



Photochemical degradation of hydroxy PAHs in ice: Implications for the polar areas



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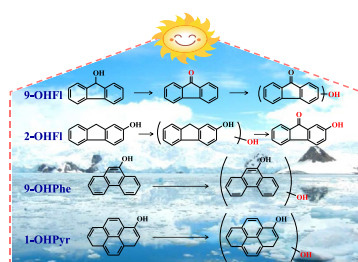
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HIGHLIGHTS

- It is first reported on photochemical behaviour of 4 hydroxylated PAHs in ice.
- Photolysis kinetics varied substantially due to different structures and properties.
- Photoinduced hydroxylation formed multiple hydroxylated intermediates.
- Photodegradation is prominent in determining the OH-PAH fate in polar sunlit snow/ice.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydroxyl polycyclic aromatic hydrocarbons (OH-PAHs) are derived from hydroxylated PAHs as contaminants of emerging concern. They are ubiquitous in the aqueous and atmospheric environments and may exist in the polar snow and ice, which urges new insights into their environmental transformation, especially in ice. In present study the simulated-solar ($\lambda > 290$ nm) photodegradation kinetics, products and pathways of four OH-PAHs (9-Hydroxyfluorene, 2-Hydroxyfluorene, 1-Hydroxypyrene and 9-Hydroxyphenanthrene) in ice were investigated, and the corresponding implications for the polar areas were explored. It was found that the kinetics followed the pseudo-first-order kinetics with the photolysis quantum yields (Φ_s) ranging from 7.48×10^{-3} (1-Hydroxypyrene) to 4.16×10^{-2} (2-Hydroxyfluorene). These 4 OH-PAHs were proposed to undergo photoinduced hydroxylation, resulting in multiple hydroxylated intermediates, particularly for 9-Hydroxyfluorene. Extrapolation of the lab data to the real environment is expected to provide a reasonable estimate of OH-PAH photolytic half-lives ($t_{1/2,E}$) in mid-summer of the polar areas. The estimated $t_{1/2,E}$ values ranged from 0.08 h for 1-OHPyr in the Arctic to 54.27 h for 9-OHFl in the Antarctic. In consideration of the lower temperature and less microorganisms in polar areas, the photodegradation can be a key factor in determining the fate of OH-PAHs in sunlit surface snow/ice. To the best of our knowledge, this is the first report on the photodegradation of OH-PAHs in polar areas.

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1. Introduction

The polar areas are considered important sinks for global Persistent Organic Pollutants (POPs), due to long-range atmospheric transport of these chemicals from various sources. Polycyclic Aromatic Hydrocarbons (PAHs) are one important class of POPs, and many of them are carcinogenic, mutagenic and toxic contaminants. PAHs have been found widely in polar multimedia, such as atmosphere (Wang et al., 2013), water (Lohmann et al., 2009), sediment (Harvey et al., 2014; Martins et al., 2010), snow (Fuoco et al., 2012; Na et al., 2011) and biota (Harvey et al., 2014). In both atmosphere and water/ice environments, PAHs can be transformed to hydroxy PAHs (OH-PAHs) through chemical/biological processes (Barrado et al., 2012; Beltran et al., 1995; Dolinová et al., 2006; Johnson-Restrepo et al., 2008; Murayama and Dasgupta, 1996; Sepic et al., 2003; Zhang et al., 2011). Airborne OH-PAHs can stem from photo-oxidation of parent PAHs or hydroxyl radical addition to PAHs (Zhang et al., 2011). Barrado et al. (Barrado et al., 2012) found that OH-PAHs in atmospheric aerosol samples showed seasonal fluctuation with generally higher concentrations detected in winter. Furthermore, it was reported that PAHs underwent primarily addition-elimination reactions to form the corresponding hydroxy compounds when H₂O₂ coexisted in ice (Dolinová et al., 2006). In natural sunlit ice or snow, H₂O₂ and many kinds of radicals were indeed found (Grannas et al., 2007).

As a group of functionalized PAHs, OH-PAHs are known as pollutants of emerging concern with even higher toxicities than their parent PAHs (Mallakin et al., 1999; McConkey et al., 1997). Moreover, some OH-PAHs, such as 9-Hydroxyfluorene (9-OHFI), showed photomodified toxicity to *V. fischeri* (Ge et al., 2016). Increasing occurrences of OH-PAHs were reported in many countries. Pojana and Marcomini (Pojana and Marcomini, 2007) found that OH-PAH concentrations ranged from 15 to 68 ng L⁻¹ in final effluents from wastewater-treatment plants in Italy. Itoh et al. (Itoh et al., 2006) detected nine OH-PAHs at concentrations of 0.49–5.8 ng L⁻¹ in the seawater samples from an industrial port of Japan. While the existence of OH-PAHs in Arctic and Antarctic remains unknown, however, OH-PAHs potentially exist in the polar area due to the feasible transformation of local existing PAHs into OH-PAHs.

