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COMPARISON OF DIFFERENT PROBE MOLECULES FOR THE QUANTIFICATION OF HYDROXYL RADICALS IN AQUEOUS SOLUTION

Davide Vione,^{a,*} Marco Ponzo,^a Daniele Bagnus,^a Valter Maurino,^a Claudio Minero,^a Maria Eugenia Carlotti^b

^a *Dipartimento di Chimica Analitica, Università di Torino, Via P. Giuria 5, 10125 Torino, Italy.*

<http://www.chimicadellambiente.unito.it>

^b *Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino, Via P. Giuria 9, 10125 Torino, Italy.*

* Corresponding author. Phone +39-011-6707874; Fax +39-011-6707615;

E-mail: davide.vione@unito.it http://naturali.campusnet.unito.it/cgi.bin/docenti.pl/Show?_id=vione

Abstract

In this paper we show that the transformation reaction of benzene into phenol is a more selective probe for the hydroxyl radical than the transformation of nitrobenzene or the generation of 4-hydroxybenzoic from benzoic acid. The benzene to phenol system showed adequate performance as a probe upon irradiation of lake water samples and humic acids. We show that the use of nitrobenzene and benzoic acid as hydroxyl probes should be avoided because of poor selectivity. Moreover, all the tested probe molecules underwent important interference by irradiated anthraquinone-2-sulphonate, and considerably overestimated the formation of the hydroxyl radicals.

Keywords: surface water; photochemistry; photosensitisers; indirect photolysis; radical transients.

1. Introduction

The impact of organic and inorganic pollutants on aquatic systems is a complex function of their harmful effects on humans and ecosystems, their inputs, transport, bioavailability, and their environmental fate. The fate of organic pollutants depends on both biological and chemical processes, the latter playing a substantial role into the transformation of biorefractory compounds, including some pesticides and pharmaceuticals. Among the chemical transformation processes, photochemistry has often an important role in defining the fate of pollutants (Canonica et al., 2006; Fenner et al., 2006).

Photochemical processes in surface waters include the direct photolysis of sunlight-absorbing molecules, the transformation reactions photosensitised by the excited triplet states of dissolved organic matter

($^3\text{DOM}^*$), and the reaction with transient species generated by photoactive compounds such as nitrate, nitrite, Fe, and DOM (Boule et al., 2005; Rafqah et al., 2006). The described processes can induce the degradation of harmful pollutants, but in some cases produce intermediates that are even more harmful than the parent compounds (Brigante et al., 2005; Vione et al., 2003). Among the reactive species that are photochemically generated in surface waters there are singlet oxygen ($^1\text{O}_2$), $^3\text{DOM}^*$, and the radicals $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ (Lam and Mabury, 2005). The quantification of the rates of photoproduction and scavenging of these species and of their steady-state concentration is of considerable importance for assessing the potential of aquatic systems to induce the degradation of xenobiotic compounds. Different probe molecules can be used for this purpose: butyl chloride, nitrobenzene, benzene and benzoic acid for $\bullet\text{OH}$ (Hoigné, 1990), furfuryl alcohol for $^1\text{O}_2$ (Halladja et al., 2007), and phenolic compounds for $^3\text{DOM}^*$ (Canonica and Freiburghaus, 2001). An important issue within this context is the selectivity toward the species of interest of the reactions that involve the relevant probe molecules. To our knowledge few or no comparisons have been carried out to date between alternative probe molecules when available (see the case of $\bullet\text{OH}$), to understand up to what extent they are selective toward the reactive species that they are intended to measure. The purpose of the present paper is to carry out such a comparison. DOM as the main source of $\bullet\text{OH}$ in surface waters (Minero et al., 2007) is a key player in this context, but it also produces additional reactive species (Halladja et al., 2007). We chose as a model the water-soluble anthraquinone-2-sulphonate, because it resembles some photoactive quinonoid moieties of coloured DOM, and because the details of its photochemical reactivity have recently been elucidated (Maurino et al., 2008). For probe testing we also used humic acids, as a less characterised but nearer material to the photoactive components of DOM (Halladja et al., 2007). Finally, we compared the behaviour of the $\bullet\text{OH}$ probes by irradiation of real lake-water samples.

