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PHOTOTRANSFORMATION PROCESSES OF 2,4-DINITROPHENOL, RELEVANT TO ATMOSPHERIC WATER DROPLETS

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Abstract

This paper shows that the polychromatic quantum yield for the photolysis of 2,4-dinitrophenol (24DNP) in the wavelength interval of 300-500 nm is $(8.1\pm0.4)\times10^{-5}$ for the undissociated phenol, and $(3.4\pm0.2)\times10^{-5}$ for the phenolate. The second-order rate constants for reaction with $^\bullet$OH were determined here as $(1.76\pm0.05)\times10^{9}$ M^{-1} s^{-1} and $(2.33\pm0.11)\times10^{9}$ M^{-1} s^{-1} for the phenol and the phenolate, respectively. By combining laboratory results and a simple modelling approach of the atmospheric aqueous phase, this work shows that the direct photolysis and the reaction with $^\bullet$OH would play a comparable role in the degradation of 24DNP at pH > 4. The $^\bullet$OH reaction would prevail for pH < 4. Both pathways would be more important than the night-time reaction with $^\bullet$NO$_3$ as removal processes for 24DNP in the atmospheric waters.

Keywords: Environmental photochemistry; Direct and sensitised photolysis; UV irradiance; Aromatic nitroderivatives.

1. Introduction

2,4-Dinitrophenol (24DNP) is a toxic nitroaromatic compound that is present in both surface waters and the atmospheric aqueous phase. In particular, it is the most phytotoxic nitrophenol that occurs in the environment to a significant extent (Shea et al., 1983). The concentration of 24DNP can reach some tens µg L^{-1} in atmospheric waters (Leuenberger et al., 1988; Belloli et al., 1999; Harrison et al., 2005; Asman et al., 2005; Barrico et al., 2006). Interestingly, nitrophenol levels in plant leaves are near the values known to cause phytotoxic effects (Natangelo et al., 1999).

There is evidence that the occurrence of 24DNP in the atmospheric aqueous phase is due to the nitration of the mononitrophenols in solution: an anti-correlation has been found between the atmospheric levels of 24DNP and of 2-nitrophenol in the presence of clouds, while no 24DNP has been detected under clear-sky conditions (Lüttke et al., 1997). Furthermore, it has been shown that

24DNP can be formed upon reaction between light-excited mononitrophenols and nitrogen dioxide in aqueous solution (Vione et al., 2005a).

The assessment of the (photo)transformation kinetics of the aromatic nitroderivatives in the environment is important, considering that these compounds are often more persistent than the corresponding non-nitrated molecules (Chiron et al., 2009). To our knowledge, only one study has been focused on the photodegradation of 24DNP under simulated sunlight, showing that 24DNP can undergo direct photolysis and photosensitised transformation as significant removal pathways in seawater (Yang and Qi, 2002). The phototransformation intermediates of 24DNP are presently not known, but in the case of the mononitrophenols it has been found that the direct photolysis mainly yields dihydroxybenzenes, nitrosophenols and quinones, while the reaction with $^\bullet$OH gives hydroxylated intermediates (nitrocatechols and nitrohydroquinone) (Alif and Boule, 1991).

Among the photoinduced transformation processes that can take place in atmospheric waters, the direct photolysis and the reaction with $^\bullet$OH are the most important ones (Anastasio and McGregor, 2001; Vione et al., 2005b). For instance, they significantly contribute to the transformation of the mononitrophenols (Vione et al., 2009a). Interestingly, the steady-state [$^\bullet$OH] values are usually much higher in atmospheric compared to surface waters (10^{-14} vs. 10^{-16} M; Warneck, 1999; Takeda et al., 2004), thus the kinetics of the $^\bullet$OH-induced processes can be faster in the atmospheric hydrometeors.

The present work studies the phototransformation kinetics of 24DNP by direct photolysis and reaction with $^\bullet$OH, with the purpose of deriving the photolysis quantum yield and the second-order reaction rate constant with $^\bullet$OH (using nitrate as $^\bullet$OH source; Mack and Bolton, 1999). The experimental data are used to calculate the lifetime of the compound in the atmospheric aqueous phase, with the purpose of comparing the importance of different processes toward the removal of 24DNP from the atmosphere.

2. Experimental

2.1. Reagents and materials

2,4-Dinitrophenol (24DNP, purity grade 97 %), H_3PO_4 (85 %), $NaH_2PO_4 \cdot H_2O$ (99 %), $HClO_4$ (70 %) and triethylamine (99 %) were purchased from Aldrich, methanol (HPLC grade), acetonitrile (HPLC gradient grade), NaOH (99 %), $Na_2HPO_4 \cdot 2\,H_2O$ (98 %), and $NaNO_3$ (> 99 %) from VWR Int. All reagents were used as received, without further purification. Water used was of Milli-Q quality.

