Atmospheric Environment 45 (2011) 917–924

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Heterogeneous reactions between NO_2 and anthracene adsorbed on SiO_2 and MgO

Jinzhu Ma, Yongchun Liu, Hong He*

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

ARTICLE INFO

Article history:
Received 27 July 2010
Received in revised form
3 November 2010
Accepted 10 November 2010

Keywords:
PAH
Anthracene
Mineral oxides
NO_2
Kinetics
Oxidation products

ABSTRACT

The heterogeneous reactions of NO_2 with anthracene adsorbed on SiO_2 and MgO were investigated under dark conditions at 298 K using DRIFTS, GCMS, and UV–Vis. The pseudo-first-order rate constants of anthracene on SiO_2 and MgO were obtained by fitting the exponential decay of adsorbed PAH concentrations versus reaction time. The reaction on SiO_2 was almost two times faster than on MgO when the concentration of NO_2 was 3.69×10^{12} molecules cm^{-3}. Both 9-nitroanthracene and 9,10-anthraquinone were the products of the nitration of anthracene adsorbed on SiO_2 whereas 9,10-anthraquinone was the only product formed by NO_2 reaction with anthracene adsorbed on MgO. These results suggest that mineral oxides not only control the reaction kinetics of PAHs with NO_2 but also alter the reaction pathway for the heterogeneous reaction of PAHs with NO_2. The difference in the heterogeneous reactivity of NO_2 with anthracene adsorbed on SiO_2 and MgO was ascribed to the formation of HNO_3 on SiO_2, which can catalyze the nitration of PAHs by NO_2. Due to the formation of nitro-anthracene and oxy-anthracene, the heterogeneous reactions of NO_2 with anthracene also altered the optical properties of the mineral oxides on which anthracene were adsorbed.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) mainly originate from incomplete combustion of fossil fuels (petroleum, natural gas, and coal) and biomass burning. The global emission of atmospheric PAHs is roughly estimated to be 0.001–0.02 $TgC\ yr^{-1}$ and about 90% of PAHs emissions are anthropogenic (Calvert et al., 2002). As ubiquitous persistent organic pollutants (POPs), PAHs and their derivatives (nitro-PAHs, oxy-PAHs, etc.) have attracted much attention due to their allergenic, mutagenic, and carcinogenic properties (Finlayson-Pitts and Pitts, 1997). In particular, nitro-PAHs have been identified as a class of very potent mutagenic compounds from environmental samples (Feilberg et al., 2001; Albinet et al., 2006; Pitts et al., 1985a; Ramdahl et al., 1986; Xu and Jin, 1984). The concentration levels range from <1 pg m^{-3} to ~ 1 ng m^{-3} and are usually a factor of 10–1000 below the parent PAHs concentrations (Feilberg, 2000). However, nitro-PAHs are typically 100,000 times more mutagenic and 10 times more carcinogenic than the corresponding parent PAHs (Onchoke et al., 2009). For these reasons it is necessary and important to identify the sources of nitro-PAHs in the atmosphere.

The presence of nitro-PAHs in environmental samples may be due to their occurrence in emissions from the above mentioned sources or by homogeneous and heterogeneous reactions in the atmosphere (Pitts et al., 1978). In the gas phase, nitro-PAHs can form by the reaction of PAHs with NO_3 or OH in the presence of NO_2 (Atkinson and Arey, 1994; Atkinson et al., 1987; Bunce et al., 1997). The reactions of PAHs adsorbed on soot (Kamens et al., 1990) or glass fiber filters (Pitts et al., 1985b) with N_2O_5 or HNO_3 also lead to the formation of nitro-PAHs. Heterogeneous reactions of PAHs adsorbed on particles with NO_2 may also be an important source of nitro-PAHs. For example, Kwamena and Abbatt (2008) found that nitration of pure anthracene and pyrene by NO_2 (406 ppb) or HNO_3 (284 ppm) under dark conditions does not occur at room temperature and ambient pressure. However, Wu and Niki (1985) revealed that the half-life of pyrene on silica plates with 1 ppm of NO_2 in N_2 was only 1.4 h at 298 K. These results imply that the substrate plays an important role in the heterogeneous reaction of PAHs with NO_2. Ramdahl and Bjørseth (1984) studied the heterogeneous reactions of PAHs adsorbed on SiO_2, Al_2O_3, and charcoal particles with NO_2 (0.5 ppm) and found that the yield of nitro-PAHs on SiO_2 was higher than on Al_2O_3, which means SiO_2 has a more reactive surface than Al_2O_3. The rate constants for the heterogeneous reaction of NO_2 with various PAHs depended on the structure of the PAHs on SiO_2 particles (from 4×10^{-8} to 1.4×10^{-3} s^{-1} (Perraudin et al., 2005)), while the rate constants were in the same order of magnitude for

