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18 April 2024

UNIVERSITÀ DEGLI STUDI DI TORINO

ASSESSING THE TRANSFORMATION KINETICS OF 2- AND 4-NITROPHENOL IN THE ATMOSPHERIC AQUEOUS PHASE. IMPLICATIONS FOR THE DISTRIBUTION OF BOTH NITROISOMERS IN THE ATMOSPHERE

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Abstract

Different transformation processes for nitrophenols in the atmospheric aqueous phase were considered to assess their relative importance, and their ability to account for the higher occurrence of 4-nitrophenol (4NP) compared to 2-nitrophenol (2NP) in the atmosphere. The importance of the different processes was in the order $^\bullet OH > {}^\bullet NO_3 >$ direct photolysis $>$ nitration to 2,4-dinitrophenol. 2NP is more reactive than 4NP with the hydroxyl radical, but the difference is low. Accordingly, such a process could account for the higher atmospheric occurrence of 4NP only if the observed atmospheric nitrophenols were what is left of an almost complete degradation by $^\bullet OH$. This would imply the unlikely scenario that the known nitrophenol sources to the atmosphere were only a limited fraction of the actual ones. A more likely, tentative possibility would be connected with the higher occurrence of 4NP on particles. If the reactivity order of nitrophenols in the atmospheric compartments was water droplets $>$ gas phase $>$ particles, particulate matter could act as a reservoir of 4NP. 2NP would undergo degradation in gas phase or solution at a higher rate than 4NP on particles, which could decrease the atmospheric levels of 2NP below those of 4NP.

Keywords: nitrated phenols, phytotoxic compounds, atmospheric waters, photochemistry.

Introduction

Nitrophenols are widespread pollutants in the atmosphere, being present in the gas phase, in atmospheric hydrometeors, and on particles (Herterich and Herrmann, 1990; Levsen et al., 1990; Cecinato et al., 2005; Morville et al., 2006; Bishop and Mitra, 2007). They are one of the most abundant groups of organic compounds in rainwater (Grosjean, 1991; Schüssler and Nitschke, 2001; Asman et al., 2005; Hofmann et al., 2008), and cause concern because of their phytotoxic properties as uncoupling agents for oxidative phosphorylation (Shea et al., 1983), combined with their ability to penetrate into plant tissues (Schönherr and Riederer, 1988; Hinkel et al., 1989; Natangelo et al., 1999). Accordingly, nitrophenols could give a substantial contribution to forest decline in polluted areas (Blank, 1985; Rippen et al., 1987). Nitrophenol deposition from the atmosphere to surface waters would also pose a potential threat to aquatic organisms (Howe et al., 1994; Tenbrook et al., 2003; Martin-Skilton et al., 2006). However, another important surface-water source of nitrophenols would be the aqueous photonitration of the transformation intermediates of phenolic pesticides (Chiron et al., 2007a). Other reasons for concern deal with the potential mutagenicity of nitrophenols, which can induce oxidative damage to DNA (Chiron et al., 2007b).

A further issue is that the photolysis of gas-phase nitrophenols is a potentially important source of nitrous acid to the atmosphere (Bejan et al., 2006; Kleffmann, 2007), which could contribute to the early-morning photochemical generation of hydroxyl radicals, and therefore have a role in the chain of reactions of the photochemical smog (Atkinson, 2000).

2-Nitrophenol (2NP) and 4-nitrophenol (4NP) are major components of the family of atmospheric nitrophenols (Harrison et al., 2005a). They are formed as primary pollutants upon emission by combustion processes (Nojima et al., 1983; Tremp et al., 1993), and as secondary pollutants via phenol nitration both in the gas phase (Atkinson et al., 1992; Bolzacchini et al., 2001; Olariu et al., 2002) and in solution (Harrison et al., 2005b; Heal et al., 2007; Vione et al., 2002). Field and laboratory data also show that the mononitrophenols are possible sources of 2,4-dinitrophenol (2,4DNP), the known most powerful phytotoxic agent in atmospheric hydrometeors (Lüttke et al., 1997; Lüttke et al., 1999; Barletta et al., 2000; Vione et al., 2005).

An interesting issue about 2NP and 4NP in the atmosphere is that the latter is most often the prevailing isomer in whole atmospheric samples (gas + liquid phase + particles), while all the known primary and secondary sources yield either a comparable amount of the two isomers, or a prevalence of 2NP (Harrison et al., 2005a). The contradiction could be solved by considering the atmospheric sinks of nitrophenols, but at the moment insufficient data are available to support the hypothesis of a faster atmospheric transformation of 2NP compared to 4NP (Harrison et al., 2005a). Additionally, it is thought that the reactions in the aqueous phase could be very important sinks for atmospheric nitrophenols (Muller and Heal, 2001), even in the case of 2NP that is mainly present in the gas phase (Lüttke and Levsen, 1997).

The purpose of the present paper is to quantitatively assess the kinetics of the known transformation pathways of 2NP and 4NP in the atmospheric aqueous phase (direct photolysis,

reaction with $^\bullet$OH and/or $^\bullet$NO$_3$, photonitration to 2,4DNP). The double goal is to assess both the importance of each process, and the relative transformation rate of the two isomers. Furthermore, because 2NP and 4NP undergo different partitioning between gas phase, aqueous solution and particles (Lüttke and Levsen, 1997; Lüttke et al., 1997), a comparison of the kinetics of the known transformation processes of nitrophenols in the different phases was also carried out.

Experimental section

Reagents and materials. 2-Nitrophenol (2NP, purity grade 98%), 4-nitrophenol (4NP, >99%), NaOH (>97%), H$_3$PO$_4$ (85%) and HClO$_4$ (70%) were purchased from Aldrich, 2-propanol (gradient grade) and NaNO$_3$ (>99%) from VWR Int., acetonitrile (supergradient HPLC grade) from Scharlau. All reagents were used as received, without further purification.