2. Experimental

2.1. Reagents and materials

Phenol (purity grade >99%), benzoic acid (99%), 4-hydroxybenzoic acid (99%), furfuryl alcohol (99%), anthraquinone-2-sulfonic acid, sodium salt (97%), 3-nitrophenol (99%), 4-nitrophenol (99%), humic acid, sodium salt, H_3PO_4 (85%) and NaNO_2 (97.5%) were purchased from Aldrich, nitrobenzene (99.5%) from Fluka, 2-nitrophenol (>99%), benzene (99.8%), acetonitrile (gradient grade), 2-propanol (gradient grade), H_2O_2 (35%), NaOH (99%) and NaNO_3 (99.5%) from VWR Int. All reagents were used as received, without further purification. Water used was of Milli-Q quality. To minimise the problems caused by the change of pH as a function of the concentration of benzoic acid in the irradiation experiments, the stock solution of benzoic acid/ benzoate was prepared by titration of benzoic acid with NaOH up to pH 6.

2.2. Irradiation experiments

All the solutions (5 mL volume unless otherwise stated) were irradiated inside cylindrical Pyrex glass cells (4.0 cm diameter, 2.5 cm height), under magnetic stirring. The irradiation of solutions containing anthraquinone-2-sulphonate (AQ2S), humic acids (HUm), nitrite, and the lake water samples was carried out

under a Philips TL K05 UVA lamp. It emits radiation between 300 and 500 nm, with emission maximum at 365 nm. The UV irradiance in solution was 22 W m^{-2} , measured with a CO.FO.ME.GRA. (Milan, Italy) power meter between 290 and 400 nm. It corresponds to $8.3 \times 10^{-8} \text{ einstein s}^{-1}$. In the case of nitrate and hydrogen peroxide that only absorb UVB radiation, selective excitation was obtained under a Philips TL 01 UVB lamp. It emits radiation between 300 and 450 nm, with emission maximum at 313 nm. The UV irradiance was 5.2 W m^{-2} , corresponding to $1.7 \times 10^{-8} \text{ einstein s}^{-1}$. Figure 1a/b reports the emission spectra of the two lamps, measured with an Ocean Optics SD 2000 UV-Vis spectrophotometer, and the absorption spectra of the relevant compounds in aqueous solution, taken with a Varian Cary 100 Scan UV-Vis spectrophotometer, using Hellma quartz cuvettes (optical path length 1.000 cm).

2.3. Analytical determinations

The irradiated systems were analysed with a Merck-Hitachi High Performance Liquid Chromatograph, equipped with AS2000A Autosampler (injection volume up to 100 μL), L-6200 and L-6000 pumps for high-pressure gradients, and L-4200 UV-Vis Detector. The column used was a RP-C18 LichroCART (Merck, length 125 mm, diameter 4 mm), packed with LiChrospher 100 RP-18 (5 μm diameter). The isocratic eluent was a mixture of acetonitrile and aqueous H_3PO_4 (0.5 mM, pH 2.8), at 1.0 mL min^{-1} flow rate. Table 1 reports the eluent composition, retention time, and quantification wavelength for the different compounds under study. The detection wavelength was chosen to maximise sensitivity.

Table 1. Chromatographic data of the studied compounds.

