

## Photochemical transformations in ice: Implications for the fate of chemical species

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**Abstract.** A quantum yield of  $\phi_{ice} = 2.3 \times 10^{-4} (\pm 4 \times 10^{-5})$  was determined for the photochemical degradation of 4-nitrophenol over the wavelength range of 300 to 370 nm in ice pellets (pH 5.6). Five reaction products were identified: hydroquinone, benzoquinone, 4-nitrosophenol, nitrate, nitrite, and the likely formation of organic polymers. The similarities of these results to the observations from 4-nitrophenol photolysis in aqueous solutions indicate that similar mechanisms are operative in both phases. The photochemical decomposition of 4-nitrophenol under conditions similar to those in polar snow and ice suggests that other direct and indirect photochemical process can occur in the polar ice/snow during spring and summer.

### Introduction

Over the last decade there has been a growing interest in the chemical composition of snow packs and ice cores in polar regions (Bales and Wolff, 1995; Chappellaz et al., 1997; Legrand, 1997). In addition, there is increasing evidence for post depositional chemical alterations in the accumulated ice and snow, including photochemical processes (Honrath et al., 1999,2000; Sumner and Shepson, 1999), that may explain some of the inconsistencies in observed time-series of different chemical species (Sigg and Neftel, 1991; Delmas, 1993; Anklin et al., 1995).

There have been several previous reports of photochemical transformations in ice relative to interstellar or stratospheric ice systems (e.g. Allamandola et al. 1988; Berstein et al.,1995, 1999; Schutte and Gerakines, 1995, and Pursell et al. 1996). These studies have shown that breakage and formation of chemical bonds due to UV radiation can take place in ice. However, all of these studies were done at very low temperatures (10 K - 200 K) using thin ice films and were addressing qualitatively the photochemical processes. Recent field and lab experiments (Sumner and Shepson, 1999; Honrath et al., 1999, 2000; Jones et al., 2000) showed photochemical production of  $\text{NO}_x$  and HCHO in surface snow.

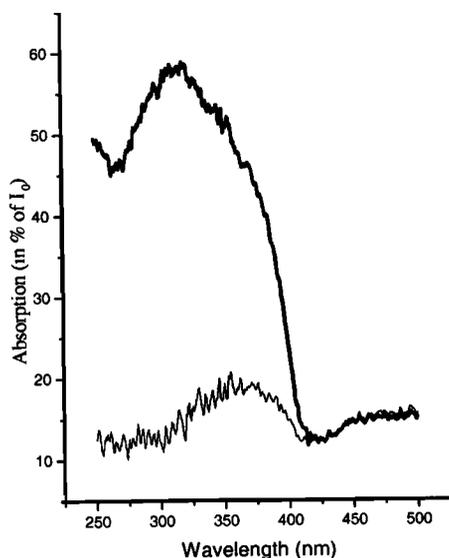
4-nitrophenol was selected for the present study as a convenient aromatic chromophore with a strong absorption over the UV range that is relevant for the earth's surface, and may represent the photochemical behavior of other simple polar aromatic compound in ice. In addition, phenols and nitrophenols are phytotoxic and have been detected in

relatively high concentrations (up to 100 $\mu\text{g/L}$ ) in rain, fog, and snow (e.g. Kawamura and Kaplan, 1986; Alber et al., 1989; Richartz et al., 1990, Herterich and Herrmann, 1990, Levsen et al., 1993). 4-nitrophenol is introduced into the environment by the following processes: combustion from motor vehicles (Trempp et al., 1993), photochemical reactions in the atmosphere during smog photochemical events (e.g. Leone and Seinfeld, 1985), and degradation of pesticides such as parathion and parathion-methyl (Kishk et al., 1976; Woodrow et al., 1977). Field measurements suggest that 4-nitrophenol is mainly particle-bound and has a longer lifetime in the atmosphere than 2-nitrophenol (Luttke et al., 1997). This suggests that 4-nitrophenol can find its way to the rural areas at the upper latitudes. In this study, the photochemical decomposition of 4-nitrophenol in uniform ice pellets under conditions that are representative of the earth's surface (258 K,  $10^5$  Pa, and under UV irradiation over the wavelength range of 300 to 370 nm) is clearly demonstrated.

