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# UNIVERSITÀ DEGLI STUDI DI TORINO

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# Formation of hydroxyl radicals by irradiated 1-nitronaphthalene (1NN): oxidation of hydroxyl ions and water by the 1NN triplet state

Babita Sur,<sup>a,b</sup> Maura Rolle,<sup>a</sup> Claudio Minero,<sup>a</sup> Valter Maurino,<sup>a</sup> Davide Vione,<sup>a,c,\*</sup> Marcello Brigante,<sup>d,e,\*</sup> Gilles Mailhot<sup>d,e</sup>

5 The excited triplet state of 1-nitronaphthalene ( $^3\text{1NN}^*$ ) reacts with  $\text{OH}^-$  with a second-order reaction rate constant of  $(1.66 \pm 0.08) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$  ( $\mu \pm \sigma$ ). The reaction yields the  $\bullet\text{OH}$  radical and the radical anion  $\text{1NN}^{\bullet-}$ . In aerated solution, the radical  $\text{1NN}^{\bullet-}$  would react with  $\text{O}_2$  to finally produce  $\text{H}_2\text{O}_2$  upon hydroperoxide/superoxide disproportionation. The photolysis of  $\text{H}_2\text{O}_2$  is  
10 another potential source of  $\bullet\text{OH}$ , but such a pathway would be a minor one in circumneutral (pH 6.5) or in basic solution ( $[\text{OH}^-] = 0.3\text{--}0.5 \text{ M}$ ). The oxidation of  $\text{H}_2\text{O}$  by  $^3\text{1NN}^*$ , with rate constant  $3.8 \pm 0.3 \text{ M}^{-1} \text{ s}^{-1}$ , could be the main  $\bullet\text{OH}$  source at pH 6.5.

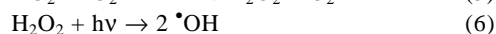
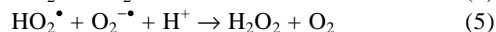
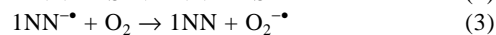
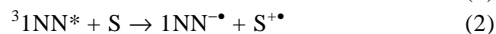
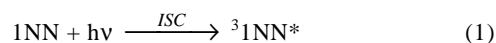
## Introduction

15 Photochemical reactions are important pathways for the transformation of naturally occurring compounds and of man-made xenobiotics in surface and atmospheric waters. The photoinduced transformation of a dissolved molecule can take place by direct photolysis or indirect photochemistry. The latter involves reaction with transient species, produced upon  
20 irradiation of sunlight-absorbing molecules called photosensitisers.<sup>1–6</sup> In surface waters, the main photosensitisers are chromophoric dissolved organic matter (CDOM), nitrite, nitrate and, probably to a lesser extent, Fe species.<sup>7–13</sup> Nitrite is also a well known photosensitiser in fog,  
25 rain and dew water.<sup>14,15</sup> A recent study has shown that sunlight-absorbing organic compounds in rainwater have a very low to nil photoactivity, thus behaving in a very different way than surface-water CDOM.<sup>16</sup>

The main transient species that are produced by the  
30 photosensitisers upon sunlight absorption are hydroxyl ( $\bullet\text{OH}$ ) and carbonate ( $\text{CO}_3^{\bullet-}$ ) radicals, singlet oxygen ( $^1\text{O}_2$ ) and the excited triplet states of CDOM ( $^3\text{CDOM}^*$ ).<sup>17</sup> CDOM is by far the main photosensitiser in surface waters: it is the only source of  $^1\text{O}_2$  and  $^3\text{CDOM}^*$ <sup>18,19</sup> and is usually the main  
35 source of  $\bullet\text{OH}$ .<sup>20,21</sup> Despite the major role of CDOM as  $\bullet\text{OH}$  producer in surface waters, the exact pathways of this process are still unknown. Several hypotheses have been formulated, including the  $\bullet\text{OH}$  generation *via* formation of  $\text{H}_2\text{O}_2$  by irradiated CDOM.<sup>22,23</sup> Photogenerated hydrogen peroxide  
40 could take part in Fenton and Fenton-like processes in the presence of Fe species<sup>24,25</sup> or undergo photolysis to yield  $\bullet\text{OH}$ .<sup>17</sup> A recent study has shown that  $\text{H}_2\text{O}_2$  may be involved in the photochemical production of  $\bullet\text{OH}$  by humic and fulvic acids under irradiation, but such a pathway would not be the  
45 only one and not even the most important.<sup>26</sup>

An alternative hypothesis for CDOM-mediated  $\bullet\text{OH}$  production could be the oxidation of water and/or  $\text{OH}^-$  by  $^3\text{CDOM}^*$ , but limited evidence is presently available of the possibility of such a process. There is more evidence of the  
50 ability of the excited triplet states to simulate the  $\bullet\text{OH}$  reactivity, by inducing the hydroxylation of  $\bullet\text{OH}$  probe molecules.<sup>27</sup> For instance, the triplet state of anthraquinone-2-

sulphonate (AQ2S) is thermodynamically unable to oxidise water to  $\bullet\text{OH}$ ,<sup>28,29</sup> but it simulates the hydroxyl radical  
55 reactivity in the presence of otherwise effective  $\bullet\text{OH}$  probe molecules such as benzene and terephthalic acid.<sup>30,31</sup> However, it is known that the excited triplet state of 1-nitronaphthalene,  $^3\text{1NN}^*$ , is able to react with  $\text{OH}^-$ .<sup>32</sup> Many features of such a reaction, studied by laser flash photolysis  
60 (LFP), are compatible with the formation of  $\bullet\text{OH}$ .<sup>33</sup> Recent evidence has been provided that irradiated 1NN yields  $\bullet\text{OH}$ , but the exact reaction pathway is still unknown.<sup>34</sup> Oxidation of  $\text{H}_2\text{O}/\text{OH}^-$  by  $^3\text{1NN}^*$  is a possibility, but an alternative pathway could involve generation of  $\text{H}_2\text{O}_2$  followed by its  
65 photolysis (in the following reaction scheme, S is a dissolved substrate and ISC = inter-system crossing):<sup>32–37</sup>



