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Atmospheric reactions of 9,10-anthraquinone

Killian Miet [a,b], Alexandre Albinet [c], Hélène Budzinski [a,b], Eric Villenave [a,b,*]

[a] Univ. Bordeaux, EPOC, UMR 5805, F-33405 Talence cedex, France
[b] CNRS, EPOC, UMR 5805, F-33405 Talence cedex, France
[c] Institut National de l'Environnement Industriel et des RISques (INERIS), Parc Technologique Alata, BP2, 60550 Verneuil en Halatte, France

HIGHLIGHTS

- The atmospheric fate of 9,10-anthraquinone still remains unknown.
- Experiments performed for all oxidants for the first time under the same conditions.
- 9,10-Anthraquinone adsorbed on silica particles showed no reactivity with O_3 and NO_2.
- Its reaction with OH radicals led to the formation of 1-hydroxy-9,10-anthraquinone.
- (9,10-Anthraquinone + OH) reaction could have an atmospheric health impact.

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ABSTRACT

The probably carcinogenic compound 9,10-anthraquinone is mainly existing in the atmosphere in the particulate phase and is often detected and measured among other oxygenated PAHs in atmospheric samples. Its fate, once released or formed in the atmosphere, still remains unknown. In this work, heterogeneous chemical oxidation processes of 9,10-anthraquinone were investigated with ozone (O_3), nitrogen dioxide (NO_2) and hydroxyl radical (OH). The study of 9,10-anthraquinone adsorbed on silica particles showed no reactivity with O_3 and NO_2. On the other hand, the reaction with OH radicals was observed and led to the formation of 1-hydroxy-9,10-anthraquinone, another oxidation product recognized as possibly carcinogenic to humans. This study showed that reactions with ozone and nitrogen dioxide are unlikely to contribute to atmospheric degradation of 9,10-anthraquinone, whereas reactions with OH radicals could be involved in 9,10-anthraquinone degradation processes, even if such reaction is probably very slow under ambient conditions.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are organic compounds widely distributed in the environment. They are mainly emitted into the atmosphere as by-products of organic matter and fossil fuel incomplete combustion (domestic heating, automobile fuel combustion, wood burning, etc). For the most part, PAHs have an anthropogenic origin in the atmosphere and once emitted, they are present in both, gaseous form and adsorbed to particles, depending on the volatility of the PAH species. Low molecular weight compounds exist mainly in the gas phase, whereas PAHs bearing five fused rings or more are predominately adsorbed onto particulate matter (Odabasi et al., 1999; Callén et al., 2008; Albinet et al., 2008).

PAHs have been extensively studied in the gas phase and adsorbed to particles with atmospheric oxidants (Pitts et al., 1985; Estève et al., 2004; Perraudin et al., 2005, 2007a; Atkinson and Arey, 2007; Gross and Bertram, 2008; Miet et al., 2009a,b). Concerning oxidation products, which seem more toxic than the parent compounds (Durant et al., 1996; Durant et al., 1998; Pedersen et al., 2004, 2005), there is a lack of data concerning their fate. Nitrated and oxygenated PAHs are often detected in ambient air samples (Castells et al., 2003; Albinet et al., 2007, 2008; Ringuet et al., 2012a) as compounds directly emitted during combustion processes or as oxidation products formed in the atmosphere by photolysis and reaction of PAHs with oxidants (NO_x, OH, O_3, SO_x). Among such compounds, quinones are often detected in atmospheric aerosol samples (König et al., 1983; Lewis et al., 1995; Allen et al., 1997; Cho et al., 2004; Shimmo et al., 2004; del Rosario Sienra and Rosazza, 2006; Jakober et al., 2006; Albinet et al., 2007, 2008; Andreou and Rapsomanikis, 2009; Ringuet et al., 2012a) and are suspected to contribute to the toxicity of ambient particles. Their toxic effects are

* Corresponding author at: Univ. Bordeaux, EPOC, UMR 5805, F-33405 Talence cedex, France. Tel.: +33 540006350.
E-mail address: eric.villenave@u-bordeaux.fr (E. Villenave).

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often attributed to their ability to form reactive oxygen species (ROS) (Lemaire and Livingstone, 1997; Kumagai and Shimojo, 2001), but also for their mutagenicity (Chesis et al., 1984; Durant et al., 1996; Pedersen et al., 2004, 2005). Recently, the IARC has classified 9,10-anthraquinone as a group 2B chemical, signifying its carcinogenic probability to humans (IARC, 2012) and highlighting the study of the fate of this compound.

The formation of quinones has been highlighted in some works as oxidation products from PAHs by photolysis or reactions with O_3, NO_3 and OH (Helmig and Harger, 1994; Dabestani et al., 1995; Barbas et al., 1996; Mallakin et al., 2000; Kwamena et al., 2006; Perraudin et al., 2007b; Wang et al., 2007; Yu, 2002; Vione et al., 2004), leading to the formation of compounds such as 9,10-phenanthrenequinone or 9,10-anthraquinone. Despite its high concentration levels observed in ambient air, very few works investigated the fate of 9,10-anthraquinone whatever the degradation pathway.

In this work, the heterogeneous reactivity of 9,10-anthraquinone was investigated with three oxidants of tropospheric interest (O_3, NO_2 and OH). 9,10-Anthraquinone was coated on silica particles as a model for mineral particles. Atmospheric particulate matter constitutes a complex medium and silica, which constitutes an important fraction of mineral particles, allows to simplify the solid substrate (Harrison and Yin, 2000; Rodriguez et al., 2008) in order to obtain better reproductility in kinetic measurements. This kind of particle has been used in previous studies (Behymer and Hites, 1985; Alebic-Juretic et al., 1990; Barbas et al., 1996; Wang et al., 1999; Perraudin et al., 2005, 2007a; Miet et al., 2009a,b), showing that such particles constitute a good model in order to investigate heterogeneous reaction processes.