### Experimental Methods

In order to create uniform ice samples that are suitable for light absorption measurements and chemical analysis, a new method was used. Solutions of 250  $\mu\text{M}$  4-nitrophenol in milli-Q water were frozen and then pulverized at 77 K. Pulverization was achieved using a porcelain mortar and pestle, which were cooled with liquid nitrogen before and during pulverization. 13 mm  $\times$  4 mm polycrystalline ice pellets were made from the ice powder under an applied pressure of 89.6 MPa using a French press. After annealing overnight at 248 K under ambient pressure ( $10^5$  Pa), the pellets were irradiated with light over the wavelength range of 300-370 nm. A high pressure 1000 W Hg-Xe arc lamp was used as a light source in combination with a 320 nm band filter and a 300 nm cutoff filter. The incident light intensity was determined to be  $8.5 \times 10^{16}$  photons $\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$  using Aberchrome-540 as a chemical actinometer (Heller, 1978). During the experiments, the ice pellets were placed (one at a time) in an isolated slot in a copper block, which was maintained at a constant temperature of 258 K. After irradiation, the pellets were thawed and analyzed using liquid chromatography (HP 1090), ion chromatography (Dionex BIO-LC) and total organic carbon analysis (Shimadzu TOC-5000A). As a result of light scattering and the uncertainties associated with the path length of light propagation through the ice, the light absorbance of the 4-nitrophenol in the pellets was determined using a UV-VIS spectrophotometer (Shimadzu UV-2101 PC) with an attached integrating sphere (Shimadzu ISR-260). This was accomplished with a duplicate set of pellets. The average intensity of scattered light was measured by a photomultiplier located at the bottom of the integrating sphere, which quantifies the light transmission through the pellet, with air used as a reference. The reflections

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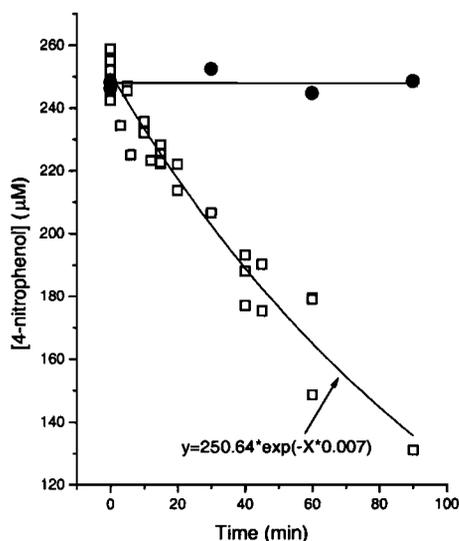


**Figure 1:** The absorption spectrum (in percent of the incident light) of 250  $\mu\text{M}$  4-nitrophenol in an ice pellet (thick line) and of pure water ice pellet (thin line). Both pellets are 4 mm thick. The light absorption by the 4-nitrophenol is given by the difference spectrum.

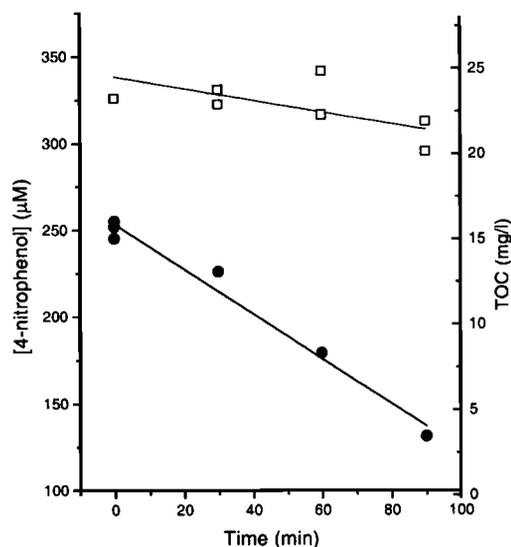
from the pellets were measured off of the ice pellets contained in a slit at the wall of the integrating sphere (with a depth equal to the pellet thickness), with pressed  $\text{BaSO}_4$  powder used as a reference.