Irradiation experiments. Aqueous samples for irradiation experiments (5 mL, containing 50 to 100 µM 2NP or 4NP and, where relevant, HClO$_4$, NaOH or NaNO$_3$) were put into Pyrex glass cells (4.0 cm diameter, 2.3 cm height, 0.4 cm optical path length), and magnetically stirred during irradiation. The direct photolysis of nitrophenols was studied upon irradiation under a Solarbox (CO.FO.ME.GRA., Milan, Italy), equipped with a 1500 W Philips xenon lamp and a filter to simulate sunlight under summertime conditions. The irradiance reaching the cells in the 290-400 nm interval was 22 W m^{-2}, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter. The excitation of nitrate was achieved under a UV-Vis Philips TL01 lamp, with emission maximum at 313 nm and 5.2 W m^{-2} UV irradiance. Figure 1 reports the emission spectra of the two lamps, measured with an Ocean Optics SD 2000 CCD spectrophotometer. The spectra (p°(λ)) are expressed in units of einstein L^{-1} s^{-1} nm^{-1} (V = 5×10^{-3} L) to facilitate calculations of absorbed photon fluxes and photolysis quantum yields, and therefore to enable the comparison with the experimentally determined rates of the photochemical reactions.

Adopted instrumentation. After irradiation the solutions were analysed by High-Performance Liquid Chromatography coupled to Diode Array Detection (HPLC-DAD). The adopted instrument was a VWR-Hitachi HPLC equipped with L-2200 autosampler, L-2130 quaternary pump for low-pressure gradients, L-2300 column oven, and L-2455 DAD detector. The column used was a LiChroCART RP18 (VWR Int., 125×4 mm), packed with LiChrospher 100 RP 18 material (5 µm diameter). The isocratic eluent was a 30:70 mixture of acetonitrile and aqueous H$_3$PO$_4$ (pH 3), with 1.0 mL min^{-1} flow rate, and the retention time and quantification wavelength were: 7.05 min and 210 nm for 2NP; 3.95 min and 315 nm for 4NP. The time evolution curves of nitrophenols were fitted with pseudo-first order kinetic equations of the form C$_t$ = C$_o$ exp($-$k t), where C$_t$ is the concentration of either 2NP or 4NP at the time t, C$_o$ is the initial concentration, and k is the pseudo-first order degradation rate constant. The use of pseudo-first order kinetics in direct photolysis and photooxidation experiments is justified by the fact that the additional reactants (photons, $^\bullet$OH) would be approximately constant in the systems under study. The initial degradation rate of

nitrophenols would be k C$_o$, and the associated error bound (μ±σ) represents the goodness of the fit of the kinetic curve to the experimental data (intra-series variability).

Transient absorption experiments in the 20 ns to 400 μs time scale were carried out on a nanosecond laser flash photolysis spectrometer from Applied Photophysics (LKS 60). Excitation (λ = 355 nm) was from the third harmonic of a Quanta Ray GCR 130-01 Nd:YAG laser (pulse width ≈ 5 ns), and was added into right angle geometry with respect to the monitoring light beam. A 3 mL volume of solution was used in a quartz cuvette and was stirred after each set of pulse. The transient absorbances at pre-selected wavelength were monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator, and a 1P28 photomultiplier. The kinetic studies were performed by analysing at the maximum of the transient absorbance. 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.

Results and Discussion

Direct photolysis under simulated sunlight. The direct photolysis of 2NP and 4NP under monochromatic irradiation (254 and/or 365 nm) has been studied by Alif et al. (1987, 1991). However, the goal of the present paper is the assessment of the transformation kinetics of nitrophenols under environmentally significant conditions (polychromatic irradiation by sunlight, pH representative of the atmospheric aqueous phase). The single-wavelength data might not be directly applicable to the environment because, for instance, the quantum yield of the photolysis of 2NP is strongly dependent on wavelength (Alif et al., 1991).

Figure 2 reports the absorption spectra of 2NP (2a) and 4NP (2b) at different pH values. It is apparent that the phenolates show higher absorption than the undissociated phenols above 350-380 nm, and the opposite takes place at shorter wavelengths. Generally speaking the phenolates are able to absorb a considerably higher fraction of sunlight, but the undissociated phenols show higher absorption of more energetic radiation at shorter wavelengths. The latter radiation could be capable, at least theoretically, to induce the direct photolysis to a higher extent.

Figure 3 reports the initial degradation rates of nitrophenols because of direct photolysis under simulated sunlight. As a general trend, the occurrence of the nitrophenolate under basic conditions (pKa ≈ 7; Martell and Smith, 1974) favours the photolysis in the case of 2NP and inhibits it for 4NP. In the latter case the wavelength-averaged photolysis quantum yield would show a much higher decrease with pH than the rate of photolysis, because the phenolate absorbs sunlight at a far higher extent. This datum is in agreement with the findings of Alif et al. (1987) for the photolysis quantum yield of 4NP at 365 nm, which decreased by three times between pH 2 and pH 8.3. Additionally, with the exception of very basic conditions of no atmospheric significance, the rate of

the direct photolysis is considerably higher for 4NP compared to 2NP. At pH 6 that is significant for atmospheric hydrometeors, one gets that the initial rates of photolysis of $C_o = 50$ μM 2NP and 4NP are $(1.02\pm0.35)\times10^{-10}$ and $(4.31\pm0.39)\times10^{-10}$ M s^{-1}, respectively (Rate = k C_o). The respective pseudo-first order rate constants k are $(2.04\pm0.70)\times10^{-6}$ and $(8.62\pm0.78)\times10^{-6}$ s^{-1}.
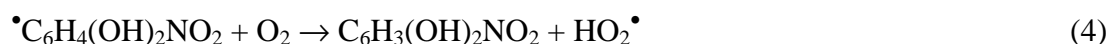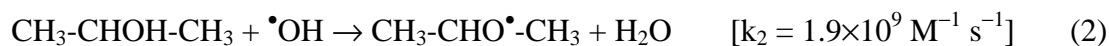
The absorption peak of 4NP at around 320 nm is about 3 times higher than that of 2NP at 350 nm, but the radiation absorption of 2NP is extended at longer wavelengths. The absorption of simulated sunlight by each nitrophenol (NP) in our irradiation experiments ($C_o = 50$ μM, optical path length b = 0.4 cm) can be calculated as $P_a^{NP} = \int_\lambda p^o(\lambda)\ (1-10^{-\varepsilon(\lambda)\,bC_o})\,d\lambda$ (Braslavsky, 2007),

where $p^o(\lambda)$ is the lamp spectrum reported in Figure 1, and $\varepsilon(\lambda)$ is the molar absorption coefficient at pH 6. The two nitrophenols would absorb radiation at a similar extent: $P_a^{2NP} = 1.2\times10^{-6}$ einstein L^{-1} s^{-1}, and $P_a^{4NP} = 1.3\times10^{-6}$ einstein L^{-1} s^{-1}. The average photolysis quantum yields Φ_{ave} in the relevant wavelength intervals (300-500 nm for 2NP, and 300-430 nm for 4NP) can be calculated from photolysis rates (Rate^{NP}) and absorption intensities (P_a^{NP}). One gets that $\Phi_{ave} = \text{Rate}^{NP}\,(P_a^{NP})^{-1}$ $= 8.4\times10^{-5}$ for 2NP, and 3.3×10^{-4} for 4NP.