Compound	$\text{CH}_3\text{CN} : \text{aqueous H}_3\text{PO}_4$	Retention time (min)	Wavelength (nm)
Benzene	40:60	7.70	210
Phenol	40:60	2.50	210
Benzoic acid	20:80	7.70	210
4-Hydroxybenzoic acid	20:80	2.60	210
Nitrobenzene	40:60	5.90	210
2-Nitrophenol	40:60	4.80	210
3-Nitrophenol	40:60	3.20	210
4-Nitrophenol	40:60	2.95	210
Furfuryl alcohol	10:90	3.70	215

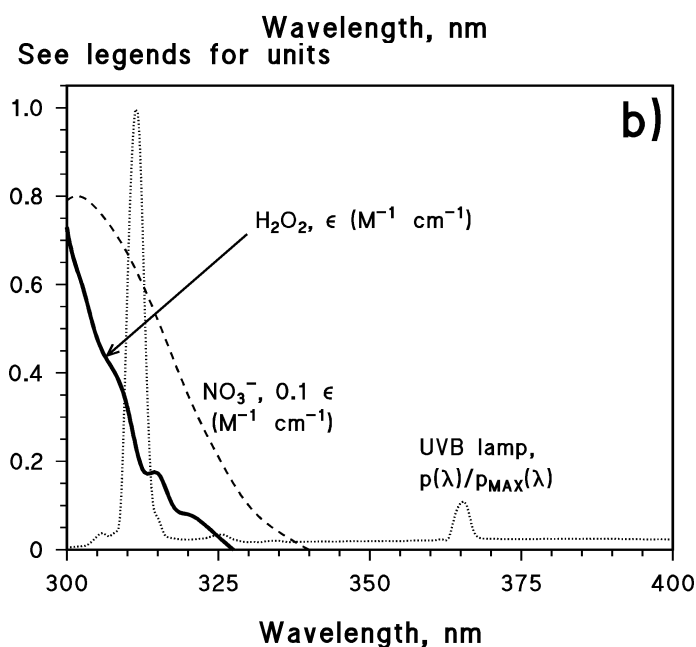
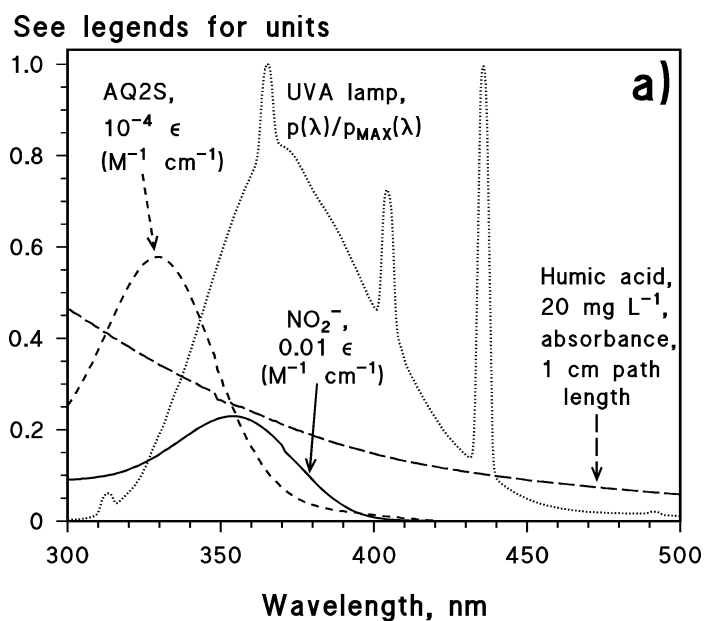
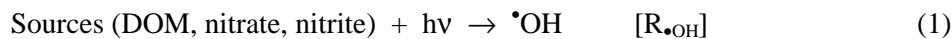


Figure 1. Emission spectra of the adopted UV lamps (UVA: TL K05; UVB: TL01). Absorption spectra of AQ2S, HU_m, nitrite, nitrate, and hydrogen peroxide. Units are $\text{M}^{-1} \text{ cm}^{-1}$ for ϵ , and cm^{-1} for the absorbance of HU_m; $\rho(\lambda)/\rho_{\text{MAX}}(\lambda)$ is a ratio between homogeneous quantities.