2.2. Irradiation experiments

Irradiation of aqueous samples (5 mL, containing 2 to 100 µM 2,4-DNP and, where relevant, 0.1 M $NaNO_3$) was carried out in magnetically stirred Pyrex glass cells (0.4 cm optical path length). To determine the reaction rate constant between 24DNP and $^\bullet$OH, it was adopted a competition

kinetics between 24DNP and methanol. The pH, adjusted by addition of HClO$_4$ or NaOH, was measured with a Metrohm 713 pH meter, equipped with a combined glass electrode. To achieve excitation of nitrate as much selectively as possible in the presence of 24DNP, it was adopted for irradiation a Philips TL01 lamp with emission maximum at 313 nm, very near the absorption maximum of nitrate. In this case, the irradiation time was up to 4 h. The direct photolysis of 24DNP was studied under a set of three Philips TL K05 UVA lamps with emission maximum at 365 nm, which are able to excite 24DNP in about the same spectral interval as sunlight (300-500 nm), although with a quite different emission spectrum. In the direct photolysis experiments, the solutions were buffered at the chosen pH value with 0.05 M phosphate (H$_3$PO$_4$ + NaH$_2$PO$_4$ or NaH$_2$PO$_4$ + Na$_2$HPO$_4$). Irradiation time was up to 165 h. The UV irradiance reaching the top of the cells, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter (290 – 400 nm), was 5.4±0.6 W m^{-2} and 4.8±0.5 W m^{-2} for the TL01 and TL K05 lamps, respectively. The photon fluxes in solution (P$_o$) were 3.5×10^{-6} einstein L^{-1} s^{-1} and 3.6×10^{-6} einstein L^{-1} s^{-1}, respectively (measured by ferrioxalate actinometry; Kuhn et al., 2004).

2.3. Quantum yield calculations

To obtain the spectrum of a lamp ($p°(\lambda)$), measurements were initially carried out with an Ocean Optics SD2000 charge coupled device (CCD) spectrophotometer. Let $q(\lambda)$ be the spectrum thus derived. The transmittance $T(\lambda)$ of the Pyrex-glass upper face of the irradiation cells was measured with a Varian Cary "100 Scan" UV-Vis spectrophotometer. $T(\lambda)$ is reported in Figure A in the Supplementary Material (hereafter SM). Let $p(\lambda) = T(\lambda) q(\lambda)$. The spectrum thus obtained should finally be normalised ($p(\lambda) \rightarrow p°(\lambda)$) to the actinometrically measured photon flux P_o, so that $P_o = \int_\lambda p°(\lambda) \, d\lambda$. Figure 1 reports the values of $p°(\lambda)$ for the two lamps, together with the absorption spectra of 24DNP at pH 2.5 (undissociated compound) and 9 (phenolate), taken with the UV-Vis scan spectrophotometer. Note that the transmittance was measured in the presence of a light beam perpendicular to the Pyrex glass, which is not always the case for the irradiated solutions. However, Pyrex absorption modifies very little the shape of the 313 nm peak of the UVB lamp (note that nitrate practically only absorbs UVB radiation), or the spectrum of the UVA one. Accordingly, large errors while applying the described procedure are not foreseen.

The absorbed spectral photon flux density p$_a$(λ) of 24DNP under irradiation is (Braslavsky, 2007):

$$p_a(\lambda)_{24DNP} = p°(\lambda) \cdot (1 - 10^{-\varepsilon_{24DNP}(\lambda) \cdot b \cdot [24DNP]})$$ (1)

where p°(λ) is the incident spectral photon flux density, ε_{24DNP}(λ) the molar absorption coefficient of 24DNP (different for the phenol and the phenolate, see Figure 1) and b = 0.4 cm, the optical path length of the irradiated solution. The photon flux absorbed by 24DNP is $P_a^{24DNP} = \int_\lambda p_a(\lambda)_{24DNP} \, d\lambda$

(Braslavsky, 2007). The integration interval (300-500 nm) is referred to the overlap between the

emission spectrum of the lamp and the absorption spectrum of 24DNP (see Figure 1). The polychromatic photolysis quantum yield in the 300-500 nm range is $\Phi_{24DNP} = Rate_{24DNP} (P_a^{24DNP})^{-1}$, where $Rate_{24DNP}$ is the transformation rate of 24DNP.

2.4. Analytical determinations

Analyses were carried out by liquid chromatography, adopting a VWR-Hitachi Elite HPLC (Milan, Italy). It was used a RP-C18 LichroCART column (Merck, 125 mm × 4.6 mm × 5 µm). Isocratic elution (1 mL min^{-1}) was performed with a 40/60 (v/v) mixture of acetonitrile/aqueous phosphate buffer (0.050 M, pH 2.8). The injection volume was 60 µL using an autosampler system. The retention time of 24DNP was 5.1 min, the column dead time 0.9 min, the detection wavelength 258 nm. To confirm the peak purity of 24DNP, HPLC runs were also carried out at 210 nm, where the absorption coefficient of 24DNP is similar to that at 258 nm.

A preliminary survey of the phototransformation pathways of 24DNP was carried out by HPLC-MS. It is suggested that the main reaction intermediate under both direct photolysis and irradiation with nitrate is probably a trinitrophenol. Further details are reported as Supplementary Material (hereafter SM).

2.5. Kinetic treatment of data

The time evolution of 24DNP by direct photolysis followed a pseudo-zero order trend and the data were linearly fitted. Let m be the (negative) slope of the *[24DNP] vs. time* fitting line; the initial transformation rate of 24DNP is $Rate_{24DNP} = -m$. In the presence of nitrate under irradiation, the trend of 24DNP could be fitted well with a pseudo-first order equation of the form: $C_t = C_o exp(-k\,t)$, where C_t is the concentration of 24DNP at the time t, C_o the initial concentration, and k the pseudo-first order degradation rate constant. The initial transformation rate of 24DNP is $Rate_{24DNP} = k\,C_o$. The errors associated to the rates (±σ) were derived from the scattering of the experimental data around the fitting curve (intra-series variability). The reproducibility of repeated runs (inter-series variability) was around 15%.