The half-life time of 2NP and 4NP under the adopted irradiation conditions would be $t_{1/2} = 0.693\ k^{-1}$, where k is the pseudo-first order degradation rate constant (already reported). One gets $t_{1/2} =$ $(3.40\pm1.17)\times10^5$ s for 2NP, and $t_{1/2} = (8.04\pm0.73)\times10^4$ s for 4NP. In the described experiments (simulated sunlight) we adopted constant irradiation intensity (22 W m^{-2} UV irradiance), which is not the case for actual sunlight. In previous studies it has been shown that the sunlight UV energy reaching the ground in a whole summer sunny day (15 July) at 45°N latitude is equivalent to that emitted during 10 h irradiation under 22 W m^{-2} irradiance as adopted in the present work (Minero et al., 2007a). It is therefore possible to transform the half-life time $t_{1/2}$ under the lamp into outdoor sunny summer day (SSD) equivalents, by dividing $t_{1/2}$ by 10 h = 3.6×10^4 s. One obtains $(t_{1/2})_{SSD} =$ 9.44±3.24 days for 2NP, and 2.23±0.20 days for 4NP. However, the calculated $t_{1/2}$ values would be higher than the real ones: in fact, the spherical symmetry of atmospheric water droplets induces several reflection/refraction phenomena at the air/water interface. These phenomena would considerably increase the effective path length of the radiation. Accordingly, the probability for dissolved species to absorb radiation could be significantly higher in a droplet than in a planar slab of comparable dimension (Mayer and Madronich, 2004; Nissenson et al., 2006). This effect would be equivalent to an enhancement of the radiation intensity compared to the surrounding gas phase, which for droplets of lower diameter than 10 μm would be of around 1.7-1.8 times (Mayer and Madronich, 2004). The resulting half-life times for 2NP and 4NP would therefore be reduced to about 5.4 and 1.3 days, respectively. Especially in the case of 4NP, the direct photolysis could be a significant removal pathway under summertime irradiation conditions. However, it could not account for the higher atmospheric occurrence of 4NP compared to 2NP, because 4NP undergoes photolysis at a higher rate.

Reaction with the hydroxyl radical. To our knowledge the reaction rate constants with $^\bullet$OH of both undissociated nitrophenols, which could allow an assessment of their relative reactivity, are

not available (Barzaghi and Herrmann, 2004; Buxton et al., 1988). To allow a proper comparison, in this paper the two cited rate constants were measured under the same conditions by competition kinetics with 2-propanol, a compound of known reaction rate constant with the hydroxyl radical (1.9×10^9 M^{-1} s^{-1}; Buxton et al., 1988). Nitrate photolysis was used as source of $^\bullet OH$ (Mack and Bolton, 1999), which would induce the following reactions in a system containing also 2-propanol (CH_3-$CHOH$-CH_3) and 2NP or 4NP ($C_6H_4(OH)NO_2$):

$$NO_3^- + h\nu + H^+ \rightarrow {}^\bullet OH + {}^\bullet NO_2 \qquad [R_{\bullet OH}] \qquad (1)$$

$$CH_3\text{-}CHOH\text{-}CH_3 + {}^\bullet OH \rightarrow CH_3\text{-}CHO^\bullet\text{-}CH_3 + H_2O \qquad [k_2 = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}] \quad (2)$$

$$C_6H_4(OH)NO_2 + {}^\bullet OH \rightarrow {}^\bullet C_6H_4(OH)_2NO_2 \qquad [k_{2NP,\bullet OH} \text{ or } k_{4NP,\bullet OH}] \qquad (3)$$

$${}^\bullet C_6H_4(OH)_2NO_2 + O_2 \rightarrow C_6H_3(OH)_2NO_2 + HO_2^\bullet \qquad (4)$$

The application of the steady-state approximation to [$^\bullet OH$] yields the following equation to describe the initial degradation rate of a nitrophenol (NP, either 2NP or 4NP), as a function of its initial concentration and of that of 2-propanol, [2Pr]:

$$-\frac{d[NP]}{dt} = \frac{R_{\bullet OH} \, k_{NP,\bullet OH} \, [NP]}{k_{NP,\bullet OH} \, [NP] + k_2 \, [2\text{Pr}]} \qquad (5)$$

Figure 4 reports the initial degradation rates of 2NP and 4NP (initial concentration 0.1 mM) upon UV-Vis irradiation of 0.10 M NO_3^- ($NaNO_3$ + HNO_3), at pH 3, as a function of the initial concentration of 2-propanol. The pH value was chosen to ensure the presence of the nitrophenols in the associated form, which prevails under the typical conditions of the atmospheric aqueous phase. Note that an almost complete inhibition of the degradation of nitrophenols was observed at the highest adopted concentration of 2-propanol, suggesting that the transformation of nitrophenols is accounted for almost exclusively by reaction with $^\bullet OH$. This finding is consistent with the results of control runs, which showed that the direct photolysis of nitrophenols was negligible compared to the degradation rate observed in the presence of nitrate. The possible reaction between nitrophenols and $^\bullet NO_2$, which is not affected by 2-propanol, would also be negligible compared to $^\bullet OH$.

The fitting of the experimental data of Figure 4 with equation (5) yielded $k_{2NP,\bullet OH} = 5.8 \times 10^9$ M^{-1} s^{-1} and $k_{4NP,\bullet OH} = 5.0 \times 10^9$ M^{-1} s^{-1}. The value of $R_{\bullet OH}$ derived from the fit was 1.6×10^{-8} M s^{-1}, equal in the two cases as expected under the adopted experimental set-up.