The two alternative pathways for  $\bullet\text{OH}$  production by irradiated 1NN ( $\text{H}_2\text{O}/\text{OH}^-$  oxidation by  $^3\text{1NN}^*$  or  $\text{H}_2\text{O}_2$   
75 generation and photolysis) have a very interesting parallelism with the processes under debate for the photochemical generation of  $\bullet\text{OH}$  by CDOM.<sup>26</sup> Therefore, 1NN under irradiation could be a very useful model system to understand the pathways of  $\bullet\text{OH}$  production by organic matter in surface  
80 waters. The goal of the present study is the elucidation of the processes involved in  $\bullet\text{OH}$  formation by irradiated 1NN. This implies a study of the reaction between  $^3\text{1NN}^*$  and  $\text{OH}^-$ , as well as the assessment of  $\text{H}_2\text{O}_2$  photoproduction by 1NN under irradiation.

85 The formation of  $\bullet\text{OH}$  by irradiated 1NN has been demonstrated by use as probe reactions of both benzene and terephthalic acid hydroxylation (to phenol and 2-hydroxyterephthalic acid, respectively).<sup>34</sup> Such processes can be suitable for the assessment of  $\bullet\text{OH}$  photoproduction by  
90 1NN at circumneutral pH, but they would not be recommended to study reactions that occur in the presence of  $\text{OH}^-$  in basic solution. Phenol has  $pK_a = 10$ <sup>38</sup> and, therefore,

its yield from benzene and/or its stability in aqueous solution could be modified at basic pH. As far as terephthalic acid is concerned, we have recently found that its yield of hydroxylation has a significant pH dependence<sup>31</sup> that could bias the interpretation of the experimental results of the present study. The transformation of nitrobenzene (NB) is not selective enough as probe reaction for  $\cdot\text{OH}$  generation in surface waters,<sup>30,39</sup> but it can satisfactorily be exploited in simplified laboratory solutions where the probability of interfering processes is much lower.<sup>40</sup> Moreover, NB transformation has been found to undergo interference by the AQ2S triplet state to a lesser extent than the hydroxylation of benzene.<sup>30</sup> For these reasons, coupled with the fact that it does not take part to acid-base equilibria, NB was chosen as  $\cdot\text{OH}$  probe molecule under basic conditions after a preliminary control of the absence of interference by  $^3\text{1NN}^*$ .

In contrast, the hydroxylation of benzene to phenol was adopted as  $\cdot\text{OH}$  probe reaction under circumneutral conditions. Under such circumstances the production rate of  $\cdot\text{OH}$  is fairly low (*vide infra*) and the transformation of a primary compound (NB) would not be sensitive enough. Indeed, low  $\cdot\text{OH}$  formation rates require a low initial NB concentration for the detection, otherwise a too limited fraction of NB would be transformed. However, low NB gives detection problems and does not ensure scavenging of the majority of photoproducted  $\cdot\text{OH}$ . A high initial NB concentration would scavenge the majority of  $\cdot\text{OH}$ , but the reaction would produce a very limited percentage transformation of NB. The variation of NB concentration with time would thus be comparable to or even lower than the analytical reproducibility, preventing a proper measurement of  $\cdot\text{OH}$  formation. In contrast, benzene at relatively high concentration can be used to detect  $\cdot\text{OH}$  when the formation rate of the latter is low. Under such conditions there would be formation of low but still detectable amounts of phenol.<sup>20</sup>

## Experimental

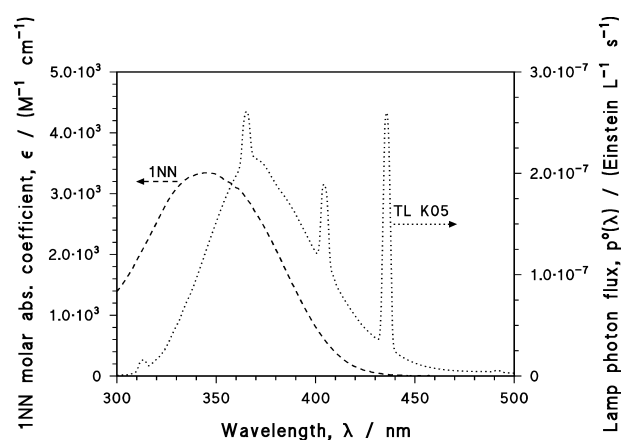
### Reagents and materials

1-Nitronaphthalene (1NN, purity grade 99%), nitrobenzene (>99%), methanol (gradient grade), NaOH (99%) and phenol (>99%) were purchased from Aldrich, 2-propanol (LiChrosolv gradient grade), benzene (for gas chromatography) and  $\text{H}_3\text{PO}_4$  (85%) from VWR Int. All reagents were used as received, without further purification.