3. Results and Discussion

3.1. Direct photolysis

Figure 2 reports the time evolution of 0.1 mM 24DNP upon UVA irradiation, at pH 2.4 and 7.3 where the prevailing species are the undissociated phenol and the phenolate, respectively (the pK$_a$ of 24DNP is around 4.1; Martell et al., 1997). The solution pH was practically constant during irradiation. The direct photolysis quantum yield is $\Phi_{24DNP} = Rate_{24DNP} (P_a^{24DNP})^{-1}$. At pH 2.4 we obtained $Rate_{24DNP} = (1.26\pm0.06)\times10^{-10}$ M s^{-1}, $P_a^{24DNP} = 1.55\times10^{-6}$ Einstein L^{-1} s^{-1}, and $\Phi_{24DNP} = (8.13\pm0.39)\times10^{-5}$. At pH 7.3 we obtained $Rate_{24DNP} = (1.60\pm0.07)\times10^{-10}$ M s^{-1}, $P_a^{24DNP} = 4.64\times10^{-6}$

Einstein L^{-1} s^{-1}, and $\Phi_{24DNP} = (3.45\pm0.15)\times10^{-5}$. The values of Φ_{24DNP} are slightly lower than the photolysis quantum yields of the mononitrophenols (Alif et al., 1987 and 1991). Moreover, similarly to 4-nitrophenol (Vione et al., 2009a), in the case of 24DNP the phenolate has lower photolysis quantum yield than the undissociated compound. Runs in the dark were carried out in magnetically stirred vials, wrapped with aluminium foil. No dark transformation of 24DNP was detected in the studied samples.

3.2. Reaction with $^{\bullet}$OH

For the measurement of the second-order reaction rate constant between 24DNP and $^{\bullet}$OH, $k_{\bullet OH,24DNP}$, the photolysis of nitrate was adopted as a source of $^{\bullet}$OH (Mack and Bolton, 1999) and a competition kinetic between 24DNP and methanol was exploited. Figure 3 reports the trend of Rate$_{24DNP}$ as a function of the concentration of methanol, upon UVB irradiation of 0.1 mM 24DNP + 0.1 M NaNO$_3$ at pH 2.5 (undissociated phenol) and at pH 8.7 (phenolate). Without methanol, Rate$_{24DNP} \approx 9\times10^{-9}$ M s^{-1}, which is almost two orders of magnitude higher than the rate of 24DNP direct photolysis under the adopted irradiation device. To derive $k_{\bullet OH,24DNP}$, the following reactions were included in the relevant kinetic model that neglects the direct photolysis of 24DNP:

$$NO_3^- + h\nu + H^+ \rightarrow {}^{\bullet}OH + {}^{\bullet}NO_2 \qquad [R_{\bullet OH,NO3-}] \qquad (2)$$

$$24DNP + {}^{\bullet}OH \rightarrow Products \qquad [k_{\bullet OH,24DNP}] \qquad (3)$$

$$CH_3OH + {}^{\bullet}OH \rightarrow CH_3O^{\bullet} + H_2O \qquad [k_{\bullet OH,CH3OH}] \qquad (4)$$

From the literature it is derived $k_{\bullet OH,CH3OH} = 9.7\times10^8$ M^{-1} s^{-1} (Buxton et al., 1988). Upon application of the steady-state approximation to [$^{\bullet}$OH], one gets the following expression for the degradation rate of 24DNP:

$$Rate_{24DNP} = \frac{R_{\bullet OH,NO_3^-} \; k_{\bullet OH,24DNP} \; [24DNP]}{k_{\bullet OH,24DNP} [24DNP] + k_{\bullet OH,CH_3OH} [CH_3OH]} \qquad (5)$$

Figure 3 shows that the added alcohol inhibits the transformation of 24DNP, as can be expected by a process that involves $^{\bullet}$OH, but Rate$_{24DNP}$ reaches a plateau at elevated [CH$_3$OH]. The plateau rate is an order of magnitude or more higher than the rates of the direct photolysis. It could be accounted for by reactions involving 24DNP and the radical intermediates that are formed from methanol and $^{\bullet}$OH (see *e.g.* reaction (4)). To fit the experimental data, the equation (5) should be modified to include a constant term *c* that describes the plateau at elevated [CH$_3$OH], as follows:

$$Rate_{24DNP} = \frac{R_{\bullet OH,NO_3^-} \; k_{\bullet OH,24DNP} \; [24DNP]}{k_{\bullet OH,24DNP} [24DNP] + k_{\bullet OH,CH_3OH} [CH_3OH]} + c \qquad (5a)$$

The fit with equation (5a) is reported in Figure 3. One gets $k'_{\bullet OH,24DNP} = (1.76\pm0.05)\times10^9$ M^{-1} s^{-1} at pH 2.5 (undissociated phenol), and $k''_{\bullet OH,24DNP} = (2.33\pm0.11)\times10^9$ M^{-1} s^{-1} at pH 8.7 (phenolate). The $k'_{\bullet OH,24DNP}$ value obtained for the undissociated phenol compares well with a previous estimate, made with UV-H$_2$O$_2$ at pH 2.5 as $^\bullet$OH source (García Einschlag et al., 2002). Interestingly, the rate constant values obtained in the present study are of the same order of magnitude but a bit lower compared to those of the mononitrophenols (which are in the range of $(4-9)\times10^9$ M^{-1} s^{-1}; Buxton et al., 1988). The difference might be accounted for by the electron-withdrawing character of the nitro groups, which could decrease the substrate reactivity towards $^\bullet$OH.