2. Experimental

2.1. Preparation of the particles

Silica particles IT70-5 were supplied by Interchim. According to their certificate of analysis, the silica particles have an average particle diameter of 5 μm and an average pore diameter of 70 Å. Their specific surface area is about 500 $m^2 g^{-1}$. The diameter of these particles is situated in the coarse particle mode. These particles have well-defined properties already detailed in a previous work by Perraudin et al. (2005).

Silica particles were first cleaned by ultrasonication using dichloromethane (HPLC grade, Acros Organics). After drying, the particles were introduced in a solution of dichloromethane containing 9,10-anthraquinone (97%, Aldrich). The solvent was then evaporated using a rotary evaporator (at atmospheric pressure and $T = 35$ °C). Coated particles were finally stored in amber glass flasks at ambient temperature until reactivity experiments.

2.2. Analytical procedures

After the addition of a surrogate standard (fluoranthene-d10, 99.2%, MSD isotopes), coated particles were extracted using pressurized fluid extraction (ASE® 200, Dionex) with dichloromethane ($P = 100$ bars, $T = 100$ °C, heat time of 5 min and 2 static extraction cycles of 8 min). Extracts were then evaporated in the ASE extract-collecting flask and changed to isooctane (HPLC Grade, Scharlau) using a vacuum evaporation system (Rapidvap, Labconco), with the following parameters: 70%, 900 mbar, 50 °C during 20 min.

After the addition of a internal standard (pyrene-d10, 98%, MSD isotopes) (used to quantify surrogate standard), samples were analysed by gas chromatography (HP model series 6890 Gas Chromatograph, Agilent Technologies) coupled to mass spectrometry (HP model 5973 mass selective detector, Agilent Technologies), using a HP-5MS capillary column (30 m × 0.25 mm ID × 0.25 μm film thickness, Hewlett Packard). The temperature program was 70 °C during 2 min up to 300 °C at a rate of 10 °C min^{-1} and held at 300 °C during 5 min. The carrier gas was helium (He 99.9999+% purity, Linde Gas) at a constant flow rate of 1 mL min^{-1}. The interface temperature was kept at 280 °C during analysis. The mass spectrometer was operating under electron impact ionisation (70 eV) and mass detection was carried out in selected ion monitoring (SIM) mode (dwell time = 100 ms, number of cycles per second = 1.16 and electron multiplier voltage = (2400 ± 50) V).

The analysis performed by GC–MS allowed to evaluate the initial 9,10-anthraquinone particulate concentration: (592 ± 27) μg g^{-1} of silica ($n = 22$). Extraction efficiencies were also determined using the surrogate standard recovery yield, obtained from its quantification related to pyrene-d10: (98 ± 3) % ($n = 22$). This value, close to 100%, shows that 9,10-anthraquinone extraction from silica particles is very efficient.

2.3. Experimental reaction setups

All experiments were performed in a total darkness to avoid any photodegradation and to only account for the 9,10-anthraquinone degradation in the reactors. 9,10-Anthraquinone oxidation was followed by measuring the remaining concentration present on silica particles versus oxidant exposure time.

2.3.1. Ozone setup

The ozone setup used in this study was developed in our laboratory by Perraudin et al. (2007a). It consists of a photolysis cell in which a mixture of nitrogen and oxygen is introduced and photolysed at 185 nm by a low pressure mercury lamp (NIQ 120/80, Heraeus SAS). The ozone concentration was controlled by varying the oxygen ratio (total flow constant at 3 L min^{-1}), and the distance between the photolysis cell and the lamp. The $N_2/O_2/O_3$ flow was then directed to the reactor in which a filter, with the coated particles, was placed. The output of the reaction cell was directed to the O_3 measurement cell (41.5 cm long), in which O_3 concentration was measured by its well-known absorption at 254 nm, the irradiation being emitted from a deuterium lamp (L7296, Hamamatsu Photonics). The monochromator (Jobin Yvon) wavelength was regularly calibrated using a low-pressure mercury lamp.

2.3.2. OH and NO_2 setup

The OH and NO_2 experimental setup was similar to that previously used in our laboratory to study heterogeneous reactivity (Estève et al., 2003, 2004; Miet et al., 2009c; Ringuet et al., 2012b). It consists of a fast flow-tube reactor (2.4 cm inside diameter/48 cm long Pyrex tube) in which a movable injector (1 cm inside diameter, 60 cm long quartz tube) slides. Gases were introduced in the main reactor through the injector, which was wall-coated inside with halocarbon wax (Halocarbon Products Corporation, series 1500) in order to minimize heterogeneous recombination on the walls. The reactor pressure was regulated by a two-stage primary pump (Alcatel T2060) and monitored with a capacitance gauge (Edwards Barocel 600, 0–10 Torr). Total pressure was held at (1.8 ± 0.1) Torr during all experiments. Total flow in the reactor was approximately 1 L min^{-1} and was laminar in all experiments based on the Reynolds number.

NO_2 concentration was controlled by dilution of NO_2 (5% NO_2 in Helium 99.995% purity, Alphagaz, Air liquide) in helium (Alphagaz 1, Air liquide) using calibrated mass flow controllers (FC260 and FC2900 Mykrolis).

OH radicals were generated in situ at the upstream of the movable injector by the fast reaction between nitrogen dioxide and a hydrogen atom, produced by hydrogen impurities from helium (Alphagaz 1, Air liquide), the main carrier gas, passing through