In the first-order approximation one derives that the nitrophenol (NP) lifetime upon reaction with $^\bullet OH$ is $t_{1/2} = 0.693 \, (k_{NP,\bullet OH} \, [^\bullet OH])^{-1}$, where NP can be 2NP or 4NP. For typical continental clouds the steady-state [$^\bullet OH$] would be 5×10^{-14} M under noon, fair-weather equinox conditions at 48°N (Warneck, 1999), which would correspond to about 30 W m^{-2} sunlight UV irradiance (Frank and Klöpffer, 1988). As far as constant irradiation intensity is considered, the half-life time would be 2.4×10^3 s for 2NP and 2.8×10^3 s for 4NP. Considering that the standard SSD equivalent adopted in the present paper (15 July, 45°N) would correspond to 7.3 h = 2.6×10^4 s at 30 W m^{-2}, one obtains
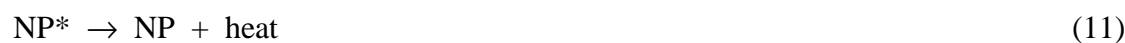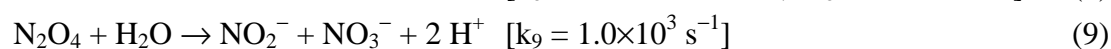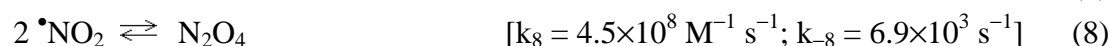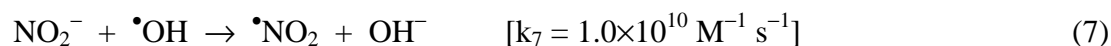
$(t_{1/2})_{SSD}$ = 0.09 days (2.2 hours) for 2NP and 0.1 days (2.5 hours) for 4NP. In the midday hours the half-life times could be significantly lower (1 h or less). The calculated lifetimes with $^\bullet OH$ are considerably lower than those of the direct photolysis, which suggests that the reaction with the hydroxyl radical could be a more important transformation pathway for nitrophenols. From the literature rate constants of the reaction of the nitrophenolates with $^\bullet OH$ (9.2×10^9 M^{-1} s^{-1} for 2NP and 7.6×10^9 M^{-1} s^{-1} for 4NP; Buxton et al., 1988) one derives that the degradation rate of nitrophenols would be increased, albeit not substantially, at the higher edge of the pH interval of the atmospheric aqueous phase.

Interestingly, 2NP is expected to be slightly more reactive than 4NP toward $^\bullet OH$. To have an idea of what this means, let us initially consider 2NP and 4NP at equal concentration in the atmospheric aqueous phase, at the sunrise of a sunny day (SSD as defined above). Under the simplified hypothesis that no external sources are present, the concentration of the two compounds would only be determined by their degradation kinetics. The kinetics could be assumed to follow a pseudo-first order law of the form $[NP]_t = [NP]_0 \exp(-k_{NP} t)$, where NP = 2NP or 4NP, $[NP]_t$ is the concentration at the time t, $[NP]_0$ the initial concentration, and k_{NP} the pseudo-first order degradation rate constant. For one SSD and for reaction with $^\bullet OH$ one has t = 2.6×10^4 s (remember the equivalence reported above) and $k_{NP} = k_{NP,\bullet OH} [^\bullet OH]$, with $[^\bullet OH] = 5 \times 10^{-14}$ M (Warneck, 1999; Frank and Klöpffer, 1988). It would therefore be $[4NP]/[2NP] = \exp[t [^\bullet OH] (k_{2NP,\bullet OH} - k_{4NP,\bullet OH})]$. Based on these premises, at the sunset 4NP would be 2.9 times more concentrated than 2NP. This effect could account for the higher occurrence of 4NP compared to 2NP in atmospheric waters. However, after irradiation for a whole SSD, 2NP would be reduced to just 0.05% of its initial concentration, and 4NP to 0.14%. Accordingly, almost quantitative nitrophenol disappearance should be hypothesised for the reaction with $^\bullet OH$ to adjust the concentration ratio in favour of 4NP.

It is interesting to make a comparison between the reaction of nitrophenols with $^\bullet OH$ and that with $^\bullet NO_3$, another very reactive transient in atmospheric waters. The relevant reaction rate constants for the undissociated compounds are $k_{2NP,\bullet NO3} = 2.3 \times 10^7$ M^{-1} s^{-1} and $k_{4NP,\bullet NO3} = 7.1 \times 10^7$ M^{-1} s^{-1} (Umschlag et al., 2002; Barzaghi and Herrmann, 2004). With $[^\bullet NO_3] \approx 10^{-13}$ M in the atmospheric aqueous phase (Vione et al., 2006), one would get $t_{1/2} \approx 3.5$ days for 2NP, and 1 day for 4NP. Although not negligible, the reaction would be considerably slower than for $^\bullet OH$ and, additionally, would foresee a faster degradation kinetics of 4NP compared to 2NP. It would therefore not be able to account for the higher atmospheric occurrence of 4NP.

Nitration to 2,4DNP. Vione et al. (2005) have found that the nitration of 2NP and 4NP to 2,4DNP is due to the reaction between radiation-excited nitrophenols (NP*) and $^\bullet NO_2$. They have also reported that the formation rate of 2,4DNP is 3.2×10^{-11} M s^{-1} upon UVA irradiation of 1 mM 2NP and 0.10 M NaNO$_2$, and 1.3×10^{-11} M s^{-1} upon UVA irradiation of 1 mM 4NP and 0.10 M NaNO$_2$, at pH 6. The following reactions would be involved in the nitration process (Mack and Bolton, 1999; Vione et al., 2005):

$NO_2^- + h\nu + H^+ \rightarrow {}^{\bullet}OH + {}^{\bullet}NO$ (6)

$NO_2^- + {}^{\bullet}OH \rightarrow {}^{\bullet}NO_2 + OH^-$ [$k_7 = 1.0 \times 10^{10}$ M^{-1} s^{-1}] (7)