### Irradiation experiments

Irradiation was carried out under a set of five 40 W Philips TL K05 UVA lamps, with emission maximum at 365 nm. The lamp irradiance between 300 and 400 nm was  $20 \pm 1 \text{ W m}^{-2}$ , measured with a CO.FO.ME.GRA. (Milan, Italy) power meter. The samples (5 mL total volume) were placed into cylindrical Pyrex glass cells (4.0 cm diameter, 2.3 cm height) closed with a lateral screw cap, and were magnetically stirred during irradiation. The incident radiation reached the cells mainly from the top, and the optical path length of the solution was  $b = 0.4 \text{ cm}$ . The incident photon flux in solution

was actinometrically determined using the ferrioxalate method. The absorption spectrum of  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$  and the variation with wavelength of the quantum yield of  $\text{Fe}^{2+}$  generation were taken into account.<sup>41</sup> If one knows, as a function of the wavelength, the fraction of radiation absorbed by  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ , the quantum yield of  $\text{Fe}^{2+}$  photoproduction and the shape of the lamp spectrum (*vide infra*), it is possible to use the measured formation rate of  $\text{Fe}^{2+}$  to fix the value of the incident spectral photon flux density  $p^\circ(\lambda)$ . The photon flux  $P_o = \int_{\lambda} p^\circ(\lambda) d\lambda$  was  $1.6 \times 10^{-5} \text{ Einstein L}^{-1} \text{ s}^{-1}$ . The irradiation temperature was around 305 K. Figure 1 reports the emission spectrum of the adopted lamps, measured with an Ocean Optics SD 2000 CCD spectrophotometer and normalised to the actinometry results, as well as the absorption spectrum of 1NN, taken with a Varian Cary 100 Scan UV-Vis spectrophotometer.



**Figure 1.** Spectral photon flux density  $p^\circ(\lambda)$  of the adopted UVA lamp. Molar absorption coefficient  $\epsilon$  of 1NN.

### Analytical determinations

After irradiation the solutions were allowed to cool for 10-15 min under refrigeration, to minimise the volatilisation of 1NN and, when applicable, that of benzene. Analysis was then carried out by High Performance Liquid Chromatography coupled with UV-Vis detection (HPLC-UV). The adopted Merck-Hitachi instrument was equipped with AS2000A autosampler (100  $\mu\text{L}$  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  $\times$  4.6 mm  $\times$  5  $\mu\text{m}$ ), and L-4200 UV-Vis detector (detection wavelength 220 nm). In the case of 1NN alone and of 1NN + NB, isocratic elution was carried out with 60:40  $\text{CH}_3\text{OH}$ :aqueous  $\text{H}_3\text{PO}_4$  (pH 2.8) at  $1.0 \text{ mL min}^{-1}$  flow rate. In the case of 1NN + benzene, the eluent was a 50:50 mixture of the already cited components. The retention times were (min): phenol (2.9), benzene (8.9), NB (4.0), 1NN (11.1 or 24.7). The column dead time was 0.90 min.

## Kinetic treatment of the data

The time evolution data of NB were fitted with pseudo-first order equations of the form  $C_t = C_o \exp(-k t)$ , where  $C_t$  is the concentration of NB at the time  $t$ ,  $C_o$  its initial concentration, and  $k$  the pseudo-first order degradation rate constant. The initial transformation rate of NB is  $Rate_{NB} = k C_o$ . The time evolution of phenol (formed from benzene +  $\bullet OH$ ) was fitted with  $C_t = k_p^f C_o (k_p^d - k_B^d)^{-1} [\exp(-k_B^d t) - \exp(-k_p^d t)]$ , where  $C_t$  is the concentration of phenol at the time  $t$ ,  $C_o$  the initial concentration of benzene,  $k_p^f$  and  $k_p^d$  the pseudo-first order formation and transformation rate constants of phenol, respectively, and  $k_B^d$  the pseudo-first order transformation rate constant of benzene. The initial formation rate of phenol is  $Rate_p = k_p^f C_o$ . The reported errors on the rates were derived from the scattering of the experimental data around each fitting curve and represent  $\mu \pm \sigma$ . The reproducibility of repeated runs was around 10-15%.

## Laser flash photolysis experiments

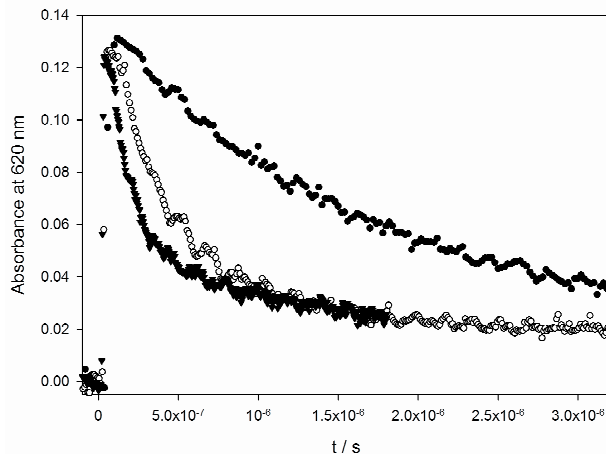
A Nd:YAG laser system instrument (Quanta Ray GCR 130-01) operated at 355 nm (third harmonic) with typical energies of 60 mJ (the single pulse was  $\sim 9$  ns in duration) was used to study the reactions involving the excited state of 1NN ( $^3 1NN^*$ ). Individual cuvette samples (3 mL volume) were used for a maximum of two consecutive laser shots. The transient absorbance at the pre-selected wavelength was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator and a photomultiplier (1P28). A spectrometer control unit was used for synchronising the pulsed light source and programmable shutters with the laser output. The signal from the photomultiplier was digitised by a programmable digital oscilloscope (HP54522A). A 32 bits RISC-processor kinetic spectrometer workstation was used to analyse the digitised signal.

Solutions of 1NN and, when relevant, NaOH, 2-propanol and NB were prepared in Milli-Q water and their stability was regularly checked by means of UV spectroscopy. The decay of the triplet state of 1NN ( $^3 1NN^*$ ) and the formation of the radical anion ( $1NN^{\bullet -}$ ) were monitored at 620 and 380 nm, respectively. The pseudo-first order decay and growth constants were obtained by fitting the absorbance vs. time data with single or double exponential equations. The error was calculated from the fit of the experimental data. All the experiments were performed at ambient temperature ( $295 \pm 2$  K) in aerated solution.