3.3. Half-life times in the atmospheric aqueous phase

The direct photolysis quantum yields and the reaction rate constants with $^\bullet$OH of the undissociated and dissociated forms of 24DNP allow the assessment of the corresponding half-life times in atmospheric droplets. The adopted sunlight spectrum is referred to a UV irradiance (290-400 nm) of 22 W m^{-2} and is reported in Figure B-SM (Frank and Klöpffer, 1988). The reported conditions can for instance occur in a summer sunny day such as 15 July at 45°N latitude, at 10 am or 2 pm (Vione et al., 2009b). As far as the direct photolysis is concerned, the term ε_{24DNP} b *[24DNP]* of equation (1) is quite low because in a single water droplet the optical path length $b \approx 1$ µm (the same order of magnitude as the droplet diameters; Finlayson-Pitts and Pitts, 2000), and [24DNP] is usually 10^{-8} M or lower (Harrison et al., 2005). In the atmospheric aqueous phase it would thus be

$$\left(\lim_{A_\lambda^{24DNP}\to 0} (1-10^{-A_\lambda^{24DNP}}) \right) = \ln(10) \cdot A_\lambda^{24DNP} = 2.3 \cdot A_\lambda^{24DNP}, \quad \text{with} \quad A_\lambda^{24DNP} = \varepsilon_{24DNP}(\lambda) \cdot b \cdot [24DNP].$$

Moreover, because b is very low, all the light-absorbing species will have low absorbance values and there would be negligible competition for irradiance between them. Accordingly, in the droplet such species can be treated as independent absorbers with excellent approximation.

In the hypothesis of a spherical drop of diameter d, the paths of the incident light will constitute different spherical chords of length $l = d \sin \alpha$, where 2α is the angle of aperture of the chord that can vary from 0 to π (therefore, $0 < \alpha < \pi/2$). On average, the path length b of the light inside the droplet will be equal to the length of the average chord, thus $b = \dfrac{2d}{\pi} \displaystyle\int_0^{\pi/2} \sin\alpha \, d\alpha = \dfrac{2d}{\pi}$.

Moreover, the sunlight irradiance inside the droplet is different than in the surrounding gas phase. A first issue is that the droplets on top of clouds experience higher irradiance than the ground in a sunny day, because they also receive light that is reflected by the lower layers of the cloud. However, this is compensated by the fact that the droplets in the bottom cloud layers receive less light, because most of the irradiance has been reflected away by the upper layers. Another issue is that the radiation in a spherical drop can undergo different total reflections at the water-air interface, which increases the path length and, therefore, the probability that radiation is absorbed by the photoactive compounds. This is equivalent to an increase of the irradiance of sunlight: it has been shown that the radiation intensity can be increased by around 1.8 times in droplets with $d < 10$ µm,

compared to the surrounding gas phase (Mayer and Madronich, 2004; Nissenson et al., 2006). Based on all the reported considerations, equation (1) would be modified as follows:

$$p_a(\lambda)_{24DNP} \approx 8.3 \cdot \pi^{-1} \cdot p°(\lambda) \cdot \varepsilon_{24DNP}(\lambda) \cdot d \cdot [24DNP] \tag{6}$$

Note that, for P_a^{24DNP} to be expressed in einstein L^{-1} s^{-1}, the units of $p_a(\lambda)_{24DNP}$ and, as a consequence, of $p°(\lambda)$ should be [einstein L^{-1} s^{-1} nm^{-1}]. The spectrum of sunlight, i°(λ), is usually expressed in einstein cm^{-2} s^{-1} nm^{-1} (see Figure B-SM), *e.g.* referred to sunlight incident over a circular surface $S = \pi d^2$. In a spherical volume $V = \pi d^3/6$, if the path length and the diameter are expressed in cm, it would be $i°(\lambda) = 10^{-3} p°(\lambda) d/6$. Accordingly, $p_a(\lambda)_{24DNP}$ would be expressed as follows:

$$p_a(\lambda)_{24DNP} = 1.6 \cdot 10^4 \cdot i°(\lambda) \cdot \varepsilon_{24DNP}(\lambda) \cdot [24DNP] \tag{7}$$

The photolysis rate constant of 24DNP is $k_{24DNP} = \Phi_{24DNP} P_a^{24DNP} [24DNP]^{-1}$. For the calculations it will be adopted the approximation that the polychromatic photolysis quantum yield measured under the TL K05 lamps adopted in this study (referred to the 300–500 nm wavelength range) is also valid for the same range where the spectra of 24DNP and sunlight overlap (negligible absorption of either phenol or phenolate takes place above 500 nm, see Figure 1). The absorbed photon flux P_a^{24DNP} is the integral over wavelength of $p_a(\lambda)_{24DNP}$. Moreover, in a first-order approximation the photolysis half-life time of 24DNP is $\tau_{24DNP} = ln\ 2\ (k_{24DNP})^{-1}$, from which one gets:

$$\tau_{24DNP} = \frac{\ln 2}{1.6 \cdot 10^4 \cdot \Phi_{24DNP} \cdot \int_\lambda i°(\lambda) \cdot \varepsilon_{24DNP}(\lambda)\ d\lambda} \tag{8}$$