## Results

The percentage of light transmittance ( $T$ ) through the ice and the reflectance ( $R$ ) off of the ice pellets as measured with an integrating sphere technique (see methods) are shown in Fig 1. The percent of incident light absorbed by a 250  $\mu\text{M}$  4-nitrophenol solution distributed in ice pellets was determined based on a light flux balance, as described in equation 1, where pure  $\text{H}_2\text{O}$  ice pellets were used as a reference blank.



**Figure 2:** 4-nitrophenol concentration vs. time for the irradiation of ice pellets by light over the wavelength range of 300 to 370nm light (open squares) and at wavelengths  $\geq 420$  nm (solid circles).  $[\text{4-nitrophenol}]_0 = 250 \mu\text{M}$ ,  $T = 258 \text{ K}$ .



**Figure 3:** Concentration of hydroquinone (squares), benzoquinone (circles), and 4-nitrophenol (triangles) vs. irradiation time,  $[\text{4-nitrophenol}]_0 = 250 \mu\text{M}$ ,  $T = 258 \text{ K}$ .

$$\frac{I_a}{I_0} = \left\{ (100 - T - R)_{\lambda, 4\text{NP ice}} - (100 - T - R)_{\lambda, \text{H}_2\text{O ice}} \right\} \quad (1)$$

Where:  $I_a/I_0$  is the percent of incident light absorbed by 250  $\mu\text{M}$  4-NP in an ice pellet,  $I_a$  = absorbed light flux,  $I_0$  = incident light flux,  $(100 - T - R)_{\lambda, 4\text{NP ice}}$  = light absorption by an ice pellet containing 250  $\mu\text{M}$  4-NP (in % of  $I_0$ ),  $(100 - T - R)_{\lambda, \text{H}_2\text{O ice}}$  = light absorption by pure  $\text{H}_2\text{O}$  pellet (in % of  $I_0$ ),  $T$  = light transmission through the ice pellet (in % of  $I_0$ ), and  $R$  = light reflection from the ice pellet (in % of  $I_0$ ).

The calculations described in eq. 1 were performed over the wavelength range of 200 to 500 nm in intervals of  $\Delta\lambda = 0.2 \text{ nm}$ . Over the range of wavelengths (300 nm to 370 nm) for active photochemistry 38.9%  $\pm$  3.6% of the incident light is absorbed by a frozen 250  $\mu\text{M}$  4-nitrophenol solution in a 4 mm-thick ice pellet.

During irradiation of the ice pellets ( $300\text{nm} \leq \lambda \leq 370\text{nm}$ ) the measured 4-nitrophenol concentration decreased with time according to apparent pseudo-first order kinetics (Fig. 2) with an observed rate constant of  $7.2 \times 10^{-3} \text{ min}^{-1}$  ( $\pm 4 \times 10^{-4}$ ). Three aromatic compounds, hydroquinone, benzoquinone and 4-nitrosophenol (Fig. 3) and two inorganic anions, nitrate and nitrite (data are not shown) were detected as reaction products of the solid ice-phase photolysis of 4-nitrophenol. Even though the sum of the detected aromatic reaction products did not account for the total amount of 4-nitrophenol that disappeared, TOC analysis showed that the latter did not change significantly over a time period of 90 min (Fig. 4).

Above 420 nm, where the light absorption by 4-nitrophenol is very small (Fig. 1), no apparent change in the 4-nitrophenol concentration was observed (Fig. 2) and none of the aromatic degradation products were detected. Nitrate and nitrite were detected in the ice pellets of the control experiment but no increase in their concentration with time was observed.

