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# Identification and quantification of ozonation products of anthracene and phenanthrene adsorbed on silica particles

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## Abstract

Primary products of the reactions of gas-phase ozone with anthracene and phenanthrene adsorbed on silica model particles have been investigated. Silica was selected as proxy for mineral atmospheric particles. The particles, coated with anthracene or phenanthrene and placed on a filter, were exposed in a reaction cell to a gaseous ozone flow. Ozone concentration was constant ($(6.0 \pm 0.6) \times 10^{13}$ molecule cm$^{-3}$) during the experiments. Anthracene, phenanthrene and their ozonation products were then extracted by focused microwave-assisted extraction or fluid pressurized extraction and analyzed by gas chromatography coupled to mass spectrometry. Anthraquinone and anthrone on the one hand, and 1,1′-biphenyl-2,2′-dicarboxaldehyde on the other hand were identified as the products of anthracene and phenanthrene, respectively and quantified versus time of ozone exposure. This kinetical approach allowed to show that anthraquinone, anthrone and 1,1′-biphenyl-2,2′-dicarboxaldehyde are the primary products of the studied reactions, and to determine their formation yields (respectively, $0.42 \pm 0.04$, $0.056 \pm 0.005$ and $1.0 \pm 0.4$).

*Keywords:* Polycyclic aromatic hydrocarbons (PAH); Ozonation products; GC/MS analysis; Heterogeneous reactivity

## 1. Introduction

By penetrating inside the respiratory system, atmospheric particles, and particularly fine particles (diameter <2.5 μm), may induce physical damages and expose the human body to organic and metallic contaminants associated to the particles. Amongst the wide range of contaminants found on atmospheric aerosols, polycyclic aromatic hydrocarbons (PAHs) and by-products are intensively studied because of their potentially carcinogenic and direct-mutagenic activities. PAHs are emitted into the atmosphere mainly through incomplete combustion processes such as fossil fuel and biomass burning, and about 90% of PAH emissions are anthropogenic (Finlayson-Pitts and Pitts, 1986). Due to their low vapor pressure, PAHs are partitioned in the atmosphere between the gas and the solid phases. PAH gas/particle distribution studies have shown that gas/solid partitioning depends on the PAH vapor pressure, on the temperature, on the relative

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humidity and on the aerosol concentration (Calvert et al., 2002).

In the atmosphere, PAHs may undergo photochemical degradation and thereby form by-products, such as hydroxy-PAHs, nitro-PAHs, quinones, whose toxicity, carcinogenicity or mutagenicity have been shown to be elevated (Calvert et al., 2002). In this work, ozone was chosen as the chemical oxidant as it is measured at high concentrations in the troposphere, and as it may be present in some urban areas concomitantly with high PAH level emissions. Some kinetic data are already available in the literature for the reactions of particulate PAHs with ozone (Kamens et al., 1985; Alebić-Juretić et al., 1990; Pöschl et al., 2001; Kwamena et al., 2004, 2006; Perraudin et al., 2007) and the rate constants reported highlight that these reactions are relevant under atmospheric conditions. Consequently, the reaction products need to be identified in order to assess the atmospheric and health impact of gas–solid PAH ozonation. The identification of some PAH ozonation products has already been reported for liquid-phase reactions, involving benzo[*a*]anthracene (Yao et al., 1998a), pyrene (Yao et al., 1998b), acenaphtene (Rivas et al., 2000), chrysene (Luster-Teasley et al., 2002), and anthracene (Mmereki et al., 2004). Concerning gas–solid reactions, the previous studies focused mainly on benzo[*a*]pyrene (Pitts et al., 1980; Van Cauwenberghe et al., 1984; Letzel et al., 1999). Only a very recent study was published on both kinetics and product yield of ozonation of anthracene but adsorbed on Pyrex tubes (Kwamena et al., 2006).

The present study reports the identification of phenanthrene and anthracene gas-surface heterogeneous ozonation products. Anthracene and phenanthrene were selected because of their both atmospheric relevance and the lack of data about their heterogeneous reactivity. Particulate concentrations of phenanthrene and anthracene were determined to be, respectively, equal to $17.0 \pm 2.8$ and $0.038 \pm 0.008\,\mu\mathrm{g\,g^{-1}}$ in diesel exhaust reference material (May and Trahey, 2000) and $4.14 \pm 0.37$ and $0.432 \pm 0.082\,\mu\mathrm{g\,g^{-1}}$ in urban dust reference material (May and Trahey, 2001). Phenanthrene is amongst the most abundant particulate PAHs, whereas anthracene is about 10 times less abundant (Calvert et al., 2002). Moreover, as two isomers, the influence of the structure of the molecule on the product distribution was finally discussed. The choice of the particle surface for such study of atmospheric gas/solid reactions is particularly difficult considering the criteria of repeatability and representativity. Atmospheric particles may contain such a complex mixture of inorganic and organic compounds, such as alkanes, alkenes, aromatics, halogen organics as well as oxygenated and nitrated derivatives (Finlayson-Pitts and Pitts, 1986), that it is not possible to properly study a single reaction and isolate the products formed along this reaction. To avoid any interference, simple and well-characterized particles were considered to be better proxies for atmospheric particles than macroscopic surfaces. Similarly to previous works (Wu et al., 1984; Alebić-Juretić et al., 1990; Murray et al., 1991; Underwood et al., 2001), silica particles were selected to model mineral atmospheric particles. As a matter of fact, silicon, along with aluminum and calcium, is one of the most frequent element in inorganic continental particles (Carrico et al., 2003; Murr and Bang, 2003; Sobanska et al., 2003), the $SiO_2/Al_2O_3$ ratio in mineral dust varying usually between 2.5 and 3.5 (Putaud et al., 2004).

## 2. Material and methods

### 2.1. Particles

The silica particles (IT70-5, Interchim) selected for this study have well-defined granulometric properties (diameter = $5\,\mu\mathrm{m}$, average pore size = 70 Å, specific surface area = $500\,\mathrm{m^2\,g^{-1}}$). The particles were first cleaned by ultrasonication (3 times) in dichloromethane (Ultra resi-analyzed JT Baker, Atlantic Labo) and allowed to dry at room temperature. Anthracene and phenanthrene were coated on silica particles using liquid–solid adsorption. The coating procedure was already described in a previous work and the coating yield was measured to be higher than 80% (Perraudin et al., 2007). Particulate anthracene or phenanthrene concentrations were about $500\,\mu\mathrm{g\,g^{-1}}$. The surface coverage was calculated, assuming a homogeneous PAH deposition on the surface, to be lower than 10% of a monomolecular layer. Since particulate PAH photodegradation may occur rapidly, especially in the case of silica particles (Korfmacher et al., 1979; Behymer and Hytes, 1985), all the prepared particles were stored at room temperature, in the dark and in amber glass flasks.

### 2.2. Ozone reaction

Reactions of ozone with particulate anthracene and phenanthrene were performed using the