$2\,{}^{\bullet}NO_2 \rightleftarrows N_2O_4$ [$k_8 = 4.5 \times 10^8$ M^{-1} s^{-1}; $k_{-8} = 6.9 \times 10^3$ s^{-1}] (8)

$N_2O_4 + H_2O \rightarrow NO_2^- + NO_3^- + 2\,H^+$ [$k_9 = 1.0 \times 10^3$ s^{-1}] (9)

$NP + h\nu \rightarrow NP^*$ (10)

$NP^* \rightarrow NP + heat$ (11)

$NP^* + {}^{\bullet}NO_2 \rightarrow 2,4DNP$ [k_{12}] (12)
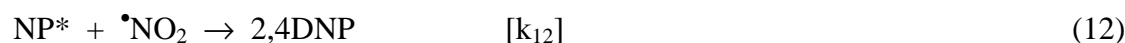
Where NP = 2NP or 4NP. From reaction (12) one gets that the formation rate of 2,4DNP would be $r_{2,4DNP} = k_{12}$ [NP*] [${}^{\bullet}NO_2$]. The value of $r_{2,4DNP}$ has been experimentally measured (Vione et al., 2005), and the determination of k_{12} requires the assessment of both [${}^{\bullet}NO_2$] and [NP*]. The calculation of the two concentration values, in the presence of 1 mM 2NP or 4NP and 0.10 M NaNO$_2$ under UVA irradiation (2.3×10^{-5} einstein L^{-1} s^{-1}), required the combination of laser flash photolysis experiments and multi-wavelength calculations of radiation absorption in the mixture. The adopted procedures and the calculations are reported in the Supplementary Material.

In the case of 1 mM 2NP and 0.10 M NaNO$_2$ it is [${}^{\bullet}NO_2$] = 3.9×10^{-8} M and [2NP*] = 1.0×10^{-11} M; for 1 mM 4NP and 0.10 M NaNO$_2$ it is [${}^{\bullet}NO_2$] = 3.7×10^{-8} M and [4NP*] = 6.0×10^{-12} M. From reaction (12) one gets $k_{12} = r_{2,4DNP}$ ([NP*] [${}^{\bullet}NO_2$])$^{-1}$. From the experimental values of $r_{2,4DNP}$ (Vione et al., 2005) it is possible to obtain $k_{12(2NP)} = 7.9 \times 10^7$ M^{-1} s^{-1}, and $k_{12(4NP)} = 5.9 \times 10^7$ M^{-1} s^{-1}.

The value of k_{12} is the basis for the assessment of the atmospheric significance of the reported reactions, also considering that in the atmospheric aqueous phase it is [${}^{\bullet}NO_2$] $\cong$ 1 nM (Minero et al., 2007b). The details of the calculations are reported in the Supplementary Material. The result is that the reaction between NP* and ${}^{\bullet}NO_2$ is too slow to be a significant pathway for nitrophenol removal from the atmosphere. Dinitrophenol formation has been reported to increase by over two orders of magnitude in the presence of hematite (α-Fe$_2$O$_3$) (Vione et al., 2005), but even such an enhancement would not be sufficient to make the process competitive with the reaction with ${}^{\bullet}OH$ or with the direct photolysis.

Comparison between gas-phase and condensed-phase reactivity. In this paper it is shown that the mononitrophenol lifetime in the atmospheric aqueous phase could be as low as a few hours because of the reaction with ${}^{\bullet}OH$. The actual reaction kinetics could be further accelerated by accumulation phenomena at the droplet surface (Vione et al., 2007). As far as the reactivity of 2NP with ${}^{\bullet}OH$ and ${}^{\bullet}NO_3$ in the gas phase is concerned, the reported rate constants are $k_{2NP,\bullet OH} = 9.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 1992), and $k_{2NP,\bullet NO3} < 2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1994). With 24-h averaged concentration values in the gas phase of 10^6 molecule cm^{-3} for ${}^{\bullet}OH$ and 2.5×10^8 molecule cm^{-3} for ${}^{\bullet}NO_3$ (Arey, 1998), the life-time of 2NP in the gas phase would be around 13 days for the reaction with ${}^{\bullet}OH$, and > 2 days for the reaction with ${}^{\bullet}NO_3$.

Nitrophenols strongly absorb in the atmospherically relevant UV range 300–400 nm (Harrison et al., 2005a), corresponding to the $S_0 \rightarrow S_1$ transition as reported for the liquid phase (Ishag and

Moseley, 1977). Recently published data (Bejan et al., 2006) indicate that the gas-phase photolysis of *ortho*-nitrophenols could be an important source of HONO. The reported photolysis frequency J(2NP→HONO) under simulated atmospheric conditions is $(2.9\pm0.6)\times10^{-5}$ s^{-1}. This could imply a half-life time of around 7 h for 2NP in the gas phase, suggesting that the direct photolysis could be a more important removal pathway for gas-phase 2NP than the reaction with $^{\bullet}$OH or $^{\bullet}$NO$_3$. The lifetime of gas-phase 2NP would be a bit longer compared to 4NP in solution, under typical atmospheric conditions.

To account for the higher occurrence of 4NP compared to 2NP in the atmosphere, it could be considered that the phase partitioning of nitrophenols (and especially of the less volatile 4NP) would also involve particles. Indeed, the fraction of 4NP that is present on particles is much higher than for 2NP (Lüttke and Levsen, 1997). The reactivity of organic compounds on particulate matter might be relatively low, because the organic loading of particles can protect adsorbed substrates against the reaction with transient species ($^{\bullet}$OH, $^{\bullet}$NO$_3$). The direct photolysis would be a more significant removal pathway on particulate matter than the radical reactions, but black carbonaceous particles are able to screen sunlight and therefore protect the adsorbed compounds from direct photodegradation. Direct photolysis would therefore be slower on fine particles than in solution (Dunstan et al., 1989).

It is possible to roughly compare the reactivity of 4NP on particles with that of 2NP in the gas phase. Take the $t_{1/2}$ of 4NP due to the direct photolysis in solution, without considering the multiple refraction phenomena in spherical water droplets, as a lower limit for the corresponding $t_{1/2}$ on particles ($t_{1/2}^{4NP} \geq 2.23\pm0.20$ SSD days, with SSD = 15 July, 45°N). The corresponding $t_{1/2}$ of 2NP in the gas phase would be 7 hours. After a whole SSD irradiation, 4NP on particles would be decreased by 30% or less, 2NP in the gas phase by around 90%. In this case the faster transformation of 2NP could explain the higher atmospheric occurrence of 4NP compared to 2NP.