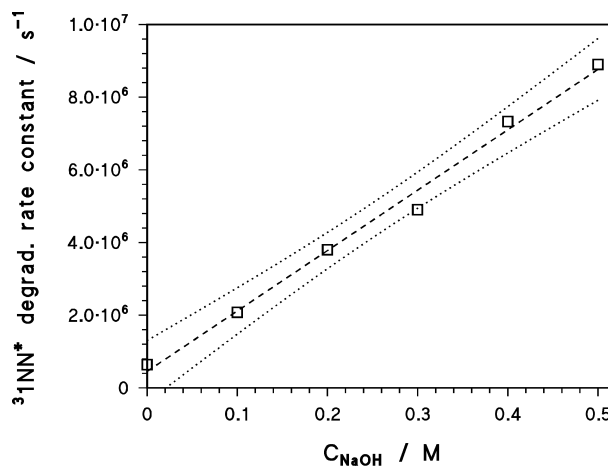
## Results and discussion

### Laser flash photolysis experiments

In a first series of experiments it was studied the reactivity between  $^3 1NN^*$ , monitored at 620 nm, and the  $OH^-$  ion. Figure 2 shows the time evolution of the  $^3 1NN^*$  spectral traces as a function of the concentration of added NaOH, while the pseudo-first order rate constants of  $^3 1NN^*$  vs. NaOH concentration are reported in Figure 3.



**Figure 2.** Decay of  $^3 1NN^*$  (monitored at 620 nm) as a function of NaOH concentration. The traces were obtained upon LFP (355 nm) excitation of 1NN (0.1 mM) (full circles), with addition of 0.1 mM NaOH (open circles) or 0.3 mM NaOH (full triangles).



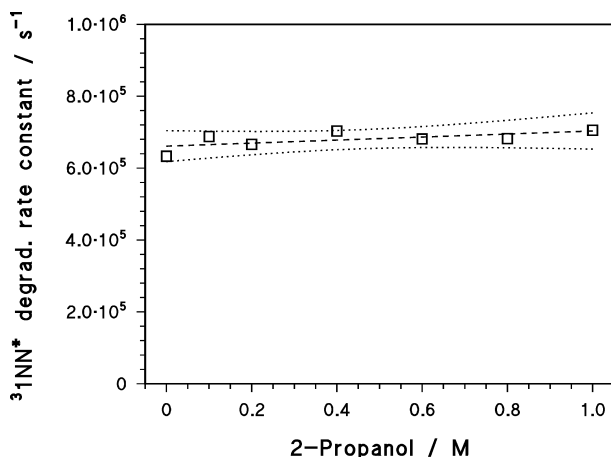
**Figure 3.** Pseudo-first order degradation rate constant of  $^3 1NN^*$ , produced upon irradiation of 0.1 mM 1NN, as a function of the concentration of added NaOH. Laser pulse: 60 mJ, 355 nm, aerated solution. Error bars derived at the  $3\sigma$  level simply from the scattering of the experimental data. Regression line is dashed, 95% confidence bands are dotted.

The slope of the regression line shown in Figure 3 gives the second-order reaction rate constant between  $^3 1NN^*$  and  $OH^-$ , which is  $k_{31NN^*, OH^-} = (1.66 \pm 0.08) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$  ( $\mu \pm \sigma$ ). Considering that  $^3 1NN^*$  usually behaves as a single-electron oxidant,<sup>32</sup> it is likely that its reaction with  $OH^-$  yields  $\bullet OH$  and the radical anion of 1NN,  $1NN^{\bullet -}$ . The formation of  $1NN^{\bullet -}$  is supported by the detection of a signal at 380 nm, which is the well-known absorption maximum of the radical anion.<sup>32-34</sup> However, demonstrating the actual formation of  $\bullet OH$  by  $^3 1NN^* + OH^-$  requires more direct evidence, which was obtained from steady irradiation experiments (*vide infra*).

The reactivity between  $^3 1NN^*$  and 2-propanol was also studied, considering that the alcohol can be a useful  $\bullet OH$  scavenger in steady irradiation experiments. Figure 4 reports the pseudo-first order degradation rate constant of  $^3 1NN^*$  as a function of 2-propanol concentration. From the fit line one

gets a second-order rate constant  $k_{3\text{INN}^*, 2\text{-propanol}} = (4.2 \pm 2.2) \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . 2-Propanol up to 1.0 M concentration is not able to behave as an effective scavenger of  $^3\text{INN}^*$ . Therefore, the addition of the alcohol to an irradiated system would cause significant scavenging of  $\cdot\text{OH}$  but not of  $^3\text{INN}^*$ .

Lack of significant reactivity was found between  $^3\text{INN}^*$  and NB, the latter adopted up to 0.6 mM initial concentration. This means that NB is not expected to undergo transformation upon reaction with  $^3\text{INN}^*$ , which would allow the use of NB as a selective  $\cdot\text{OH}$  probe in the presence of irradiated INN.

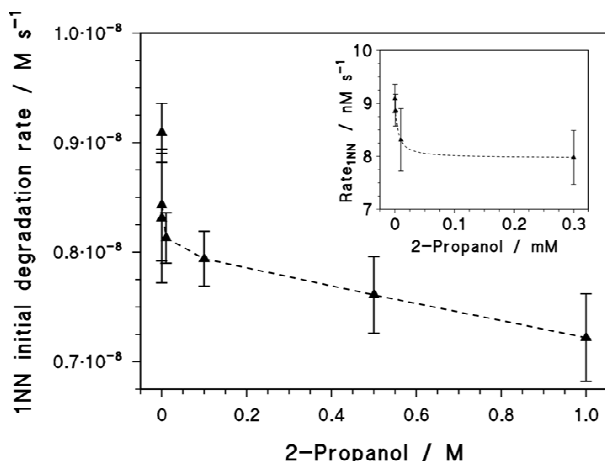


**Figure 4.** Pseudo-first order degradation rate constant of  $^3\text{INN}^*$  as a function of the concentration of 2-propanol. Laser pulse: 60 mJ, 355 nm, pH 6.5, aerated solution. Error bars derived at the  $3\sigma$  level simply from the scattering of the experimental data. Regression line is dashed, 95% confidence bands are dotted.