Note that both Φ_{24DNP} and $\varepsilon_{24DNP}(\lambda)$ would depend on pH because of the phenol/phenolate equilibrium. Assume that Φ'_{24DNP} and $\varepsilon'_{24DNP}(\lambda)$ are the quantities related to the phenol, and Φ''_{24DNP} and $\varepsilon''_{24DNP}(\lambda)$ those referred to the phenolate. From the rules of spectral overlap one gets $\Phi_{24DNP} = (10^{-pH} \Phi'_{24DNP} + K_a \Phi''_{24DNP}) (10^{-pH} + K_a)^{-1}$ and $\varepsilon_{24DNP}(\lambda) = (10^{-pH} \varepsilon'_{24DNP}(\lambda) + K_a \varepsilon''_{24DNP}(\lambda)) (10^{-pH} + K_a)^{-1}$. Note that $[H^+] = 10^{-pH}$. As a consequence, equation (8) would be modified as follows:

$$\tau_{24DNP} = \frac{4.4 \cdot 10^{-5} \ (10^{-pH} + K_a)^2}{(10^{-pH} \cdot \Phi'_{24DNP} + K_a \cdot \Phi''_{24DNP}) \cdot \left(10^{-pH} \cdot \int_\lambda i°(\lambda) \cdot \varepsilon'_{24DNP}(\lambda)\ d\lambda + K_a \cdot \int_\lambda i°(\lambda) \cdot \varepsilon''_{24DNP}(\lambda)\ d\lambda \right)} \tag{9}$$

Figure 4 reports the pH trend of τ_{24DNP}, which is referred to 22 W m^{-2} sunlight irradiance in the UV. Note that τ_{24DNP} is expressed in hours, and that the sunlight energy reaching the ground in a summer sunny day (SSD) such as 15 July at 45°N latitude is equivalent to approximately 10 irradiation hours at constant 22 W m^{-2} sunlight UV irradiance (Minero et al., 2007). Accordingly, it is possible to obtain a rough assessment of the value of τ_{24DNP} in SSD units by diving τ_{24DNP} (hours) by 10. With this approach one gets that the half-life time of 24DNP by direct photolysis in the atmospheric aqueous phase could vary from a few hours to approximately one day, and the latter only under strongly acidic conditions. Also note that the (little pronounced) minimum of τ_{24DNP} is located at pH 4-4.5, which is consistent with an acidified atmospheric aqueous phase. Interestingly, the minimum shown in Figure 4 is linked to the ~9.2 times higher absorption of sunlight by the phenolate compared to the phenol. Figure C-SM reports further information on the behaviour of equation (9) for different parameter values.

The reaction with $^\bullet OH$ would involve both the phenol and the phenolate, depending on the solution pH. Let k'$_{\bullet OH,24DNP}$ = 1.8×10^9 M^{-1} s^{-1} be the reaction rate constant of the phenol, and k''$_{\bullet OH,24DNP}$ = 2.3×10^9 M^{-1} s^{-1} that of the phenolate. From the acid-base equilibrium one gets $k_{\bullet OH,24DNP} = (10^{-pH}\ k'_{\bullet OH,24DNP} + K_a\ k''_{\bullet OH,24DNP})\ (10^{-pH} + K_a)^{-1}$; the half-life time of 24DNP because of the reaction with $^\bullet OH$ would be $\tau_{\bullet OH,24DNP} = ln\ 2\ (k_{\bullet OH,24DNP}\ [^\bullet OH])^{-1}$. From the above considerations one gets:

$$\tau_{\bullet OH,24DNP} = \frac{\ln 2 \cdot (10^{-pH} + K_a)}{(10^{-pH} \cdot k'_{\bullet OH,24DNP} + K_a \cdot k''_{\bullet OH,24DNP}) \cdot [^\bullet OH]} \tag{10}$$

In average continental clouds, under sunlight irradiance equivalent to the summer solstice at noon (about 30 W m^{-2} UV irradiance; Frank and Klöpffer, 1988), one has [$^\bullet OH$] ≈ 5×10^{-14} M (Warneck, 1999). The occurrence of $^\bullet OH$ in the aqueous phase depends on photoinduced reactions involving dissolved compounds, on processes started by species that are photochemically formed in the gas phase, and on the phase transfer of $^\bullet OH$ from the gas phase. Considering that both the aqueous-phase and the gas-phase photoreactions are initiated by sunlight, and that the concentration of gas-phase $^\bullet OH$ is directly proportional to the sun irradiance (Finlayson-Pitts and Pitts, 2000), it may be assumed that also [$^\bullet OH$] in the aqueous phase would be directly proportional to the irradiance. Under 22 W m^{-2} UV irradiance one gets [$^\bullet OH$] ≈ 3.5×10^{-14} M. However, in his calculations Warneck (1999) did not consider the increase of radiation intensity in spherical droplets. Such an effect would enhance the photoproduction of $^\bullet OH$ by the dissolved compounds, which amounts to about 10-15% of the total if the intensity enhancement is not considered (Warneck, 1999). Therefore, an increase by 1.8 times of the radiation intensity in the droplet (Mayer and Madronich, 2004) could increase [$^\bullet OH$] by about 10%, to give [$^\bullet OH$] ≈ 3.8×10^{-14} M. In contrast, the possible (but hardly known) pH dependence of the $^\bullet OH$ photogeneration rate in the atmospheric aqueous phase was neglected here in the calculations, which assume equal [$^\bullet OH$] at all the pH values. The pH trend of $\tau_{\bullet OH,24DNP}$ is reported in Figure 4. The reaction with $^\bullet OH$ and the direct photolysis

would play a comparable role in the degradation of 24DNP at pH > 4 (τ_{24DNP} = 5-7 hours in either case), while the $^\bullet$OH-mediated process would prevail at pH < 4. In both cases the phenolate is expected to be more reactive than the undissociated phenol, but the difference would be more marked for the direct photolysis.