Conclusions

This paper considered a series of nitrophenol degradation processes in the aqueous phase, to see if they can account for the higher occurrence of 4NP compared to 2NP in the atmosphere, despite the higher atmospheric input of 2NP by the known primary and secondary sources.

Reaction with $^{\bullet}$OH would be the fastest removal process for nitrophenols in the aqueous solution. 2NP would be more reactive than 4NP, but the difference is small. For the reaction with $^{\bullet}$OH to account for the higher atmospheric occurrence of 4NP, the detected nitrophenols in the atmosphere should be only a very minor fraction of the input burden, the remainder having undergone degradation. Given the reasonable match between the observed atmospheric concentrations and the known sources (Harrison et al., 2005a), this would imply the very unlikely scenario that the nitrophenol inputs to the atmosphere have been largely underestimated.

Other possible transformation processes in the aqueous phase are the reaction with $^{\bullet}$NO$_3$ and the direct photolysis. Under average atmospheric conditions they would be considerably slower than

the reaction with $^\bullet$OH, and would lead to a faster transformation rate of 4NP compared to 2NP. The reaction between NP* and $^\bullet$NO$_2$ is also unlikely to be a significant nitrophenol sink under typical atmospheric conditions. However, this paper elucidated for the first time the detailed kinetics of the photonitration process that yields 2,4DNP.

The transformation of 2NP in the gas phase is dominated by the direct photolysis (Bejan et al., 2006), which is sufficiently fast to ensure an efficient removal of 2NP from the sunlit atmosphere. Furthermore, the transformation of gas-phase 2NP is expected to be much faster than for 4NP on particles. Considering that 4NP undergoes extensive partitioning to airborne particulate matter (Lüttke and Levsen, 1997), particles could be seen as an atmospheric reservoir of 4NP that could account for its higher occurrence compared to 2NP.

Overall the aqueous phase would be the most efficient atmospheric reactor for nitrophenol transformation, and $^\bullet$OH would quickly consume the dissolved compounds. Significant degradation could also involve the nitrophenols reaching the solution from other atmospheric compartments. The mass transfer of gas-phase 2NP to water droplets (Lüttke and Levsen, 1997) should be faster than that of particle-adsorbed 4NP, which would constitute an additional protective effect of particles toward 4NP. However, further research would be required into the degradation kinetics of 4NP on particles, to prove or disprove the proposed scenario.

Supplementary Material Available. The Supplementary Material reports the study of the reaction between radiation-excited mononitrophenols and nitrogen dioxide to yield 2,4-dinitrophenol. The calculations to assess the atmospheric significance of the reaction are also reported.

