, because of the effect of H$^+$, the first-order rate constant of C degradation would be about double at pH 4 compared with pH 6 (see Supplementary Information, Figure ESI5). This is to be compared with the 3.8-fold increase of the rate constant between FFA and C in the same pH interval: a higher fraction of C is therefore expected to react with FFA at pH 4 compared with pH 6. Also note that the reaction rate constant between A and FFA is increased by almost 50% between pH 4 and 2 (see Figure 2).

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Therefore, A might contribute somewhat to the increased degradation rate of FFA at low pH, but under such conditions also the competitive reaction between A and H^+ would be faster. The higher reactivity of both A and C toward FFA at low pH could be accounted for by the fact that the excited AQ2S has an oxidising nature,[17-19] and its reduction would yield the semiquinone radical (AQ2SH$^\bullet$) or its conjugate base (AQ2S$^{-\bullet}$ + H^+). The occurrence of the former would be favoured under acidic conditions. The fact that reaction (4) is endothermic suggests that at low pH the photoredox reactions could be favoured because they yield AQ2SH$^\bullet$, which is the most stable intermediate.

The degradation of FFA in the presence of AQ2S under irradiation is interesting because FFA is usually adopted as a probe molecule for $^1O_2$.[21-23] In the system under study, a significant formation of $^1O_2$ is highly unlikely given the lack of reactivity between A, B or C and molecular oxygen. Furthermore, it has been shown that $^1O_2$ plays no role in the degradation of phenol in the presence of irradiated AQ2S.[19] The degradation of FFA would thus represent an interference, if the alcohol is used as a probe to measure $^1O_2$ in systems that contain AQ2S or compounds with similar behaviour. The data reported in Figure 5 suggest that such an interference would be more important under acidic or basic compared with circumneutral conditions. Similar processes could possibly take place in the environment. In fact, a non-negligible fraction of FFA degradation upon irradiation of river water could be caused by reactive species derived from dissolved organic matter (possibly the excited triplet states). These processes could complicate the quantification of $^1O_2$ by using FFA as a probe molecule.[21]

Figure 6 shows the degradation rate of 1 mM AQ2S and the formation rate of phenol from 0.1 mM benzene, upon UVA irradiation. Both rates decrease with decreasing pH.
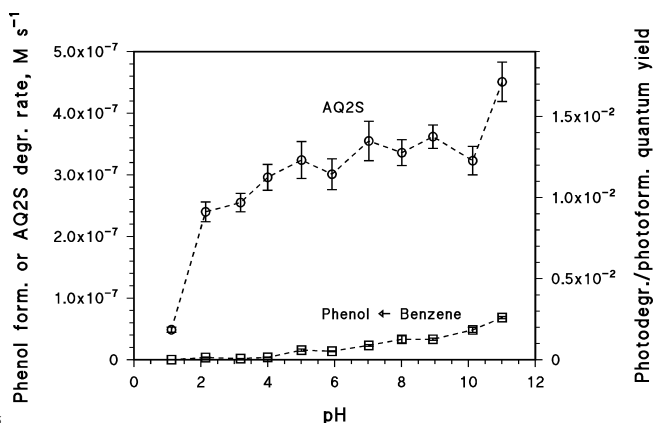
Figure 6. Initial degradation rate of 1 mM AQ2S and initial formation rate of phenol from 0.1 mM benzene, upon UVA irradiation, as a function of pH adjusted with HClO$_4$ or NaOH. Irradiation time was up to 1 h. The right Y axis reports the average photodegradation quantum yields, calculated as $\Phi_i = \text{Rate}_i\,(P_a^{AQ2S})^{-1}$ (i = AQ2S or Phenol).

Interestingly, the LFP data indicate that $k_{C,AQ2S}$ has a negligible pH trend, while little or no reaction between C and benzene is observed in the pH interval 4-6. A non-null value of $k_{C,Benzene}$ can be observed at pH 2 (Figure ESI9), but it is quite low when compared with, for instance, $k_{C,AQ2S}$.

Moreover, at pH 2 the reaction between C and benzene would be in competition with the fast disappearance of C, possibly because of reaction with H^+. As a consequence, a limited amount of C would be available to react with benzene at pH 2. Comparison between Figures ESI8 and ESI9 suggests that benzene would mainly undergo transformation upon reaction with A. Interestingly, $k_{A,Benzene}$ is higher at low pH (about 40% higher at pH 2 compared with pH 6), but also the pseudo-first order transformation rate constant of A is 2-3 times higher at pH 2 than at pH 6 (Figures ESI5 and ESI8). Overall, at pH 2 there would be less A available for the reaction with benzene, compared with pH 6.

Figure 7 shows the degradation rates of 0.1 mM nitrobenzene (NBz) and of 1 mM AQ2S upon UVA irradiation. The degradation of NBz is quite slow, making it the least reactive substrate toward irradiated AQ2S among the tested ones. Interestingly, the phototransformation rates are in the order FFA > Benzene → Phenol > Nitrobenzene, which reflects the reactivity of the substrates with A ($k_{A,FFA}$ > $k_{A,Benzene}$ > $k_{A,NBz}$), and the fact that FFA is considerably more reactive than either benzene or nitrobenzene toward C.