## Discussion

During the freezing process, most solutes are excluded from the growing ice crystals resulting in higher concentrations on crystals surfaces and between the adjacent ice crystals (Takenaka et al. 1996). Because of the low

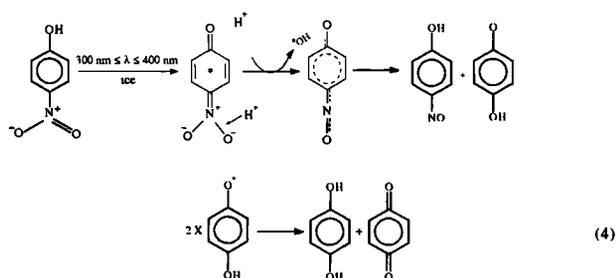
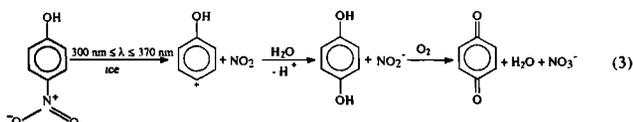
aqueous-phase solubility of 4-nitrophenol, these inclusions are too dilute with respect to the solute to remain exclusively in the liquid phase. Extrapolation of the 4-nitrophenol solubility data of Benes and Dohnal (1999) to temperatures below 273 K, shows that the mole fraction of 4-nitrophenol can not exceed  $10^{-3}$ . These concentrations are too small for freezing point depression down to 258 K. Thus, for our experiments, 4-nitrophenol is trapped in the solid ice phase.

Based on the observed photolysis rate, the incident light intensity and the fraction of the measured light absorbed by the 4-nitrophenol, a quantum yield of  $2.3 \times 10^{-4}$  ( $\pm 4 \times 10^{-5}$ ) was determined for the UV photolysis of 4-nitrophenol according to eq. 2 as follows:

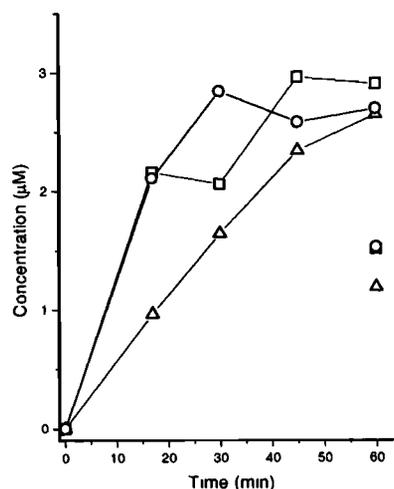
$$\phi(4\text{-NP}, 300\text{-}370\text{ nm}) = \frac{\left(\frac{d[4\text{-NP}]}{dt}\right)_0}{I_{\text{absorbed}}(300\text{-}370\text{ nm})/dt} \quad (2)$$

Where:  $\phi(4\text{-NP}, 300\text{-}370\text{ nm})$  is the apparent quantum yield for 4-NP photolysis over the wavelength range of 300 to 370 nm,  $(d[4\text{-NP}]/dt)_0$  is the initial loss of 4-NP when irradiated at this wavelength range ( $\text{mole}\cdot\text{s}^{-1}$ ), and  $I_{\text{absorbed}}(300\text{-}370\text{ nm})/dt$  is the photon flux (over 300 to 370 nm) absorbed by the 4-NP ( $\text{einstein}\cdot\text{s}^{-1}$ ).

Both the quantum yield and the products observed in the ice photolysis experiments are similar to those observed in homogeneous aqueous-phase measurements for the photolysis of 4-nitrophenol (Masayuki and Crosby, 1974; Alif et al., 1987). This similarity in observed photochemical product arrays suggests a similar mechanism for photochemical decomposition for both phases (eqs. 3 and 4, after Alif et al., 1987):