## Steady irradiation experiments

### Effect of 2-propanol on the direct photodegradation of INN

Figure 5 reports the initial transformation rates of 0.1 mM INN upon UVA irradiation at the natural pH (6.5), as a function of the concentration of added 2-propanol.



**Figure 5.** Initial transformation rates of 0.1 mM INN as a function of the concentration of 2-propanol. UVA irradiation, pH 6.5, aerated solution. The insert shows the rate trend for 2-propanol concentration values up to 0.3 mM. The dashed curve is the fit of the experimental data with  $\text{Rate}_{\text{INN}} = R_{\text{INN}, \cdot\text{OH}} (\text{equation } 7) + c$ .

The INN rate data have a double trend, with a very marked initial decrease of the rate for relatively low alcohol concentrations, followed by a further but less steep decrease above 0.1 M 2-propanol. Considering that the alcohol is an effective  $\cdot\text{OH}$  scavenger but that it does not react with  $^3\text{INN}^*$ , as is shown by laser flash photolysis data, a likely explanation is that the transformation of INN upon UVA irradiation follows two pathways:

(i) A minor pathway ( $< 15\%$ ) could be the reaction between INN and  $\cdot\text{OH}$ , photogenerated by  $^3\text{INN}^*$ . In such a case there would be competition between 2-propanol and INN for reaction with  $\cdot\text{OH}$ . Although the reaction rate constant between INN and  $\cdot\text{OH}$  in aqueous solution is not known, it is reasonable that 2-propanol at mM levels is able to effectively inhibit reaction between 0.1 mM INN and  $\cdot\text{OH}$ . If this hypothesis is correct, the data reported in the insert of Figure 5 allow the determination of the reaction rate constant between INN and  $\cdot\text{OH}$ ,  $k_{\cdot\text{OH}, \text{INN}}$ . Assume  $k_{\cdot\text{OH}, 2\text{-prop}} = 1.9 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$  as the second-order reaction rate constant between 2-propanol and  $\cdot\text{OH}$ ,<sup>42</sup> and  $R_{\cdot\text{OH}}$  as the formation rate of  $\cdot\text{OH}$ . The rate of INN transformation because of reaction with  $\cdot\text{OH}$ ,  $R_{\text{INN}, \cdot\text{OH}}$  is given by  $R_{\cdot\text{OH}}$  times the fraction of  $\cdot\text{OH}$  that reacts with INN, in competition with 2-propanol. Therefore, one obtains:

$$R_{\text{INN}, \cdot\text{OH}} = \frac{R_{\cdot\text{OH}} k_{\cdot\text{OH}, \text{INN}} [\text{INN}]}{k_{\cdot\text{OH}, \text{INN}} [\text{INN}] + k_{\cdot\text{OH}, 2\text{-prop}} [2\text{-propanol}]} \quad (7)$$

In addition to reaction with  $\cdot\text{OH}$ , INN also undergoes other transformation processes (possibly linked with  $^3\text{INN}^*$  evolution) that would account for the plateau reached by  $\text{Rate}_{\text{INN}}$ , as reported in the insert of Figure 5. One thus obtains  $\text{Rate}_{\text{INN}} = R_{\text{INN}, \cdot\text{OH}} + c$ . The fit of the experimental data with the latter equation (with  $R_{\text{INN}, \cdot\text{OH}}$  described by equation 7) yielded  $k_{\cdot\text{OH}, \text{INN}} = (8.25 \pm 0.38) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .

(ii) The main pathway of INN transformation would involve  $^3\text{INN}^*$ , which could *e.g.* be able to oxidise ground-state INN, in analogy with results concerning the photochemistry of anthraquinone-2-sulphonate.<sup>28</sup> Figure 4 suggests that 2-propanol at the studied concentration values is not expected to scavenge  $^3\text{INN}^*$  to a significant extent, but some secondary reactivity could involve the radical species that are formed upon reaction between 2-propanol and  $\cdot\text{OH}$ . A possibility could be the recombination between oxidised 2-propanol and  $\text{INN}^{\cdot-}$ , which would yield back 2-propanol and INN and decrease the rate of INN transformation. An additional possibility could be the oxidation of 2-propanol radical species by oxidised INN, which would probably yield back INN (thereby lowering its transformation rate) together with acetone.<sup>43</sup> The latter compound was actually detected upon irradiation of INN and 2-propanol (data not shown), by adopting a pre-column derivatisation reaction with 2,4-dinitrophenylhydrazine followed by HPLC-UV analysis.<sup>43</sup>

### Photodegradation of NB induced by INN under irradiation in the presence of NaOH

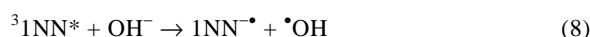
NB was used as  $\cdot\text{OH}$  probe in basic solution. Absence of direct NB photolysis under the adopted irradiation conditions

was preliminary checked and confirmed. Table 1 reports the initial transformation rate of 0.01 mM NB ( $R_{NB}$ ) upon UVA irradiation, in the presence of 0.1 mM INN and with different concentration values of NaOH. The increase of  $R_{NB}$  with increasing NaOH is consistent with the generation of  $\bullet OH$  by irradiated INN under basic conditions.