---

* Corresponding author. Tel.: +86 10 62849123; fax: +86 10 62923563.
E-mail address: honghe@rcees.ac.cn (H. He).

1352-2310/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2010.11.012

different PAHs on graphite (from 2.0×10^{-3} to 8.4×10^{-3} s^{-1} (Esteve et al., 2004)) or diesel exhaust particles (from 1.7×10^{-3} to 3.2×10^{-3} s^{-1} (Esteve et al., 2006)). These results suggest that the reactivity of PAHs with NO_2 on the surface may greatly depend on the nature of the substrates. However, it is unclear that what the essence for this substrate effect is.

Mineral dust, which mainly originates from arid and semi-arid regions with global source strength of about 1000–3000 Tg yr^{-1} (Dentener et al., 1996), is one of the most important contributors to the loading of atmospheric particle matters. In the atmosphere, PAHs are able to partition between the gas phase and atmospheric particulate matter. Recently, field measurements also found that PAHs usually adsorb on mineral dust in real atmospheric particulate matter (Wu et al., 2005; Fu et al., 2009). Therefore, it is very significant to investigate the chemical behavior of PAHs on mineral dust. Unfortunately, the mechanism for how mineral dust affects the heterogeneous reactions of PAHs with NO_2 remains unclear. The reaction of NO_2 with anthracene adsorbed on MgO has never been carried out. In this study, we selected SiO_2 and MgO as model mineral particles and anthracene as the representative PAH compound to investigate the effect of mineral substrates on the heterogeneous reaction of PAHs with NO_2. The results will help understand the chemical behavior of PAHs and the source of nitro-PAHs in the atmosphere.

2. Experimental

2.1. Particles and characterization

The SiO_2 sample was prepared from SiO_2 (Degussa 304N) by calcining at 1273 K for 3 h. The MgO sample was supplied by Haizhong Chemicals Plant in Tianjin. The specific surface area of these samples was measured using Nitrogen Brunauer–Emmett–Teller (BET) physisorption (Quantachrome Autosorb-1-C). The crystalline phase for these samples were identified to be amorphous (SiO_2) and periclase (MgO) by a D/max-RB automatic powder X-ray diffractometer (XRD) using Cu Kα irradiation.

2.2. Sample preparation and storage

Before adsorption of anthracene, SiO_2 and MgO were cleaned three times by ultrasonication in dichloromethane (Chromatographic Grade), followed by drying at room temperature. The concentration of PAHs in the extract of cleaned particles and the pure solvent can not be detected by the gas chromatography–mass spectrometer (Agilent 6890/5973).

Anthracene was adsorbed on particles by the impregnation method. Approximately 1.0 g of cleaned particles was added to 20.0 mL of n-hexane (Chromatographic Grade) containing 500 μg of anthracene. After stirred homogeneously, the solvent was slowly evaporated using a rotary evaporator at 303 K. Finally, the particles were dried at room temperature for 4 h. To avoid the photodegradation of adsorbed PAHs, all particles were stored in amber glass flasks at 255 K in dark.