2.4. Kinetic modelling

The time evolution data of the substrates were fitted with pseudo-first order curves of the form $C_t = C_0 e^{-kt}$, where C_t is the substrate concentration at the time t , C_0 its initial concentration, and k the pseudo-first order degradation rate constant. The initial degradation rate of the substrate is $k C_0$. For the transformation intermediates the adopted equation was $I_t = k_1^f C_0 (k_1^d - k)^{-1} [\exp(-k t) - \exp(-k_1^d t)]$, where I_t is the concentration of the intermediate I at the time t , C_0 and k as for the previous equation, and k_1^f and k_1^d are the pseudo-first order formation and degradation rate constants of I , respectively. The initial formation rate of the intermediate is $k_1^f C_0$. The error bars ($\mu \pm \sigma$) were derived from the goodness of the numerical fit of the theoretical curves to the experimental data (intra-series variability).

In the case of lake water, the competition between the added probe P and the natural scavengers, $\sum_i S_i$, for the photogenerated $\bullet\text{OH}$ radicals was accounted for by the following model:



$R_{\bullet\text{OH}}$ is the total formation rate of the hydroxyl radicals in the irradiated sample (our target in this work), I is the monitored transformation intermediate, and η the formation yield of I from the probe P and $\bullet\text{OH}$ (e.g. phenol from benzene, $\eta = 0.95$). In some cases (e.g. nitrobenzene) one measures the transformation rate of P, R_P . In other cases (e.g. benzene \rightarrow phenol) one measures the formation rate of I, $R_I = \eta R_P$. From the equations reported above one gets:

$$R_P = \frac{k_P [P] R_{\bullet\text{OH}}}{k_P [P] + \sum_i k_{S_i} [S_i]} \quad (5)$$

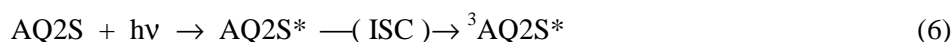
By plotting R_P^{-1} vs. $[P]^{-1}$ {or $R_I^{-1} (= [\eta R_P]^{-1})$ vs. $[P]^{-1}$ } one should obtain a straight line, from the intercept of which one derives $R_{\bullet\text{OH}}$.

3. Results and Discussion

3.1. Irradiation of AQ2S

Figure 2a reports the initial degradation rates of furfuryl alcohol (Furf), phenol (Ph) and nitrobenzene (NBz) upon UVA irradiation of 4 μM AQ2S, as a function of the concentration of the substrate (Furf, Ph, or NBz). The degradation of phenol and NBz upon irradiation without AQ2S was negligible, while in the case of Furf some transformation (photolysis and thermal degradation) was detected, accounting for around 10% of that in the presence of AQ2S. For this reason the Furf data reported in Figure 2a are corrected by subtracting the degradation rate without AQ2S. This procedure is allowed by the fact that 4 μM AQ2S absorbs a very limited fraction (around 0.5%) of the radiation reaching the solution. Also note that nitrobenzene is able to compete with AQ2S for radiation absorption. The effect would be negligible up to 10^{-4} M nitrobenzene, and would decrease AQ2S absorption by at most 25% at the highest adopted NBz levels.

The irradiation of AQ2S yields the excited triplet state, ${}^3\text{AQ2S}^*$ by inter-system crossing (ISC). The triplet state could directly react with the substrates or produce ${}^1\text{O}_2$ from dissolved O_2 (Boule et al., 2005; Halladja et al., 2007). Production of $\bullet\text{OH}$ might take place upon oxidation of water by ${}^3\text{AQ2S}^*$.



The degradation of phenol in the presence of AQ2S under irradiation has been shown to occur almost exclusively upon reaction with the excited triplet states ${}^3\text{AQ2S}^*$ (Maurino et al., 2008). This fact makes phenol a suitable probe molecule for ${}^3\text{AQ2S}^*$.