In spite of the much stronger cage effects expected in ice, the exclusion of 4-nitrophenol from the ice crystal and its concentration between the ice crystals, the photochemical reaction occurs at rates that are similar to the corresponding reaction rates in the aqueous phase at 25°C. The main difference between the two phases is that in aqueous solutions, the aromatic products account for a larger fraction of the degraded 4-nitrophenol. As can be seen from the data in Fig. 3, the detected organic reaction products reach concentrations in the micromolar range suggesting that their photochemical lifetimes are relatively short. As previously mentioned during the course of photolysis the decrease in the total organic carbon levels (TOC) is much lower than the degradation of the 4-nitrophenol. Over an irradiation exposure of 90 minutes, the TOC decreased by only 2.25 mgC/L whereas the 4-nitrophenol concentration decreased by 120



**Figure 4:** 4-nitrophenol (solid circles) and total organic carbon (open squares) concentrations vs. time of irradiation of the ice pellets for  $300\text{ nm} \leq \lambda \leq 370\text{ nm}$  at  $T = 258\text{ K}$ .

$\mu\text{M}$  (i.e., 8.64 mgC/L). Thus, it is likely that organic polymers were formed during the photodegradation of 4-nitrophenol. Formation of polymeric material was previously observed by Masayuki and Crosby (1974) during irradiation of 4-nitrophenol in aqueous solution. Oxidative polymerization of polyphenols is also a well known mechanism for the formation of humic acids in soils (Shindo, 1990; Naidja et al., 1998; Kung and McBride, 1988). The small decrease in the TOC may suggest that  $\text{CO}_2$  was produced. This requires breakage of the aromatic ring, as was observed previously during 4-nitrophenol photocatalysis in  $\text{TiO}_2$  slurries by Dieckmann and Gray (1995).

## Conclusions

In this study the photochemistry of 4-nitrophenol over the wavelength range of 300 to 370 nm in ice pellets was investigated. A quantum yield of  $\phi_{\text{ice}} = 2.3 \times 10^{-4}$  ( $\pm 4 \times 10^{-5}$ ) was determined for the photochemical degradation of 4-NP in ice pellets. This value of  $\phi_{\text{ice}}$  is of the same magnitude as the aqueous-phase quantum yield which we measured under similar irradiation conditions ( $\phi_{\text{aq}} \approx 7.7 \times 10^{-5}$ ). The observed products of 4-nitrophenol photolysis in ice were nitrate, nitrite, hydroquinone, benzoquinone, 4-nitrosophenol, and the likely formation of organic polymers. These results and their similarity to the observations from 4-nitrophenol photolysis in aqueous solutions indicate that similar mechanisms are operative in both phases. The photochemical decomposition of 4-NP under conditions similar to those in polar snow and ice (i.e., temperature, pressure, and UV wavelength range), suggests that other direct and indirect photochemical processes can occur in the polar ice/snow during spring and summer. For example, naturally-occurring organic matter (NOM) that has a substantial aromatic character and serves as an excellent absorber of UV and visible radiation, is most likely to be present in significant amounts in polar snow. Absorption of light by NOM can lead to the indirect production of hydroperoxyl radicals and eventually organic peroxides (Hoffmann, 1996). These free radicals may further react with other impurities present in the polar snow (e.g., organic matter) causing chemical changes in important species such as  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{CO}$  and  $\text{CO}_2$ . These alterations may effect the

interpretations of the time-records of these species in polar ice cores regarding the oxidation capacity of past atmospheres (Staffelbach et al., 1991) and related climate changes (Fuhrer et al., 1993).

The present results are consistent with recent studies by Honrath et al. (1999, 2000), Jones et al. (2000), and Sumner and Shepson (1999), who reported on the photochemical production of NO<sub>x</sub> and HCHO in surface accumulated snow. These observations were interpreted in terms of nitrate photolysis in snow, followed by the production of hydroxyl radical which, in turn, is expected to lead to the production of H<sub>2</sub>O<sub>2</sub>, HCHO, and other organic compound destruction in polar snow during spring and summer.

Since polar ice cores are used extensively to probe the atmospheric paleo-chemistry and to predict the evolution of climate, more systematic investigations of post-depositional chemical changes due to direct and indirect photolysis are needed.

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