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Identification of products formed during the heterogeneous nitration and ozonation of polycyclic aromatic hydrocarbons

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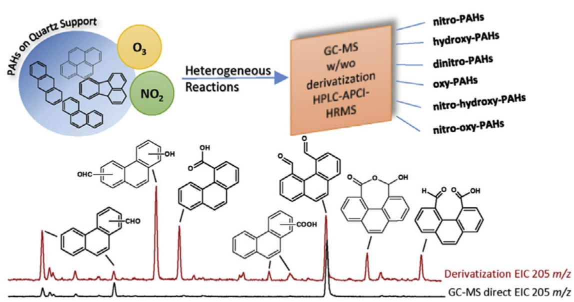
HIGHLIGHTS

- Heterogeneous oxidation of polycyclic aromatic hydrocarbons was investigated.
- Identification of reaction products with NO_2, O_3 or NO_2+O_3 was confirmed with HRMS.
- New products not previously observed for the reaction of PAHs with O_3 are reported.
- Products from the oxidation of PAHs with NO_2+O_3 are reported for the first time.

GRAPHICAL ABSTRACT



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ABSTRACT

The 3- and 4-ring polycyclic aromatic hydrocarbons (PAHs) are the most abundant of PAHs in air particulate matter (PM). Thus we have investigated heterogeneous oxidation of 3- and 4-ring PAHs in a small-scale flow reactor using quartz filter as a support. Four representative PAHs, anthracene, phenanthrene, pyrene, and fluoranthene, were exposed to either NO_2, O_3 or NO_2+O_3 (NO_3/N_2O_5) with a goal to identify and attempt quantification of major product distribution. A combination of gas chromatography with mass spectrometry (GC–MS) with/without derivatization and liquid chromatography with high resolution MS (LC-HRMS) was used for identification. For the first time, a comprehensive characterization of a broad range of products enabled identifying ketone/diketone, aldehyde, hydroxyl, and carboxylic acid PAH derivatives. Exposure to NO_3/N_2O_5 (formed by reacting NO_2 with O_3, a more powerful reactant than either O_3 or NO_2) produced additional compounds not observed with either oxidant alone. Multiple isomers of nitrofluoranthene and, for the first time, nitrophenanthrene were identified. In addition hydroxy-nitro-PAH derivatives were observed for the reaction of anthracene with NO_3/N_2O_5. Monitoring of specific common ions such as those of 176 and 205 *m/z* attributed to carbonyl phenanthrene and deprotonated phenanthrene ions respectively was shown to be a useful tool for identification of multiple pyrene oxidation products.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have long been known as an important byproduct of incomplete combustion of various fuel sources due to their pro-mutagenic character and possible connection to climatic disturbances while in the particle phase [i.e., particulate matter (PM)] (Barcelo and Kostianoy, 1998; Calvert et al., 2002; Finlayson-Pitts and Pitts, Jr., 2000; Greenberg et al., 1993; Sasaki et al., 1995). PAH sources include both anthropogenic and natural processes, with the former being the major contributor to the atmospheric budget (Pandis and Seinfeld, 2006). Some polar PAH derivatives, including nitrated (nitro-PAHs) and oxygenated species (oxy-PAHs), have been recently found to be directly mutagenic, posing a greater threat to human health than their parent PAHs (Barcelo and Kostianoy, 1998; Greenberg et al., 1993; Sasaki et al., 1995; Souza et al., 2014). These PAH oxidation products are formed through both primary (direct) processes, such as incomplete combustion of diesel fuel, and secondary processes in the atmosphere through reactions of either gas-phase or particle-bound PAHs with gas-phase atmospheric oxidants (Atkinson, 1991; Barrado et al., 2012; Calvert et al., 2000; Guo and Kamens, 1991; Kamens et al., 1990; Nielsen, 1984; Pitts et al., 1985; Sweetman et al., 1986; Van Cauwenberghe et al., 1984; Zielinska et al., 1986). Much attention has been previously given to the mechanisms that produce polar PAH oxidation products in the gas phase (Atkinson, 1991; Calvert et al., 2002; Zielinska, 2005; Zielinska et al., 1986), however, heterogeneous reactions occurring on the gas–particle interface and having rather different mechanisms received attention recently (Fan and Kamens, 1996; Henderson and Donaldson, 2012; Ma et al., 2011; Miet et al., 2009a, 2009b; Nguyen et al., 2010; Perraudin et al., 2007a, 2005).