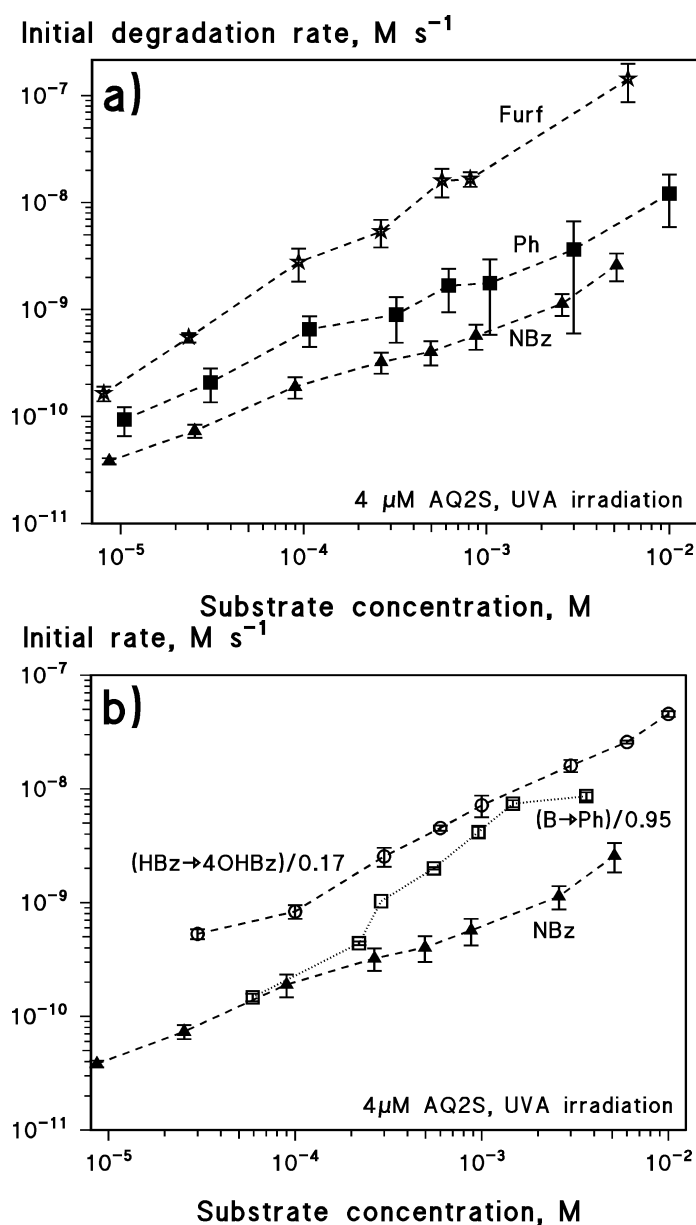


Figure 2. a) Initial degradation rates of nitrobenzene (\blacktriangle , NBz), phenol (\blacksquare , Ph) and furfuryl alcohol (\star , Furf) upon UVA irradiation of $4 \mu M$ AQ2S. Note the logarithmic scale on both axes.

b) Use of the probe molecules for the possible quantification of $\bullet OH$ generation: nitrobenzene (\blacktriangle , NBz), formation of phenol from benzene (\square , B \rightarrow Ph, 95% yield), and formation of 4-hydroxybenzoic from benzoic acid (\circ , HBz \rightarrow 4OHBz, 17% yield). The rate order is HBz > Benzene > NBz. Note the logarithmic scale on both axes. The NBz data are reported in both plots to facilitate the comparison.

The continuous increase with concentration of phenol degradation rate suggests that at low phenol, $^3AQ2S^*$ would mainly undergo thermal deactivation. This process is in competition with the reaction between phenol and $^3AQ2S^*$ (Maurino et al., 2008), which prevails at elevated phenol concentration.