Interestingly, 24DNP would also react with the radical $^\bullet$NO$_3$, with a second-order rate constant of 5.3×10^7 M^{-1} s^{-1} (Umschlag et al., 2002). With a 24-h averaged [$^\bullet$NO$_3$] $\approx 10^{-13}$ M in the atmospheric aqueous phase (Finlayson-Pitts and Pitts, 2000), one would get a half-life time of about 36 h for 24DNP (1.5 days). Such a value is higher than for the direct photolysis or the reaction with $^\bullet$OH. Therefore, the reaction with $^\bullet$NO$_3$ would lead to slower degradation of 24DNP compared to the photoinduced processes. However, the pathways would not be in direct competition because the reactions induced by $^\bullet$NO$_3$ are operational during the night, when photochemistry is not active.

4. Conclusions

The excitation of 24DNP in the wavelength interval of 300 to 500 nm gave polychromatic, direct photolysis quantum yields of $(8.1\pm0.4)\times10^{-5}$ for the undissociated phenol, and $(3.4\pm0.2)\times10^{-5}$ for the phenolate. The second-order rate constants for reaction with $^\bullet$OH were measured upon irradiation of nitrate in the presence of methanol; it was obtained $k_{\bullet OH,24DNP} = (1.76\pm0.05)\times10^9$ M^{-1} s^{-1} and $(2.33\pm0.11)\times10^9$ M^{-1} s^{-1} for the phenol and the phenolate, respectively. The reaction with $^\bullet$OH and the direct photolysis would play a comparable role in the degradation of 24DNP at pH > 4 (where the half-life time of 24DNP could be as low as 5-7 hours), while the $^\bullet$OH-mediated process would prevail at pH < 4. Additional reactions, like that with $^\bullet$NO$_3$ during the night, are expected to play a less important role than the photoinduced processes.