In order to mimic the variation in the PM matrix, a number of studies have previously been performed on various analogue surfaces, such as soot, graphite, silica, real-world (urban) organic aerosol, and ash particles (Guo and Kamens, 1991; Inazu et al., 1997; Kamens et al., 1990; Miet et al., 2009a, 2009b; Nguyen et al., 2010; Perraudin et al., 2007b, 2005; Pitts et al., 1985; Van Cauwenberghe et al., 1984; Zhang et al., 2010; Zielinska et al., 1986). These extensive studies focused mainly on the kinetic loss of PAHs during exposure to NO_2 or O_3 or, to some extent, NO which showed a lower reactivity. Several products were reported, yet, the identification of a broad range of products appears to have been beyond the scope of these studies (Fan and Kamens, 1996; Inazu et al., 1997; Miet et al., 2009a; Nguyen et al., 2010; Perraudin et al., 2005; Ringuet et al., 2012; Zhang et al., 2011, 2010). Studies on the exposure of PAHs adsorbed on particles to a more potent reagent, NO_3/N_2O_5 (formed via the reaction of O_3 with NO_2) focused mainly on PAH degradation and reported the formation of several products, some of which were not identified (Jariyasopit et al., 2014; Kamens et al., 1990; Zielinska et al., 1986; Zimmermann et al., 2013; Zondlo et al., 1998). To our knowledge, no studies have been reported identifying the broad range of products formed during the heterogeneous oxidation of PAHs with NO_2, O_3, or NO_3/N_2O_5.

The aim of this project was to study the heterogeneous PAH oxidation in the presence of either nitrogen dioxide, ozone, or both, focusing on the identification of product species in order to enable their later identification in atmospheric studies performed either in chambers or outdoor. We evaluated a wide range of oxidation products observed from the exposure of PAHs in solid state (adsorbed on a quartz filter). The study targeted the most abundant PAHs found typically in PM i.e., anthracene, phenanthrene, pyrene and fluoranthene, that is 3-ring and 4-ring PAHs, where 3-ring PAHs are known to partition between the gas phase and solid phase, while 4-ring PAHs persists in the solid phase. The products were identified using gas chromatography with mass spectrometry (GC–MS), matching the resulting MS spectra to those of standards and MS libraries. This identification was further confirmed through the analysis with high performance liquid chromatography with atmospheric pressure chemical ionization-high resolution mass spectrometry (HPLC-APCI-HRMS).

2. Materials and methods

2.1. Materials

All standards used in this study are listed in Table 1. Stock solutions were prepared in a concentration of 100 μg mL^{-1} in dichloromethane (DCM, high-resolution GC grade, Fisher Scientific, Pittsburg, PA, USA). The internal standard (IS) solution of deuterated fluoranthene in DCM (~100 μg mL^{-1}) was employed for quantification. Additionally, recovery standard (RS) solutions (100 μg mL^{-1}; listed in Table 1) were used to correct for any errors resulting from the extraction process. The derivatization agent, N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% of trimethylchlorosilane (TMCS), was obtained from Sigma–Aldrich (Atlanta, GA, USA) and used to derivatize polar PAH derivatives featuring hydroxy groups (hydroxy-PAHs) and/or carboxylic acid groups (carboxy-PAHs) to trimethylsilyl derivatives to increase the sensitivity of their analysis.

For flow reactor experiments dry breathing quality air (<7 ppm H_2O), dry industrial grade nitrogen (<3 ppm H_2O) and ultra-high purity nitrogen dioxide (380.1 ppm in dry air) were obtained from Airgas (Chicago, IL, USA).

2.2. Flow reactor

The home-built flow reactor used in this study was composed of three main parts: a gas injection/dilution system, mixing chamber, and a reaction chamber (Fig. 1). The gas injection/dilution system delivered air, nitrogen, nitrogen dioxide to a mixing chamber composed entirely of Teflon (31.5 cm length × 9.0 cm I.D.) through ¼" stainless steel tubing. Two-way stainless steel valves were used for selecting the gases used in each experiment. All gas flows through the reactor system were regulated with mass flow controllers (Alicat Scientific, Tucson, AZ, USA) to achieve the desired dilution of gases. After the mixing chamber, stainless steel tees directed the flow to the reaction chamber, gas analyzer, and exhaust vent.

During ozonation experiments, ozone levels at the outlet of the mixing chamber were measured using a photometric O_3 gas analyzer (Teledyne, Thousand Oaks, CA, USA). For nitration experiments, NO_2 concentrations were measured using a chemiluminescence NO_x analyzer (Teledyne). The gas mixtures from the mixing chamber were supplied to the Teflon reaction chamber (43 cm in length × 9.0 cm I.D.) through an inlet located on top of the chamber. A quartz window was located directly above the reaction chamber inlet where a UV light bulb (356 nm) was housed for photochemical experiments. At the bottom of the reaction chamber was a Teflon-coated aluminum filter support where 90 mm quartz filters were placed for each reaction experiment. The outlet of the reaction chamber was located under the filter support. Following the outlet of the reaction chamber, two polyurethane foam (PUF) filters were placed in series to collect residual gas phase species exiting the reaction chamber. The total flow through the reaction chamber was controlled using an oil-less pump with a mass flow controller positioned between the reaction chamber and the pump. The flow drawn by the pump was always kept lower than the gas flow exiting the mixing chamber to prevent an over pressurization of the reaction chamber.