Furfuryl alcohol is a possible probe molecule for 1O_2 . Negligible reactivity of Furf with the excited triplet states of humic acids has been reported (Halladja et al., 2007), but no data exist for the reaction with $^3AQ2S^*$. Considering that the reaction between 1O_2 and Furf (rate constant $1.2 \times 10^8 M^{-1} s^{-1}$) is in competition with the thermal deactivation of 1O_2 ($2.5 \times 10^5 s^{-1}$) (Halladja et al., 2007), one would expect the degradation

rate of Furf to reach a plateau above 2 mM Furf. Under such circumstances Furf would scavenge the majority of photogenerated $^1\text{O}_2$. In Figure 2a we show that, in contrast, the degradation rate of Furf continues increasing above 2 mM Furf. This indicates that a reaction between Furf and $^3\text{AQ2S}^*$ cannot be excluded.

The sustained production of $^3\text{AQ2S}^*$ and possibly $^1\text{O}_2$ from irradiated AQ2S, reflected by the phenol and Furf data, could interfere with the measurement of $\bullet\text{OH}$ by using nitrobenzene, benzene, and benzoic acid. In Figure 2b we compare the degradation rate of nitrobenzene with the formation rates of phenol from benzene and of 4-hydroxybenzoic from benzoic acid. To enable the comparison, the rates are divided by the yield of the reaction that involves $\bullet\text{OH}$: 95% for phenol from benzene (Minero et al., 2007, and references therein), and 17% for 4-hydroxybenzoic from benzoic acid (Lindsey and Tarr, 2000). We confirmed the literature yield of 4-hydroxybenzoic acid upon UVB irradiation of benzoic acid and nitrate. The probe molecules show very different reaction rates, which excludes that they all measure selectively the generation of $\bullet\text{OH}$. Additionally, considering that $\bullet\text{OH}$ in the studied systems could only react with the substrates or with the very little concentrated AQ2S, the reaction rates of Figure 2b would quickly reach a plateau if they measured the generation of $\bullet\text{OH}$. The fact that the plateau was still not reached for 10^{-2} M substrate indicates that interfering reactions are operational. This is further proven by the use of 2-propanol, which inhibits the processes induced by $\bullet\text{OH}$ but not those mediated by $^1\text{O}_2$ or the excited triplet states (Vialaton and Richard, 2002). We found that excess 2-propanol was not able to inhibit significantly the reactions of the adopted probe molecules, which strongly suggests interference by $^3\text{AQ2S}^*$ and/or $^1\text{O}_2$. Additionally, the interfering reactions would be much more important than the reaction with $\bullet\text{OH}$. From Figure 2b one gets that the reactivity of the different probes with $^3\text{AQ2S}^*$ and/or $^1\text{O}_2$ is benzoic acid > benzene > nitrobenzene.

3.2. Irradiation of HUm

Figure 3 reports the degradation rates of Furf, phenol and nitrobenzene upon UVA irradiation of 0.2 g L^{-1} humic acids (HUm). We also report the formation rates of phenol from benzene and of 4-hydroxybenzoic from benzoic acid, corrected for the yield of the reaction with $\bullet\text{OH}$. The trends of Furf and phenol suggest that $^1\text{O}_2$ and $^3\text{HUm}^*$ are produced in high amount. For the $\bullet\text{OH}$ probe molecules the rates are benzoic acid > nitrobenzene > benzene. The lower rate for benzene could mean better selectivity for $\bullet\text{OH}$. We found that 10 mM 2-propanol decreased by about 8 times the formation rate of phenol from 0.2 mM benzene. When alone, 0.2 mM benzene would scavenge around half of the photogenerated $\bullet\text{OH}$, the remainder being consumed by HUm. The reaction rate constant between $\bullet\text{OH}$ and benzene is 4.2 times higher than for 2-propanol (Hoigné, 1990). If all phenol in our system were formed from the reaction between benzene and $\bullet\text{OH}$, 2-propanol would reduce the rate of phenol by a factor of 7. We measured a similar, 8-time reduction. By comparison, 2-propanol under comparable conditions decreased the degradation rate of nitrobenzene by a factor of 2 only. These results are compatible with previous findings that $\bullet\text{OH}$ is not the only species involved in the degradation of nitrobenzene by irradiated HUm (Vialaton and Richard, 2002).