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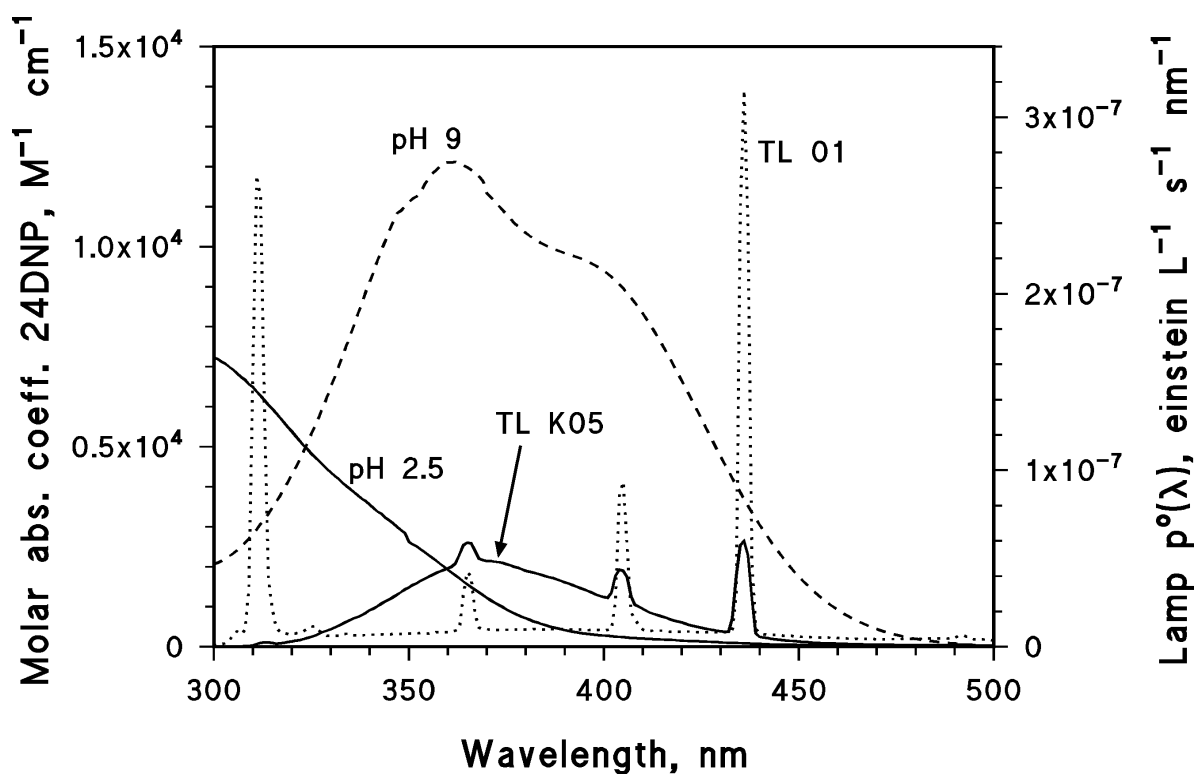
Figure 1. Absorption spectra (molar absorption coefficients) of 24DNP at pH 2.5 and 9 (adjusted with $HClO_4$ and NaOH, respectively). Emission spectra (spectral photon flux densities) of the lamps adopted for the irradiation experiments, TL01 (dotted trace) and TL K05 (solid trace).
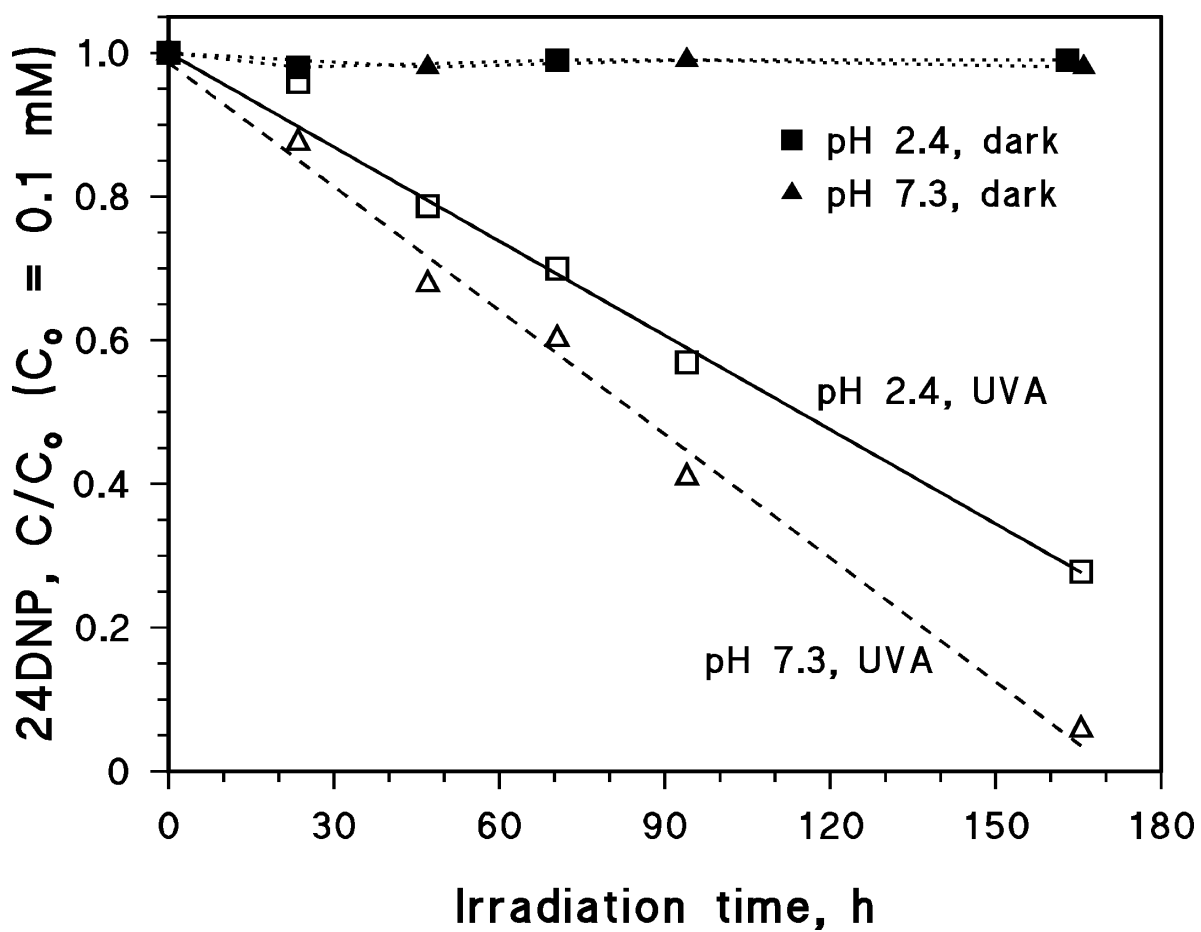
Figure 2. Time evolution of 0.1 mM 24DNP, upon irradiation under the TL K05 lamps (UVA) and in the dark. The pH values of 2.4 and 7.3 were adjusted upon addition of HClO$_4$ and NaOH, respectively.