**Table 1.** Initial transformation rates of 0.01 mM NB ( $R_{NB}$ ) upon UVA irradiation of 0.1 mM INN, for different concentration values of NaOH. Irradiation took place in aerated solution.

$C_{NaOH}, M$	$R_{NB}, M s^{-1}$
0	$(3.37 \pm 2.05) \cdot 10^{-10}$
0.3	$(2.48 \pm 0.73) \cdot 10^{-9}$
0.5	$(2.89 \pm 0.41) \cdot 10^{-9}$

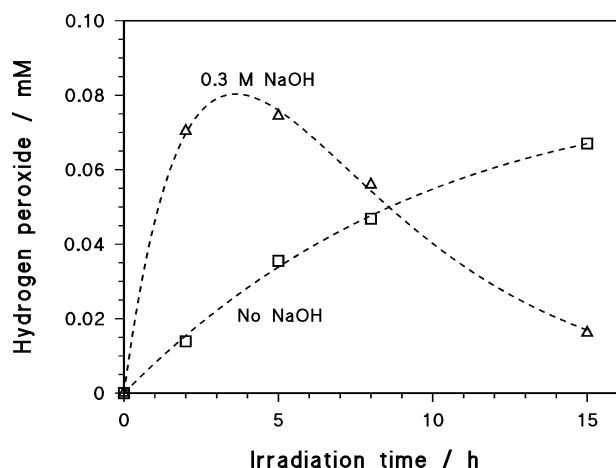
Note that NB degradation is extremely unlikely to undergo interference by  $^3INN^*$ , which showed negligible reactivity toward NB itself. Together with the data reported in Figure 3 (reactivity between  $^3INN^*$  and  $OH^-$ ), such findings suggest that the following reaction takes place in the presence of INN and NaOH under irradiation:



The formation of  $INN^{\bullet-}$  postulated in reaction (8) is consistent with the LFP signal detected at 380 nm.

#### Generation of $H_2O_2$ by INN under irradiation and its possible role in $\bullet OH$ photoproduction

Figure 6 reports the time trend of  $H_2O_2$  generated upon UVA irradiation of 0.1 mM INN and 0.01 mM NB in aerated solution, in the absence of NaOH and in the presence of 0.3 M NaOH.



**Figure 6.** Time trend of  $H_2O_2$  upon UVA irradiation of 0.1 mM INN and 0.01 mM NB in aerated solution, without NaOH and with 0.3 M NaOH.

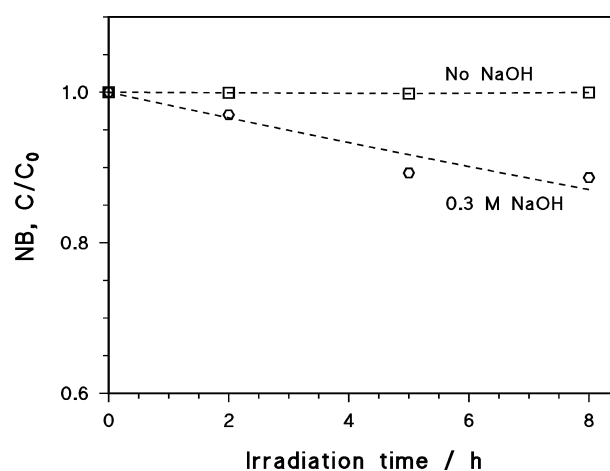
Interestingly, both the initial formation and the transformation rate of  $H_2O_2$  are higher in the presence of NaOH. The higher formation rate is probably linked with the reaction (8) between  $^3INN^*$  and  $OH^-$ , which enhances the transformation of NB (Table 1) and yields  $INN^{\bullet-}$ . In aerated solution the radical anion is expected to yield  $H_2O_2$  via reactions (3-5), and an enhanced  $INN^{\bullet-}$  generation would lead to higher  $H_2O_2$

production.

The much higher transformation rate of  $H_2O_2$  in the presence of NaOH, which yields a time evolution with a maximum after 3-5 hour irradiation, could be accounted for by an enhanced production of reactive species, including  $\bullet OH$ , under basic conditions. Moreover, with a  $pK_a$  of 11.6,<sup>38</sup>  $H_2O_2$  would be fully deprotonated to  $HO_2^-$  in the presence of 0.3 M NaOH. The conjugated base  $HO_2^-$  would be less stable than  $H_2O_2$ . For instance, the reaction rate constant between  $HO_2^-$  and  $\bullet OH$  is  $7.5 \cdot 10^9 M^{-1} s^{-1}$ , to be compared with  $2.7 \cdot 10^7 M^{-1} s^{-1}$  for  $H_2O_2$ .<sup>42</sup>

Figure 6 shows that the concentration of  $H_2O_2$  is lower than 0.1 mM for irradiation times up to 15 h. Figure 7 reports the time evolution of 0.01 mM NB upon UVA irradiation of 0.1 mM INN + 0.3 M NaOH, and of 0.1 mM  $H_2O_2$  + 0.3 M NaOH. It is apparent that 0.1 mM  $H_2O_2$  does not induce significant degradation of NB, despite the presence of  $H_2O_2$  in the system right from the start.

$H_2O_2$  could be able to induce NB transformation upon production of  $\bullet OH$  by photolysis (reaction 6).<sup>17</sup> The negligible transformation of NB upon UVA irradiation of 0.1 mM  $H_2O_2$  + 0.3 M NaOH suggests that the formation of  $\bullet OH$  by  $H_2O_2$  was negligible under the adopted irradiation conditions. This means that irradiated INN in basic solution is expected to induce NB transformation by producing  $\bullet OH$  via reaction (8) ( $OH^-$  oxidation), rather than upon formation of  $H_2O_2$  (reactions 1-5) followed by photolysis (reaction 6).