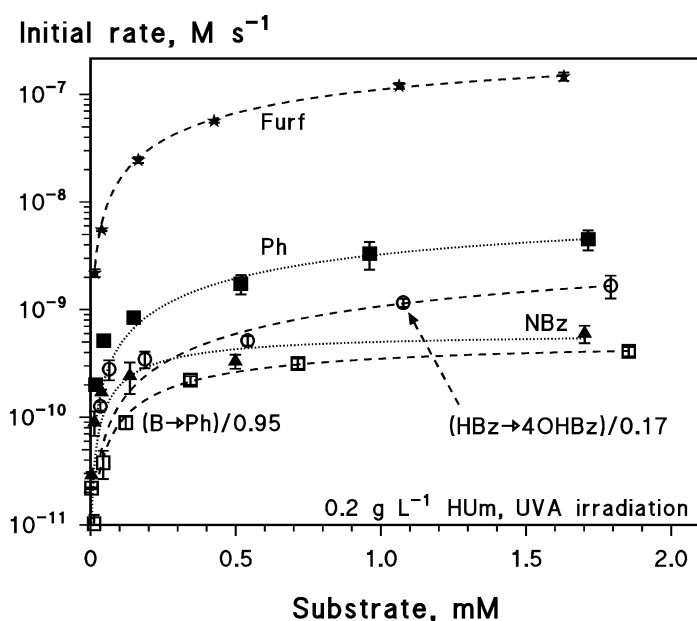


Figure 3. Initial formation rate of $\bullet\text{OH}$, upon UVA irradiation of 0.2 g L^{-1} HUM, measured by the degradation of nitrobenzene (\blacktriangle , NBz), the formation of phenol from benzene (\square , B \rightarrow Ph), and the formation of 4-hydroxybenzoic from benzoic acid (\circ , HBz \rightarrow 4OHBz). $R_{\bullet\text{OH}}$ is given by the rate at elevated substrate, and the lowest $R_{\bullet\text{OH}}$ is that measured by benzene. The Figure also reports the initial degradation rates of phenol (\blacksquare , Ph) and furfuryl alcohol (\star , Furf), the latter measuring $^1\text{O}_2$. Note the logarithmic scale in the Y axis.

For HUM, blank runs were carried out with similar procedures and results as for AQ2S. Benzene and nitrobenzene as $\bullet\text{OH}$ probes were also compared in the presence of nitrite under UVA and nitrate or H_2O_2 under UVB irradiation, all yielding $\bullet\text{OH}$ (Hoigné, 1990). With 0.13 mM benzene or nitrobenzene, the ratio $\text{Rate}(\text{NBz}) / [(0.95)^{-1} \text{Rate}(\text{B}\rightarrow\text{Ph})]$ was around 0.9 ± 0.4 for H_2O_2 , 6 ± 4 for nitrate, and 18 ± 9 for nitrite. Note that the 15% difference of the rate constants of benzene and nitrobenzene with $\bullet\text{OH}$ (Hoigné, 1990) would be largely unable to account for the results. Interestingly, the 3 nitrophenol isomers and phenol were detected as transformation intermediates of nitrobenzene. These compounds are likely formed by nitrobenzene and $\bullet\text{OH}$: nitrophenols upon ring hydroxylation, and phenol probably by *ipso* substitution of $\bullet\text{OH}$ at the NO_2 position. The overall yield of phenol and nitrophenols was around 86% of transformed nitrobenzene for H_2O_2 , 27% for nitrate, 33% for nitrite, and 16% for HUM. We can thus conclude that irradiated H_2O_2 is the system affording the most selective reaction between nitrobenzene and $\bullet\text{OH}$. It also yielded $\text{Rate}(\text{NBz}) \cong [(0.95)^{-1} \text{Rate}(\text{B}\rightarrow\text{Ph})]$. In the other systems the lower yields of $\bullet\text{OH}$ -derived intermediates suggest that nitrobenzene underwent additional reactions. In these systems it was $\text{Rate}(\text{NBz}) > [(0.95)^{-1} \text{Rate}(\text{B}\rightarrow\text{Ph})]$, indicating that benzene would be a better $\bullet\text{OH}$ probe than nitrobenzene in the presence of HUM, nitrate, and nitrite.

