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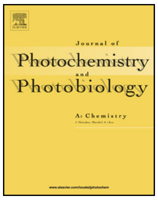

Heterogeneous photochemistry of gaseous NO_2 on solid fluoranthene films: A source of gaseous nitrous acid (HONO) in the urban environment

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ABSTRACT

Using a coated flow tube equipped with several near-ultraviolet emitting lamps, (range 300–420 nm), we examined the effect of actinic radiation on the heterogeneous loss kinetics of gaseous nitrogen dioxide on solid Polycyclic Aromatic Hydrocarbon (PAH) films deposited on a Pyrex substrate. The PAH studied was mainly fluoranthene, with additional tests on phenanthrene and pyrene. No dependence of the uptake coefficient (γ) was observed either with temperature, or with relative humidity. In the dark, the reaction was very slow but was greatly enhanced by increasing the UV-A light intensity. A linear dependency of the reaction kinetics with the photonic flux was observed. Under atmospherically-relevant NO_2 concentrations (20 ppbv), the uptake coefficient was about 1×10^{-6}. The uptake coefficient variation as a function of the NO_2 concentration suggests a Langmuir–Hinshelwood (L–H) type mechanism. This is characterized by the adsorption of NO_2 on the solid surface followed by a chemical reaction. The corresponding equilibrium constant (K') and the surface reaction rate constant (k_s^1) were found to be 3×10^{-2} ppbv^{-1} and 5×10^{-5} s^{-1} respectively for the photo-enhanced uptake of NO_2 on the fluoranthene substrate. Particular attention was given to the detection of the gas-phase products showing the photo-enhanced reduction of NO_2 to HONO and NO via a photosensitized reaction involving excited states of the PAH. Additionally we investigated the reactivity of PAH in the presence of nitrates in order to better understand if HONO generation mechanism could be explained by a first deposition of nitrates (generated via NO_2 hydrolysis) on the solid surface.

1. Introduction

Organic compounds constitute a moderate to a high fraction of the atmospheric aerosol particles but are also present in urban grime, on urban surfaces such as windows or walls [1,2]. These biogenic and anthropogenic compounds are mainly derived from biomass and fossil fuel combustion [3–6].

Polycyclic Aromatic Hydrocarbons (PAHs), are an important class of organic compounds characterized by a molecular structure with at least two fused aromatic rings and by toxic, carcinogenic or even mutagenic properties [7].

PAHs are emitted by various sources such as domestic activities, transportation (engine combustion, soot), industrial and agricultural processes, and finally natural sources (biomass burning, volcanoes). High temperatures reached during combustion lead to ubiquitous presence of PAHs with peak concentrations measured at urban sites with both traffic and nearby industrial installations.

PAHs undergo several transformation processes as well as physical and chemical removals, among them wet and dry depositions are all important. Large PAHs i.e., those containing 5 or more rings, have low vapor pressure and consequently they partition on any preexisting surfaces. Accordingly, those PAHS are mainly found on surfaces (building and aerosols, and mainly soot). Lighter PAHs, those containing 2 or 3 rings, are almost entirely present in the vapor phase. Intermediate sized PAHs (4 ring) are mainly surface-bound but can be affected by temperature changes and therefore show high seasonal variations.

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Due to their adsorption onto atmospheric particles, PAHs can act as important reactants in homogeneous [8] as well as in heterogeneous reactions with atmospheric oxidant gas such as O_3, HNO_3, $^{\bullet}OH$, $NO_3^{\bullet}$ or NO_2 [9–12].

Among these, the studies of ozone reactions with PAHs have provided the greatest amount of kinetic insight, as most of these have spanned a wide range of ozone concentrations [11,13–17], on a variety of surfaces, indicating that such reactions proceed via a Langmuir–Hinshelwood (L–H) mechanism that involves two processes: (1) equilibrium partitioning of the gas phase oxidants between the gas phase and the surface and (2) surface reaction between the oxidant and the adsorbed molecule, e.g., the PAHs. The same mechanism seems to hold for most of the systems studied to date, as well as all substrates, solid and liquid. Although heterogeneous reactions of PAHs with nitrogen dioxide have been studied for thirty years [18–20], no extensive kinetic studies over a large range of gas phase NO_2 concentrations have been published.

Moreover, these heterogeneous reactions can be considered as sources of HONO [21] which plays a fundamental role as a $^{\bullet}OH^{\bullet}$ precursor via its photolysis ($\lambda < 400$ nm) during daytime. Despite its importance, sources of HONO remain partially unresolved and it is commonly assumed that HONO formation is due to heterogeneous processes involving NO_x ($NO + NO_2$) [22]. Recently, we demonstrated that photosensitized processes on interfaces relevant to the atmosphere could enhance the conversion of NO_2 into significant amounts of both NO and HONO [23].

To date, only a handful of studies have investigated the effect of solar radiation upon the heterogeneous reaction of NO_2 on solid PAH surfaces [24,25] and many questions on the atmospheric fate of PAHs remain.

The aim of this study was to extend our knowledge of photosensitized processes involving PAHs by investigating the heterogeneous reactivity between gaseous NO_2 and mainly solid fluoranthene, with additional tests on phenanthrene and pyrene films, under UV-A irradiation by means of a coated-wall flow-tube.