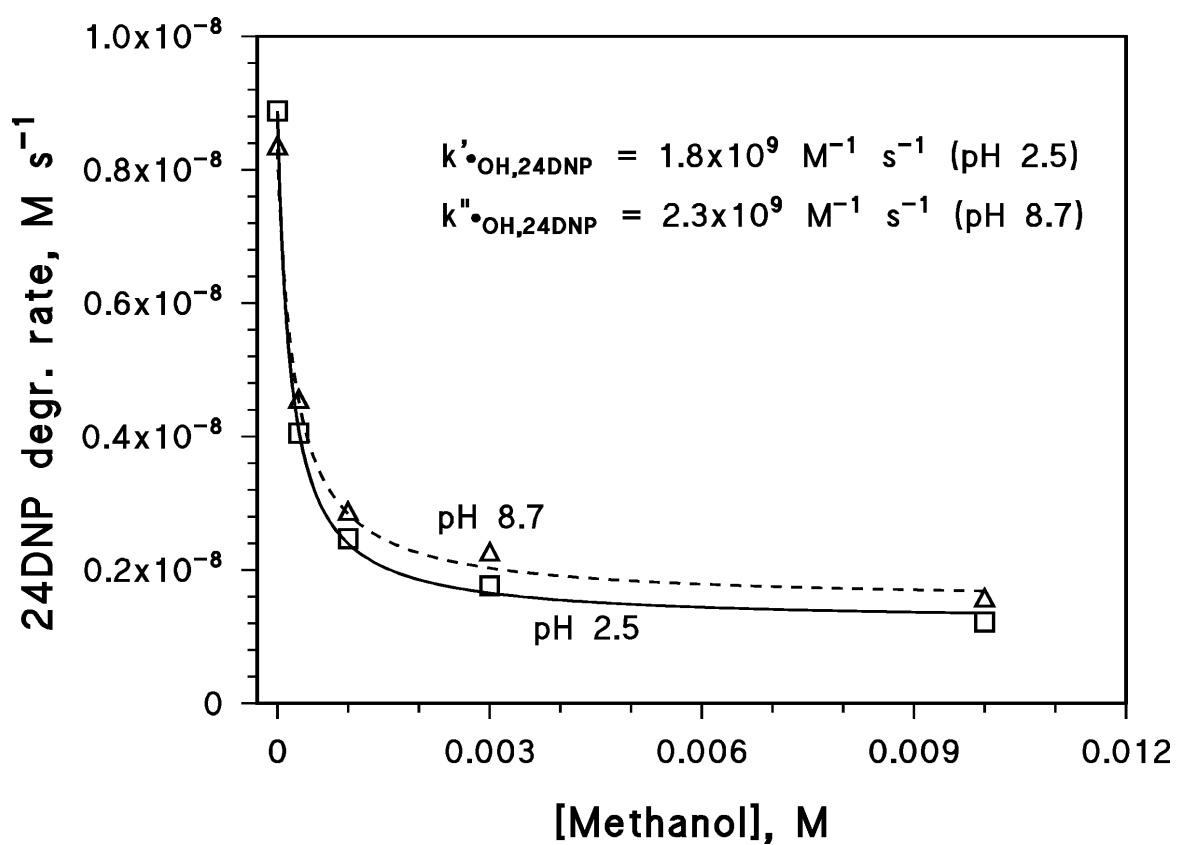
Figure 3. Initial degradation rates of 0.1 mM 24DNP upon irradiation of 0.1 M NaNO$_3$ under the TL 01 lamp (UVB), as a function of the concentration of methanol.
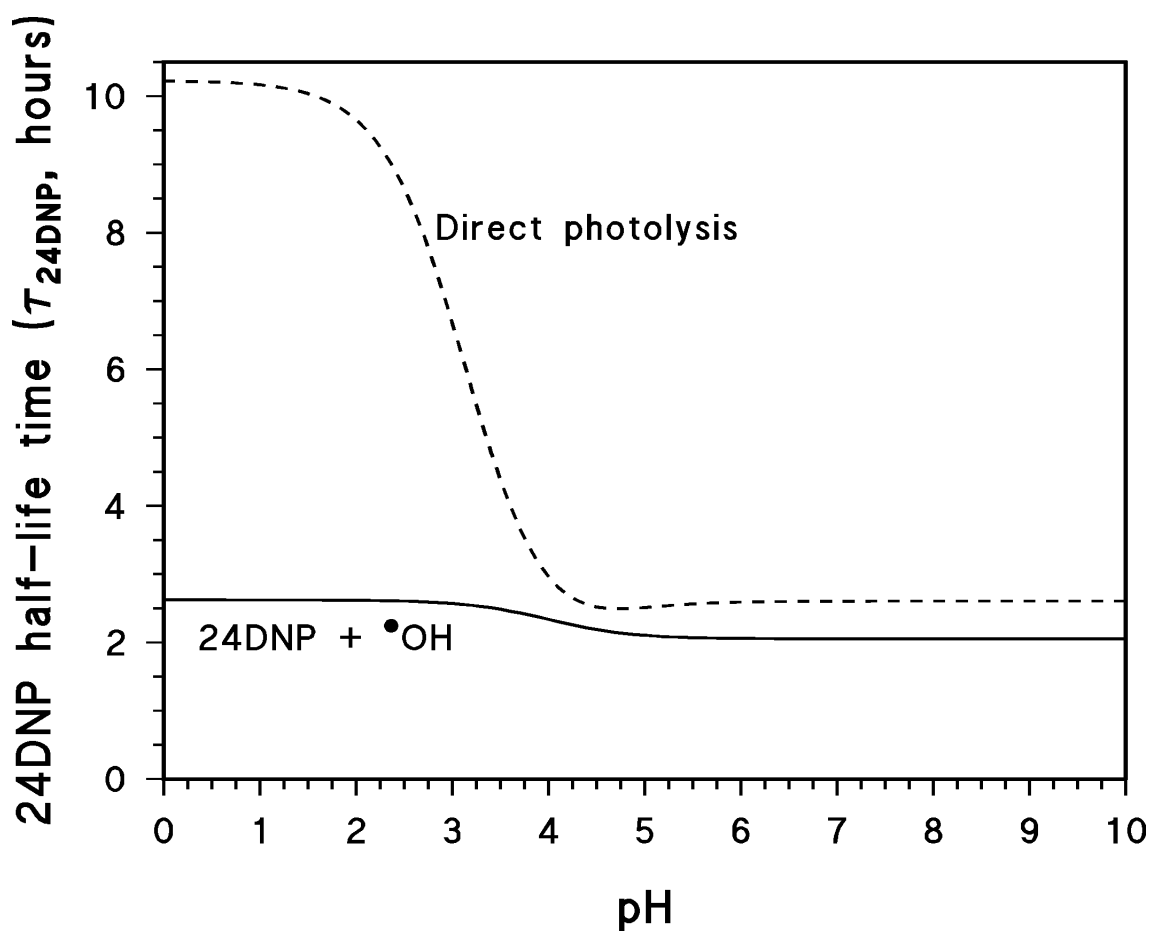
Figure 4. Half-life times of 24DNP as a function of pH, because of direct photolysis and the reaction with $^{\bullet}$OH. It was adopted [$^{\bullet}$OH] = 3.8×10^{-14} M, relevant to the atmospheric aqueous phase under a sunlight UV irradiance of 22 W m^{-2}.