3.3. Irradiation of lake water samples

We also used benzene and nitrobenzene as probes for the generation of $\bullet\text{OH}$ upon UVA irradiation of lake water samples. The samples were taken from the surface layer of the lakes Rouen, Avigliana Grande and Avigliana Piccolo, all located in Piedmont (NW Italy). For further data see Vione et al. (2006).

Benzoic acid was not used as a probe because of the poor selectivity shown with the model systems: it was at least four times more reactive than benzene with irradiated HUM, and it was also the most reactive probe

toward irradiated AQ2S. The calculation of $R_{\bullet\text{OH}}$ from the transformation rate of nitrobenzene and the formation rate of phenol from benzene was carried out as described in Section 2.4. Table 2 reports the $R_{\bullet\text{OH}}$ values obtained with benzene and nitrobenzene for the lake water samples under study. With the exception of Lake Avigliana Piccolo, for which the two measured values of $R_{\bullet\text{OH}}$ coincide, we have obtained higher values by use of nitrobenzene as a probe. These data are consistent with the results reported in Section 3.2, and suggest again a higher selectivity of the transformation reaction benzene \rightarrow phenol as a probe for $\bullet\text{OH}$. Our conclusion is supported by the fact that 2-propanol was able to quench the formation of phenol from benzene upon irradiation of the lake water samples.

Table 2. Initial formation rates of $\bullet\text{OH}$, measured by use of benzene ($R_{\bullet\text{OH}}(\text{B}\rightarrow\text{Ph})$) and nitrobenzene ($R_{\bullet\text{OH}}(\text{NBz})$) as probes, in the lake water samples under study (15 mL irradiated solution). The standard deviation of the data is in the 20-30% range.

Lake	$R_{\bullet\text{OH}}(\text{B}\rightarrow\text{Ph}), \text{M s}^{-1}$	$R_{\bullet\text{OH}}(\text{NBz}), \text{M s}^{-1}$
Rouen (45°01' N, 7°10' E, 18 Jun 06)	1.1×10^{-11}	2.9×10^{-11}
Avigliana Grande (45°04' N, 7°23' E, 19 Oct 07)	9.6×10^{-12}	2.4×10^{-11}
Avigliana Piccolo (45°03' N, 7°24' E, 19 Oct 07)	2.3×10^{-11}	2.3×10^{-11}

4. Conclusions

5.

In this paper we show that the transformation reaction of benzene into phenol is a more selective probe for the photochemical generation of $\bullet\text{OH}$, compared to the transformation of nitrobenzene or the generation of 4-hydroxybenzoic from benzoic acid. Benzene would therefore be a better choice as $\bullet\text{OH}$ probe for natural water systems. The results of the irradiation of lake water samples, humic acids, hydrogen peroxide, nitrate and nitrite show that nitrobenzene can be degraded by interfering species different from $\bullet\text{OH}$. In contrast, none of the probe molecules was suitable for the characterisation of the photochemistry of irradiated AQ2S. The selectivity of nitrobenzene as $\bullet\text{OH}$ probe could be increased upon consideration of the transformation intermediates that are generated via reaction with the hydroxyl radical, namely the three nitrophenol isomers and phenol. However, the presence of at least four reaction pathways between nitrobenzene and $\bullet\text{OH}$ is problematic because the intermediates could not be able to reach the detection limit when the rate of $\bullet\text{OH}$ generation is low. In contrast, benzene has the advantage that its reaction with $\bullet\text{OH}$ yields phenol as the only high-yield intermediate.

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