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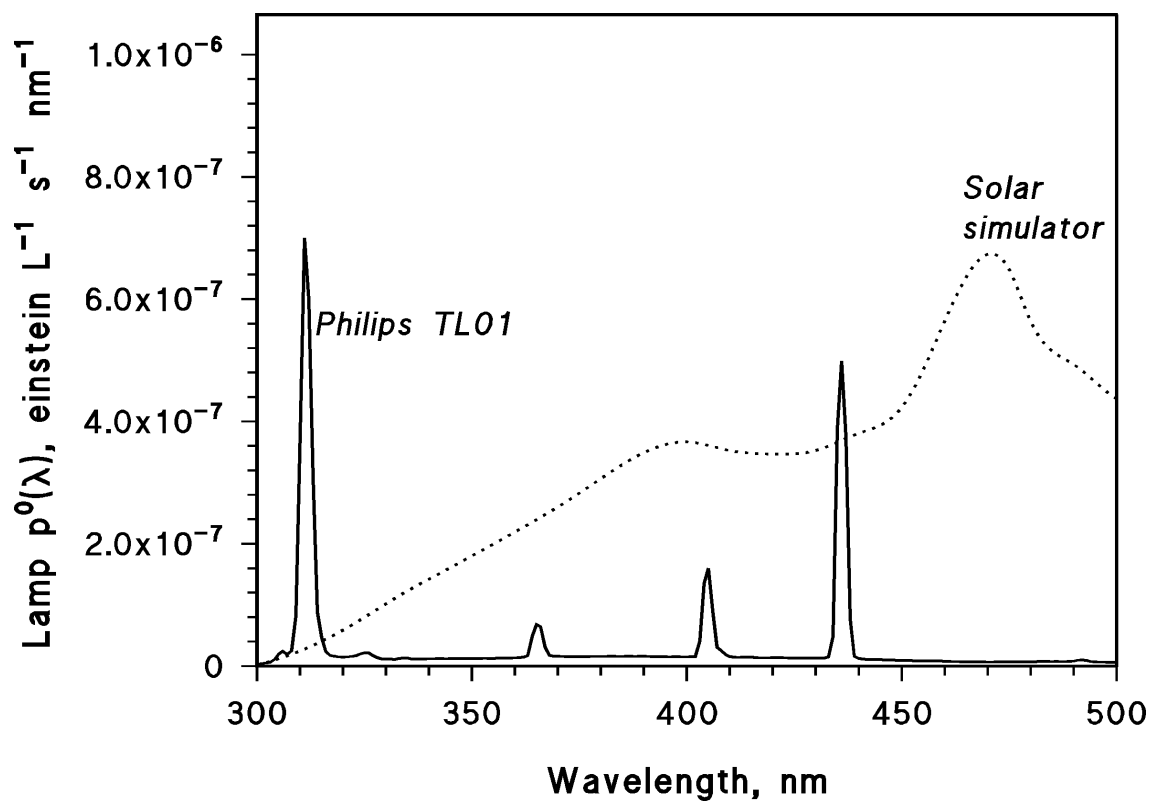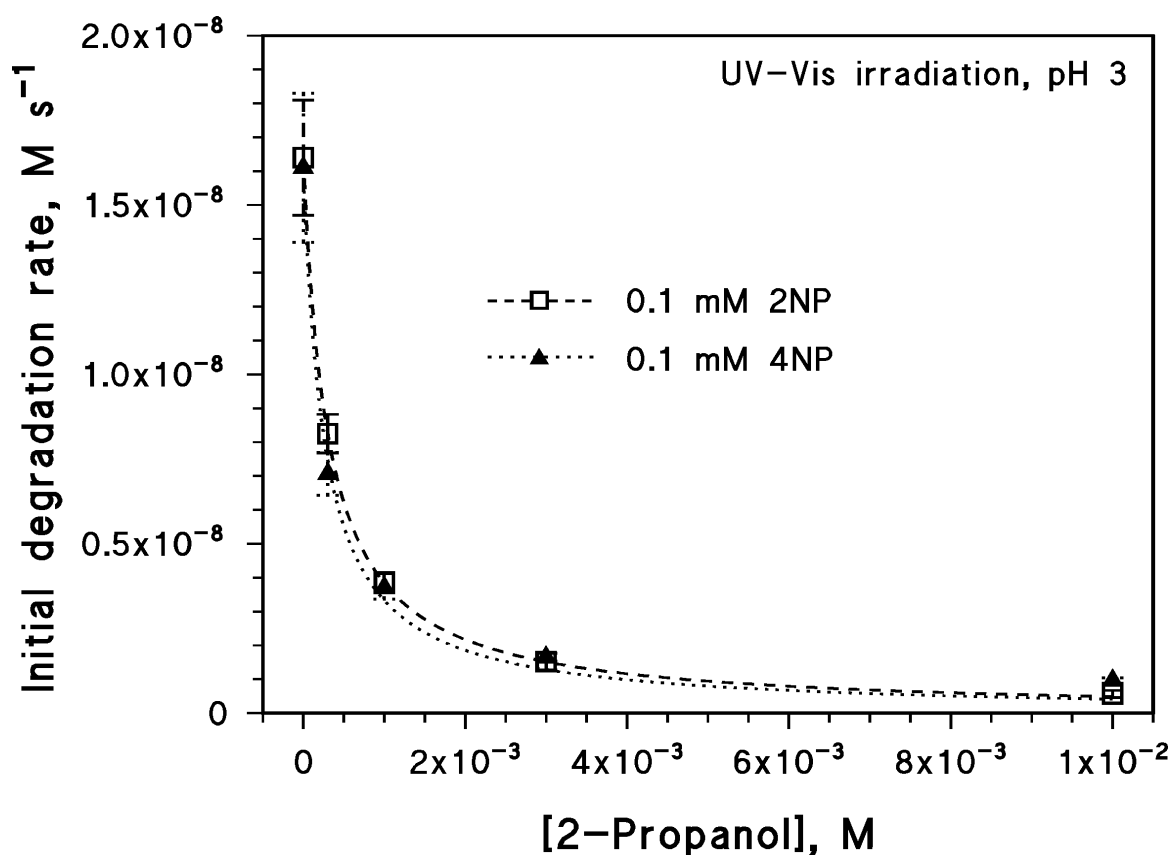
Figure 1. Emission spectra ($p°(\lambda)$) of the adopted solar simulator and of the Philips TL01 lamp. The solar simulator was used to study the direct photolysis of nitrophenols, and the TL01 lamp was used to induce the photolysis of nitrate.
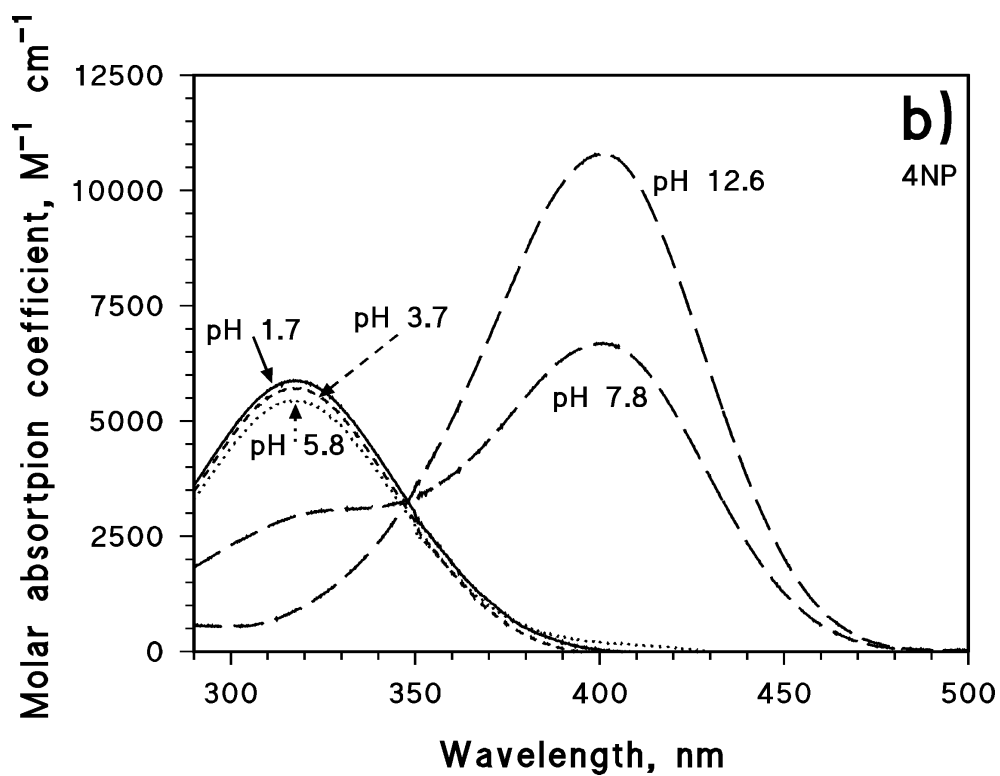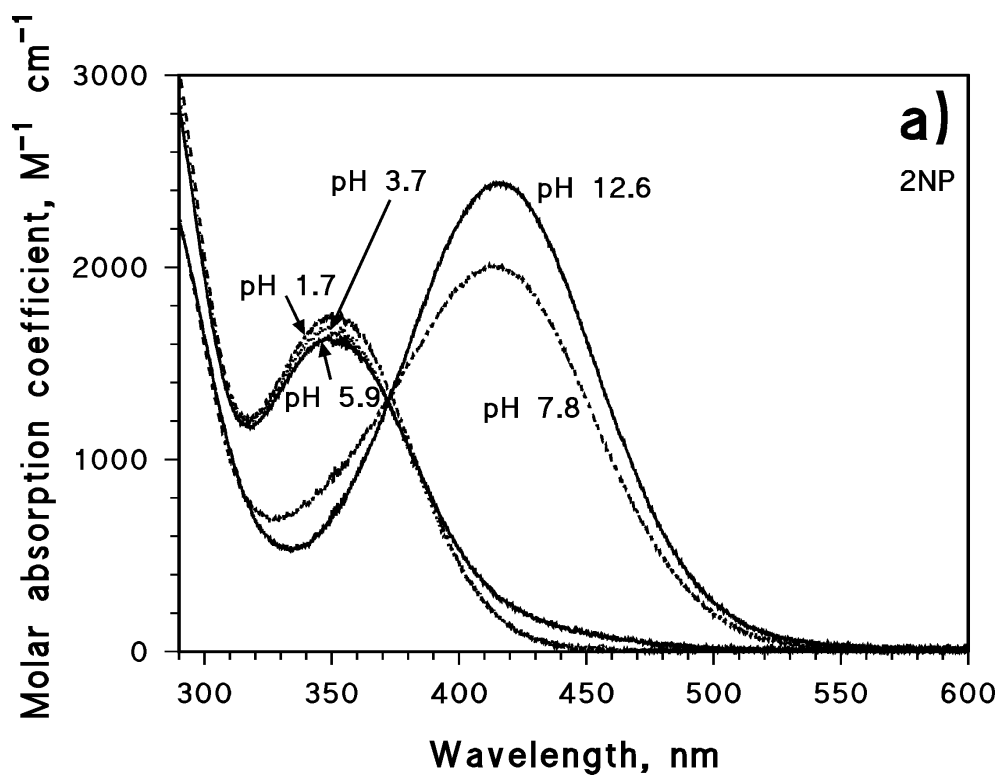
Figure 2. Absorption spectra of 2NP (2a) and 4NP (2b) at different pH values. The values of pK_a are 7.21 and 7.15 for 2NP and 4NP, respectively (Martell and Smith, 1974).
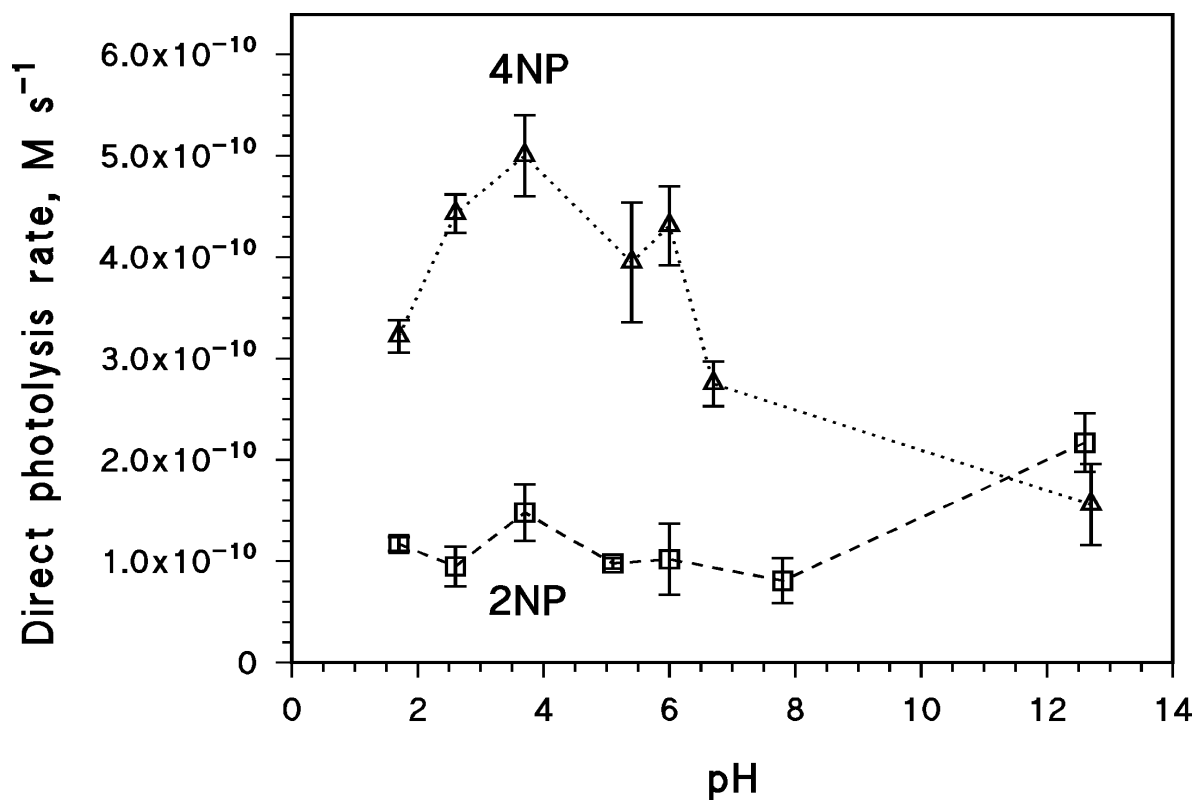
Figure 3. Direct photolysis rates of 50 μM 2NP and 50 μM 4NP under the adopted solar simulator. The error bounds (μ±σ) represent the intra-series variability (goodness of the fit of the pseudo-first order kinetic curves to the experimental data of the time evolution).

Figure 4. Initial degradation rate of 0.1 mM 2NP or 4NP upon UV-Vis irradiation of 0.10 M NO_3^- ($NaNO_3$ + HNO_3), at pH 3, as a function of the initial concentration of 2-propanol. The experimental data were fitted with equation (5) to get $k_{2NP,\bullet OH} = 5.8\times10^9$ M^{-1} s^{-1} and $k_{4NP,\bullet OH} = 5.0\times10^9$ M^{-1} s^{-1}. The error bounds ($\mu\pm\sigma$) represent the intra-series variability (goodness of the fit of the pseudo-first order kinetic curves to the experimental data of the time evolution).