Since OH-PAHs are potential polar contaminants, it is necessary to investigate their transformation in order to assess the persistence and fate in the arctic/antarctic environment. The intense solar UV irradiation and weak microorganism effects prevail on the snow and ice, making photodegradation a key process in determining the fate of polar organic pollutants (Klán and Holoubek, 2002). The ice photochemical behaviour of many organics has been reported in previous studies, such as benzene (Kahan and Donaldson, 2010), halobenzenes (Klan et al., 2001), monochlorophenols (Kang et al., 2009; Klanova et al., 2003), methyl-parathion and fenitrothion (Weber et al., 2009), and a pentabromodiphenyl ether (BDE-100) (Sanchez-Prado et al., 2012). Ram and Anastasio (Ram and Anastasio, 2009) found that the direct photolysis was the main mechanism of degradation for phenanthrene, pyrene, and fluorene in ice and snow. Kahan et al. (Kahan et al., 2010) unveiled that anthracene photolysis kinetics depended on photon flux in ice. Furthermore, Dolinová et al. (Dolinová et al., 2006) evaluated qualitatively and quantitatively photoinduced oxidation reactions that occurred on PAHs in frozen aqueous solutions in the presence of H₂O₂. These studies clarified the photochemistry for PAHs in ice or snow. In addition, the photochemical behaviour of PAHs and alkylated PAHs was well documented not only in water and gas phases (Fasnacht and Blough, 2002, 2003; Long and Niu, 2007; Niu et al., 2005) but also on solid matrix surfaces (Niu et al., 2003, 2004), which is of importance to understand their ice photochemistry. However, little is known about the ice photochemistry of

OH-PAHs. Only 9-OHFI was reported in our previous studies, which indicated its photochemical degradation and photoinduced toxicity in ices (Ge et al., 2014).

Herein, the aim of this study was to investigate the photo-degradation kinetics and intermediates of OH-PAHs in ice, and to explore their photochemical behaviours and fate in the Arctic and Antarctic ice/snow environment. Four OH-PAHs were selected, i.e. 9-OHFI, 2-Hydroxyfluorene (2-OHFI), 9-Hydroxyphenanthrene (9-OHPhe) and 1-Hydroxypyrene (1-OHPyr), because they can be transformed from their parents, fluorene, phenanthrene and pyrene (known as abundant PAHs in the environment), through chemical/biological processes (Luan et al., 2006). Moreover, these mono-hydroxylated metabolites have been widely used as biomarkers to evaluate the exposure to PAHs (Guo et al., 2013; Luan et al., 2006). To our best knowledge, this is the first comprehensive study on the ice photochemical behaviour of these four representative OH-PAHs.

2. Materials and methods

2.1. Chemicals

9-OHFI, 2-OHFI, 9-OHPhe and 1-OHPyr (purity ≥ 98%) were purchased from Sigma Aldrich, Inc. (Milwaukee, WI, USA). Their chemical structures are shown in Table S1. *p*-nitroanisole (purity > 97%) was obtained from Alfa Aesar (MA, USA), pyridine (purity > 99%) from TCI (Shanghai) Development Co., Ltd. Acetonitrile, methanol and acetone were of HPLC grade from TEDIA (Fairfield, USA). All chemicals were used as received. Ultrapure water was produced by a Milli-Q water system (Millipore, CA, USA).

2.2. Photolytic kinetic experiments

All solutions of OH-PAHs (C₀ = 0.5 μM) for photolysis were prepared in ultrapure water with acetonitrile (2% in volume) as a cosolvent. The solutions were pipetted into quartz tubes (vol. 40 mL, dia. 23 mm; manufactured by Daming Glass Instrument Plant, Dalian, China) and frozen vertically at -20 °C. After freezing, the tubes were set into a merry-go-round reactor and temperature-controlled in a freezer [-(5 ± 1) °C]. A Pyrex-well cooled and filtered high-pressure mercury lamp (500 W) was used to irradiate the solutions, where the incident light intensity was 5.46 mW cm⁻², measured by a UV radiometer (Photoelectric Instrument Factory of Beijing Normal University) at 365 nm. Pyrex-filtered mercury lamps were usually employed to simulate solar radiation (λ > 290 nm) (Dolinová et al., 2006; Matykiewiczová et al., 2007; Ziolli and Jardim, 2003).

The photolysis quantum yields (Φ_s) of OH-PAHs were determined using *p*-nitroanisole/pyridine as a chemical actinometer (Dulln and Mill, 1982; Edhlund et al., 2006) and calculated according to eq 1

$$\Phi_s = \frac{k_s \sum L_\lambda \epsilon_{\lambda,a}}{k_a \sum L_\lambda \epsilon_{\lambda,s}} \Phi_a \quad (1)$$

where *s* is the substrate OH-PAHs, *a* is the actinometer, *k* is the photolysis rate constant, *L*_λ is lamp irradiance at a specific wavelength λ, and ε_λ values are the molar absorptivities of the substrate or actinometer. Kinetic experiments and dark controls were carried out at least in triplicate. A Waters UPLC coupled with a fluorescence detector was employed to analyze the OH-PAH concentrations, detailed in the Supplementary Material.

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