2. Materials and methods

2.1. Coated-wall flow tube experiments

The heterogeneous reaction of NO_2 on solid fluoranthene films was investigated in dark and illuminated conditions by means of a coated wall flow tube. This technique has been previously used to study the photosensitized reactions of oxidants gases on organic films [21,26]. Experiments were performed in a thermostat-controlled Pyrex tube reactor (internal diameter of 1.1 cm, length 20 cm *i.e.*, a surface of 69 cm^2) surrounded by four UV-A lamps (Philips Cleo 20W) having a continuum emission within the range 300–420 nm. The spectral irradiance reaching the reactor surface, reported in Fig. 1, was measured by putting inside the flow tube an optical fiber coupled to a CCD camera (Andor Shamrock) and by calibrating the acquired spectrum with a reference deuterium lamp (DH-2000, Ocean Optics). Using four lamps, a total flux of 9.5×10^{14} photons cm^{-2} s^{-1} was measured in the wavelength range 300–420 nm.

A new solid PAH film was prepared before each experiment by introducing 250 μL of PAH in a methanol solution (5 g L^{-1}) and evaporating the solvent to dryness under a dry N_2 stream. This corresponds to a solid deposit of 18 μg cm^{-2}.Taking into account the respective molecular surface area of each PAH (*ca.* 200 $Å^2$) [27], we can estimate that in our experiments approximately a thousand layers of PAH were deposited on the inner surface of the tube.

A mixed film (PAH/KNO_3) was prepared following the same procedure before each experiment by introducing in the cylindrical Pyrex tube an aliquot (500 μL) of a methanolic solution containing a PAH (24.7 mmol L^{-1}) and KNO_3 (148.3 mmol L^{-1}).

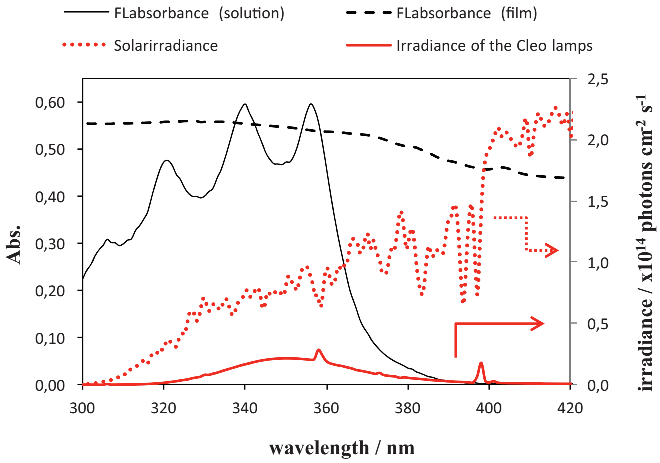

Fig. 1. Absorbance of fluoranthene in solution in methanol (5 g L^{-1}) (black solid line) and in a solid film (black dashed line – arbitrary units); red solid line shows the irradiance of the Cleo lamps in the range 300–420 nm (right axis) with a total emission intensity of 9.5×10^{14} photons cm^{-2} s^{-1}. Red dashed line represents the sun emission at the Earth surface (total intensity of 1.9×10^{16} photons cm^{-2} s^{-1} in the range 300–420 nm). The data presented for the solid film are presented in arbitrary units, and cannot directly be compared to the absorbance in solution, but they highlight a slightly broader absorption spectra as compared to the monomeric fluoranthene. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

A mixture of gaseous NO_2 with dry or humidified N_2 was introduced inside the reactor via a movable injector (internal radius of 0.3 cm) at a flow rate of 275 mL min^{-1}. Temperature and relative humidity were checked using a SP UFT75 Sensor (Partners BV) positioned before the reactor. Indirect quantification of HONO was possible during heterogeneous reactions by means of a sodium carbonate denuder tube (30 cm × 0.6 cm ID glass tube). In fact, the molybdenum converter of the NO_x analyser reduces HONO and NO_2 to NO before chemiluminescence detection and measures NO_y species (NO, NO_2 and HONO) with an equal analytical response. To avoid interferences from HONO when measuring NO_2, the gas flow exiting the reactor may be passed through the sodium carbonate denuder tube to trap HONO, allowing the measurements of NO_2 alone. By bypassing the carbonate denuder the sum of NO, NO_2 and HONO species is measured and HONO can be quantified as the difference between these two signals.

2.2. Chemicals and gases

NO_2 (1 ppmv in N_2; 99%) and N_2 (99.9%) were purchased from Alphagaz (France) and were used via Teflon tubing without further purification. The gas flows were controlled by a digital mass flow meter (Brooks Instruments). Deionised water (18 MΩ cm) was used to humidify the N_2 gas steam. Methanol was purchased from Merck (HPLC grade), fluoranthene (FL), phenanthrene (PH) and pyrene (PY) from ACROS Organics (>97%) and KNO_3 from Sigma–Aldrich (99%), and used without further purification. The UV–vis spectrum of the fluoranthene in methanol solution (5 g L^{-1}) is given as an example in Fig. 1 showing the overlap with the emission spectrum of the adopted irradiation system. When PAHs are deposited as solid films, they form complexes, and any photolysis or photosensitization that occurs is likely due to the complexes rather than to the monomers. Therefore, we also reported in Fig. 1 the UV–vis spectrum of a solid film of fluoranthene. The latter exhibits a wider unstructured spectrum which dominates absorption. In other words, it is likely that the complexes play a key role in the chemistry discussed below.