2.3. Reaction procedure and analytical methods

All experiments were performed under dark conditions at 298 K. A total of 20.0 mg of coated particles were evenly deposited on a Teflon disc (the geometric surface area is 3.39 cm^2), which was then placed in a quartz reactor. In the case of reaction on Teflon disc, 1.16 μg of anthracene dissolved in CH_2Cl_2 was evenly distributed on the Teflon disc. Before NO_2 was introduced into the quartz reactor, $O_2/NO/N_2$ with a given concentration was flowed through another blank reactor. The concentration of NO_2 was analyzed by an online Nexus 6700 FT-IR spectrometer equipped with a gas cell having an optical length of 2 m. When the concentration of NO_2 was stable, the feed gas was switched to the reactor containing adsorbed anthracene for reaction.

The reacted particle samples were ultrasonically extracted using 20.0 mL CH_2Cl_2 and were then filtered using a glass fiber filter, which had been previously cleaned in the same manner as the pure mineral oxides. Subsequently, CH_2Cl_2 was evaporated and changed to 1.00 mL n-hexane under a gentle stream of nitrogen gas at 293 K.

Analyses of PAHs samples were performed by a GC–MS. The column was an HP 5MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The methodology for the analysis of PAHs is similar to our previous study (Ma et al., 2010). 1.0 μL of each sample was introduced via EPC splitless mode injection. The injector temperature was 553 K. The oven temperature was held at 363 K for 2 min, then increased from 363 K to 603 K at a rate of 10 K min^{-1} and held at 603 K for 5 min. Helium was used as carrier gas at a constant flow of 1.5 mL min^{-1}. The interface temperature was kept at 553 K during analysis. For identification of the product, mass detection was performed in the scan mode (mass/charge ratio ranging from 50 to 500 a.u), while for quantification of the reactant, mass detection was performed in selected ion monitoring (SIM) mode (dwell time = 10 ms, number of cycles per second = 12.3). The m/z ratio of 178 was used for quantification ion and the m/z ratio of 177 and 176 were used for confirmation ion for anthracene, respectively. The concentration of PAHs in solution was measured based on an external standard and the use of a calibration curve. The recovery obtained from spike and recovery experiments for anthracene on SiO_2 and MgO was $(95.6 \pm 3.51)\%$ and $(96.9 \pm 5.03)\%$, respectively. Therefore, GCMS areas were corrected for 100% recovery before quantification with the calibration curve.

The diffuse reflectance spectra were recorded on a NEXUS 6700 (Thermo Nicolet Instrument Corporation) FT-IR, equipped with an *in situ* diffuse reflection chamber and a high-sensitivity mercury cadmium telluride (MCT) detector cooled by liquid N_2. The sample (about 11 mg) for the *in situ* DRIFTS studies was finely ground and placed into a ceramic crucible in the *in situ* chamber. The total flow rate was 100 mL min^{-1}, and the concentration of NO_2 was 4.43×10^{15} molecules cm^{-3}. Mineral oxides or mineral oxides coated with anthracene are used as the background to get the absorption spectra. The reference spectrum was measured in a synthesized air stream at 298 K. All spectra reported were recorded at a resolution of 4 cm^{-1} for 100 scans.

A UV–vis absorption spectrometer (U-3310 Spectrophotometer) was used to determine the absorption properties of the extract after the reaction. The samples were exposed to NO_2 at 298 K for 1 h and were then extracted and filtered using the same method mentioned above. Standard solution of anthracene in hexane was also prepared. Spectra were collected over a wavelength range of 190–650 nm at an interval of 1 nm and a scan speed of 600 nm min^{-1}.

2.4. Chemicals

All chemicals were chromatographic grade and used without further purification. CH_2Cl_2 and n-hexane were obtained from Baker Analyzed and Dima Technology Inc. Anthracene (99%), anthraquinone (99.5%), and 9-nitroanthracene (100 μg mL^{-1} in Toluene) were purchased from Acros Organics, Dr. Ehrenstorfer GmbH, and AccuStandard Inc., respectively. Polynuclear aromatic hydrocarbon mix (the purity of anthracene was 100% and the prepared and certified analysis concentration of anthracene was 100 and 100.3 μg mL^{-1}, respectively), which was used as the standard for calibrations, was purchased from AccuStandard, Inc. High purity N_2 (99.99%) and O_2 (99.99%) were supplied by Beijing