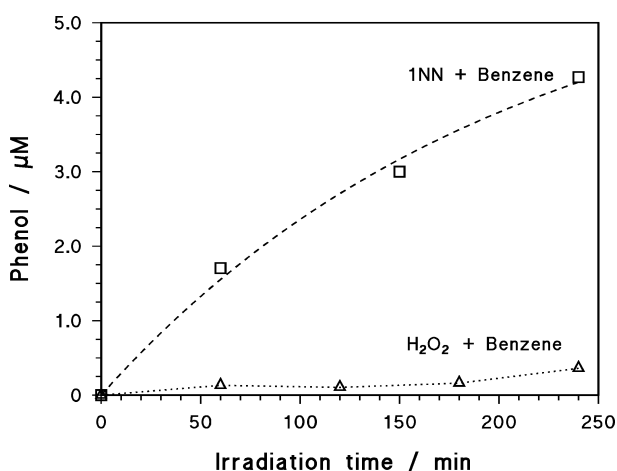


**Figure 7.** Time evolution of 0.01 mM NB upon UVA irradiation of 0.1 mM INN + 0.3 M NaOH, and of 0.1 mM  $H_2O_2$  + 0.3 M NaOH. Irradiation was carried out in aerated solution.

#### Benzene hydroxylation to phenol induced by irradiated INN in circumneutral solution

Figure 8 reports the time evolution of phenol formed from 0.5 mM benzene, upon UVA irradiation of 0.1 mM INN or of 0.1 mM  $H_2O_2$  at the natural pH of the solution (6.5). The initial level of hydrogen peroxide was chosen to be higher than the  $H_2O_2$  concentration formed upon UVA irradiation of INN without NaOH (Figure 6). It has been shown previously that phenol formation from benzene in the presence of INN under irradiation is mostly caused by the photoproduction of  $\bullet OH$ .<sup>34</sup>

Therefore, the much higher phenol formation upon irradiation of 1NN compared to H<sub>2</sub>O<sub>2</sub> suggests that H<sub>2</sub>O<sub>2</sub> generation and photolysis gives a minor to negligible contribution to <sup>•</sup>OH photoproduction by 1NN under circumneutral conditions. An alternative pathway is the oxidation of OH<sup>-</sup> or H<sub>2</sub>O by <sup>3</sup>1NN\*.



**Figure 8.** Time evolution of phenol, formed from 0.5 mM benzene, upon UVA irradiation of 0.1 mM 1NN or of 0.1 mM H<sub>2</sub>O<sub>2</sub> at pH 6.5. Irradiation was carried out in aerated solution.

Considering that the reaction between benzene and <sup>•</sup>OH yields phenol with 95% yield<sup>44</sup> and that the initial rate of phenol formation with 1NN + benzene (Figure 8) is  $R_{\text{phenol}} = (4.96 \pm 0.37) \cdot 10^{-10} \text{ M s}^{-1}$ , one gets  $R_{\text{OH}} = (0.95)^{-1} R_{\text{phenol}} = (5.22 \pm 0.39) \cdot 10^{-10} \text{ M s}^{-1}$ . By knowing the reaction rate constant between <sup>3</sup>1NN\* and OH<sup>-</sup> ( $k_{31\text{NN}^*,\text{OH}^-} = (1.66 \pm 0.08) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ), the photon flux absorbed by 1NN, and the quantum yield of <sup>3</sup>1NN\* formation upon 1NN irradiation ( $\Phi_{31\text{NN}^*} = 0.63$ ),<sup>45</sup> one can obtain the contribution of the reaction <sup>3</sup>1NN\* + OH<sup>-</sup> to <sup>•</sup>OH photogeneration at pH 6.5.

The photon flux absorbed by 1NN is  $P_a^{1\text{NN}} = \int_{\lambda} p^\circ(\lambda) [1 - 10^{-\varepsilon(\lambda)b[1\text{NN}]}] d\lambda$ , where  $p^\circ(\lambda)$  is the lamp volumetric spectral photon flux density in solution,  $\varepsilon(\lambda)$  is the molar absorption coefficient of 1NN (Figure 1),  $b = 0.4 \text{ cm}$  and  $[1\text{NN}] = 0.1 \text{ mM}$ . One gets  $P_a^{1\text{NN}} = 2.5 \cdot 10^{-6} \text{ Einstein L}^{-1} \text{ s}^{-1}$ , and the rate of <sup>3</sup>1NN\* formation is  $R_{31\text{NN}^*} = \Phi_{31\text{NN}^*} P_a^{1\text{NN}} = 1.6 \cdot 10^{-6} \text{ M s}^{-1}$ . At pH 6.5 ( $[\text{OH}^-] = 3 \cdot 10^{-8} \text{ M}$ ) the reaction with OH<sup>-</sup> is a minor <sup>3</sup>1NN\* sink and the pseudo-first order rate constant for <sup>3</sup>1NN\* deactivation is  $k_{31\text{NN}^*} = 6.4 \cdot 10^5 \text{ s}^{-1}$  (see the laser flash photolysis data of Figure 3). One gets  $[^31\text{NN}^*] = R_{31\text{NN}^*} / k_{31\text{NN}^*} = 2.5 \cdot 10^{-12} \text{ M}$ . The formation rate of <sup>•</sup>OH upon reaction (8) between <sup>3</sup>1NN\* and OH<sup>-</sup> would be  $R_{\text{OH}}^{31\text{NN}^*,\text{OH}^-} = k_{31\text{NN}^*,\text{OH}^-} [^31\text{NN}^*] [\text{OH}^-] = 1.2 \cdot 10^{-12} \text{ M s}^{-1}$ . The value of  $R_{\text{OH}}^{31\text{NN}^*,\text{OH}^-}$  thus estimated is over two orders of magnitude lower than  $R_{\text{OH}} = (5.22 \pm 0.39) \cdot 10^{-10} \text{ M s}^{-1}$ . This means that reaction (8) cannot be a significant source of <sup>•</sup>OH under circumneutral conditions.

