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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 was 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.

1. 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

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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.

2. Experimental section

2.1. Reagents and materials

2-Nitrophenol (2NP, purity grade 98%), 4-nitrophenol (4NP, >99%), NaOH (>97%), H_3PO_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.

2.2. Irradiation experiments

Aqueous samples for irradiation experiments (5 mL, containing 50–100 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. Fig. 1 reports the emission spectra of the two lamps, measured with an Ocean Optics SD 2000 CCD spectrophotometer. The spectra ($p^o(\lambda)$) are expressed in units of einstein L^{-1} s^{-1} nm^{-1} ($V = 5 \times 10^{-3}$ 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.

2.3. 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_3PO_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 $C_t = C_o \exp(-kt)$, 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 kC_o, and the associated error bound ($\mu \pm \sigma$) represents the goodness of the fit of the kinetic curve to the experimental data (intra-series variability).

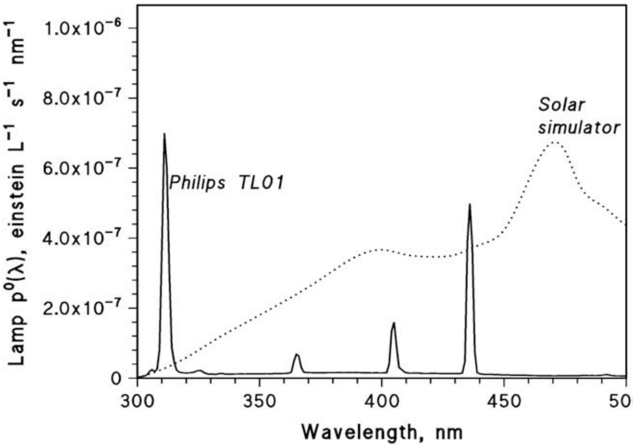

Fig. 1. Emission spectra ($p^o(\lambda)$) of the adopted solar simulator and of the Philips TL01 lamp. The solar simulator was used to study the direct photolysis of nitrophenols, and the TL01 lamp was used to induce the photolysis of nitrate.

Transient absorption experiments in the 20 ns–400 μs time scale were carried out on a nanosecond laser flash photolysis spectrometer from Applied Photophysics (LKS 60). Excitation ($\lambda = 355$ 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.

3. Results and discussion

3.1. 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