The rate of NBz degradation is slightly higher under basic compared with acidic conditions, thus the pH trend resembles that of benzene but it is less marked. A reasonable explanation is the fact that $k_{A,NBz}$ undergoes a higher increase at low pH than $k_{A,Benzene}$ (Figures ESI8 and ESI10).
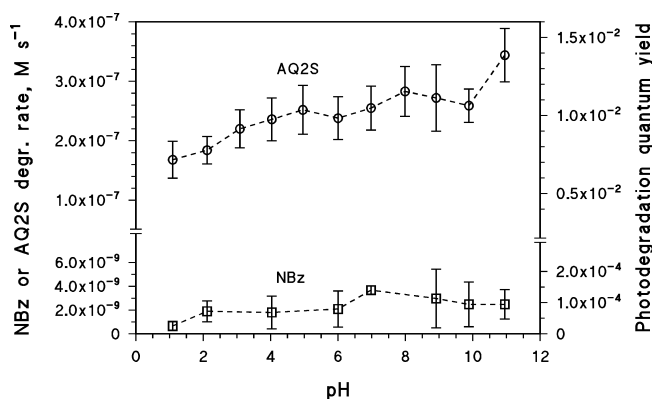
Figure 7. Initial degradation rate of 0.1 mM nitrobenzene (NBz) and of 1 mM AQ2S upon UVA irradiation, as a function of pH adjusted upon addition of HClO$_4$ or NaOH. Irradiation time was up to 2 h. Note the break in the Y-axis. The right Y axis reports the average photodegradation quantum yields, calculated as $\Phi_i = \text{Rate}_i\,(P_a^{AQ2S})^{-1}$ (i = AQ2S or NBz).

Irradiated AQ2S is an interfering agent in the determination of $^\bullet$OH by means of nitrobenzene and benzene as probe molecules.[20] The present study suggests that the main reason for the interference is the reactivity of nitrobenzene and benzene with the excited triplet state (A) of AQ2S. Interestingly, the extent of the interference would increase with pH because A undergoes faster transformation under acidic conditions (possibly because of the reaction with H^+, which competes with benzene or NBz for the consumption of A).

The comparison between Figures 5, 6 and 7 shows that, under similar conditions, the formation rate of phenol from benzene and the transformation rate of NBz are much lower than the transformation rate of FFA. Although the interference of

irradiated AQ2S on $^\bullet$OH measurement would be considerably lower in absolute terms than for $^1O_2$, it should be considered that the formation rate of $^\bullet$OH upon irradiation of natural waters is typically much lower compared with that of $^1O_2$ or the excited triplet states of coloured dissolved organic matter.[3,22] Accordingly, AQ2S or similar compounds are potential interferents for the determination of both $^\bullet$OH and $^1O_2$ in irradiated natural waters.

Conclusions

AQ2S is a photosensitiser that is able to induce the indirect photolysis of other molecules when irradiated. The irradiation of AQ2S in the UVA range yields three transients species, here indicated as A, B and C. The species A is likely to be AQ2S T_1, while B and C could be two exciplexes between AQ2S T_1 and H_2O.[17] The results of laser flash photolysis experiments suggest a lack of reactivity between the species B and other dissolved compounds, with the possible exception of the ion OH$^-$. Among the tested solutes, some of them are able to react selectively (N_3^-, Fe^{2+}) or almost selectively (benzene, nitrobenzene) with A. Additionally, ground-state AQ2S appears to react with C only, and FFA reacts with both A and C. The transient species A and C are less stable under acidic conditions, and therefore less available for indirect photolysis reactions, but they could also be more reactive at low pH. A major issue that governs the pH trend of substrate photodegradation in the presence of irradiated AQ2S seems to be the reactivity with C and the pH dependence of $k_{C,Substrate}$. FFA is degraded faster at acidic pH. Coherently, its second-order rate constant with C increases under acidic conditions, more than the overall rate constant of C degradation in the same pH interval. AQ2S, benzene and nitrobenzene all undergo slower degradation at acidic pH. At the same time, these compounds either show very limited reactivity toward C (such as benzene and nitrobenzene), or react with C but the reactivity is almost independent of pH (such as AQ2S).

Irradiated AQ2S is hardly able to produce $^\bullet$OH or $^1O_2$, but it can induce the transformation of molecules that are currently adopted as probes for the hydroxyl radical (benzene, nitrobenzene) or singlet oxygen (FFA). The degradation of FFA by irradiated AQ2S suggests the potential for quinonoid compounds to interfere with the quantification of $^1O_2$ by using furfuryl alcohol as a probe. Such a result would confirm the hypothesis, formulated in a recent field study, that species formed upon irradiation of coloured dissolved organic matter (CDOM) and $^1O_2$ can both react with FFA, and that the interference by CDOM needs to be taken into account for a correct quantification of $^1O_2$ photoproduction in natural waters.[22] In the case of AQ2S, the interference would be higher under acidic and basic compared with circumneutral conditions. The reactivity between A and N_3^- is also interesting (second-order rate constant 4.4×10^9 M^{-1} s^{-1}), because the azide anion is widely used as a scavenger of $^1O_2$.[38]

In the case of benzene, AQ2S behaves in an opposite way than freshwater CDOM, which has been shown to induce a considerably higher hydroxylation of benzene at acidic pH.[24] The present data do not enforce the hypothesis that the observed pH trend of benzene hydroxylation by irradiated natural waters reflects the photoreactivity of CDOM reactive moieties (including the quinones), rather than the actual availability of free $^\bullet$OH. Further investigations will be required to understand to what extent the pH trends observed in the present study are peculiar to the photochemistry of AQ2S, and therefore how much AQ2S is representative of the photoactive moieties of CDOM. However, the hydroxylation of benzene by irradiated CDOM is not necessarily involving CDOM T_1. A reasonable alternative explanation is that the dissolved organic matter is involved into photo-Fenton reactions, initiated by Fe(III) complexes with organic ligands,[39] which yield $^\bullet$OH when irradiated and have maximum efficiency under acidic conditions.[40]

Notes and references

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