An alternative hypothesis is that <sup>•</sup>OH is generated upon oxidation of H<sub>2</sub>O by <sup>3</sup>1NN\*. One would have  $R_{\text{OH}}^{31\text{NN}^*,\text{H}_2\text{O}} = k_{31\text{NN}^*,\text{H}_2\text{O}} [^31\text{NN}^*] [\text{H}_2\text{O}]$  (with  $[\text{H}_2\text{O}] \sim 55 \text{ M}$ ) and, under the

hypothesis that  $R_{\text{OH}}^{31\text{NN}^*,\text{H}_2\text{O}} = R_{\text{OH}}$ , one obtains  $k_{31\text{NN}^*,\text{H}_2\text{O}} = R_{\text{OH}} [^31\text{NN}^*]^{-1} [\text{H}_2\text{O}]^{-1} = 3.8 \pm 0.3 \text{ M}^{-1} \text{ s}^{-1}$ . Note that the reaction with H<sub>2</sub>O would give a first-order degradation rate constant  $k'_{31\text{NN}^*} = k_{31\text{NN}^*,\text{H}_2\text{O}} [\text{H}_2\text{O}] = 2.1 \cdot 10^2 \text{ s}^{-1}$  that would just be a small fraction of the deactivation rate constant of <sup>3</sup>1NN\* at pH 6.5 ( $k_{31\text{NN}^*} = 6.4 \cdot 10^5 \text{ s}^{-1}$ ), which is reasonable.

Kinetic considerations suggest that the oxidation of H<sub>2</sub>O by <sup>3</sup>1NN\* to produce <sup>•</sup>OH is a reasonable process, but the thermodynamic point of view is to be considered as well. The reduction potential of 1NN is  $E^\circ(1\text{NN}/1\text{NN}^{\bullet-}) = -0.40 \text{ V}$ ,<sup>46</sup> and the triplet state <sup>3</sup>1NN\* is about 2.4 eV above the ground one.<sup>47</sup> It is thus suggested that the potential  $E^\circ(^31\text{NN}^*/1\text{NN}^{\bullet-}) \sim 2 \text{ V}$ , coherently with the ability of <sup>3</sup>1NN\* to oxidise the halogenide anions to the corresponding radicals.<sup>33</sup> Such a potential has to be compared with  $E^\circ = 2.59 \text{ V}$  for the reaction <sup>•</sup>OH + H<sup>+</sup> + e<sup>-</sup> → H<sub>2</sub>O.<sup>46</sup> One obtains that at pH 6.5 the oxidation reaction of H<sub>2</sub>O to <sup>•</sup>OH by <sup>3</sup>1NN\* has  $E = -0.2 \text{ V}$ , which corresponds to an equilibrium rate constant  $K_{\text{eq}} = 0.03$ . It is thus suggested that some <sup>•</sup>OH can be formed starting from <sup>3</sup>1NN\* and H<sub>2</sub>O, with no initial <sup>•</sup>OH, but the actual position of the equilibrium will likely depend more on the concomitant decay/scavenging processes of <sup>3</sup>1NN\* and <sup>•</sup>OH than on the value of  $K_{\text{eq}}$ .

It is possible to derive an upper limit for the reaction rate constant  $k_{31\text{NN}^*,\text{H}_2\text{O}}$  from the Arrhenius equation,  $k = A \cdot e^{-E_a/RT}$ , with  $E_a = 0.2 \text{ eV} = 20 \text{ kJ mol}^{-1}$  (assuming no additional energy barrier for the reaction) and  $A = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (diffusive control in aqueous solution). One gets  $k_{31\text{NN}^*,\text{H}_2\text{O}} < 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , which is perfectly compatible with the rate constant value derived from kinetic considerations. Furthermore, with  $k_{31\text{NN}^*,\text{H}_2\text{O}} = 3.8 \pm 0.3 \text{ M}^{-1} \text{ s}^{-1}$  one gets  $E_a = 54 \text{ kJ mol}^{-1}$ , corresponding to an activation energy barrier of 34 kJ mol<sup>-1</sup> in addition to the 20 kJ mol<sup>-1</sup> for the reaction to take place. Therefore, the hypothesised oxidation reaction of H<sub>2</sub>O to <sup>•</sup>OH by <sup>3</sup>1NN\*, with the low rate constant obtained in this study and that would be sufficient to account for the experimental data, appears to be reasonable from both a thermodynamic and a kinetic point of view.

## Conclusions

1NN under UVA irradiation in basic solution is able to produce <sup>•</sup>OH radicals following reaction (8) between <sup>3</sup>1NN\* and OH<sup>-</sup>. Such a reaction has a rate constant  $k_{31\text{NN}^*,\text{OH}^-} = (1.66 \pm 0.08) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , measured by laser flash photolysis. Despite the production of sub-0.1 mM levels of H<sub>2</sub>O<sub>2</sub> upon irradiation of 1NN (reactions 1-5), the photolysis of hydrogen peroxide (reaction 6) is a minor pathway to <sup>•</sup>OH photogeneration under both basic and circumneutral conditions. Oxidation of H<sub>2</sub>O and OH<sup>-</sup> by <sup>3</sup>1NN\* would be the main sources of <sup>•</sup>OH, with the former process strongly prevailing under circumneutral conditions. The use of NB as <sup>•</sup>OH probe in basic solution and of 2-propanol as <sup>•</sup>OH scavenger is appropriate in the studied system because of the lack of reactivity of either NB or 2-propanol toward <sup>3</sup>1NN\*.



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## Notes and references

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