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Heterogeneous light-induced ozone processing on the organic coatings in the atmosphere

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ABSTRACT

Many of the more recent studies concerning heterogeneous reactions of atmospheric interest, carry, in some cases, much more details but still follow the basic philosophy of the first pioneering studies. Therefore, in this study the accent is put on the additional complexities that arise when the aerosols of interest have more complex compositions. Hence, it is attempted to identify the products following the simultaneous ozone processing and light irradiation on particles coated with 4-phenoxyphenol in the presence of 4-carboxybenzophenone as a photosensitizer. In order to reveal a more complete picture on the fate of these aromatic compounds under controlled experimental conditions, different analytical tools such as gas chromatography coupled to mass spectrometry (GC–MS) and proton transfer reaction-mass spectrometry (PTR-MS) have been applied.

Several surface bound products were identified via GC–MS and some of them (phenol, hydroquinone, catechol, 4-hydroxybenzoic acid, benzoic acid, fumaric acid, terephthalic acid, maleic acid, 1,2,4-trihydroxybenzene and 4,4′-oxydiphenol) confirmed with standards. The main volatile secondary products as identified by PTR-MS in this study were formic acid, phenol and *p*-benzoquinone.

A reaction mechanism was proposed and density functional theory calculations were performed in order to elucidate the initial steps of the ozonolysis reaction on 4-phenoxyphenol in the presence of 4-carboxybenzophenone.

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1. Introduction

During the past years there has been a surge of interest towards heterogeneous ozone and OH processing on the atmospheric aerosol surfaces (Bertram et al., 2001; Mmereki and Donaldson, 2003; McIntire et al., 2005; Kahan et al., 2006; Kwamena et al., 2007; McNeil et al., 2007; Vlasenko et al., 2008) but only a few studies (Park et al., 2006; Gomez et al., 2006; Jammoul et al., 2008) focused on the light-induced heterogeneous reactions.

Light-induced (photosensitized) heterogeneous reactions taking place on the surface of the atmospheric aerosols are extremely important because they can significantly impact the surface properties of the aerosols (Nieto-Gligorovski et al., 2008) and change its hygroscopicity. Consequently, the resulting aerosols can serve as cloud condensation nuclei, and cause significant perturbations to the transfer of infrared and UV–vis light in the atmosphere via their ability to either scatter or absorb the solar radiation (Rudich, 2003).

On the other hand, particle surface coatings are likely to play an important role in the toxicity and corresponding safety assessments of nanoparticles (Warheit, 2004). Atmospheric aerosols from biomass burning include a significant amounts of phenols, substituted phenols (4-phenoxyphenol (4-PP)) and photosensitizers, such as quinones and aromatic carbonyls (4-carboxybenzophenone (4-CB)), which may be also products of PAH photolysis (Simoneit et al., 1993; Jang and McDow, 1995; Jang and McDow, 1997; Anastasio et al., 1997; Vione et al., 2006). It was shown that, in solution, the excited triplet states of aromatic carbonyls such as 4-carboxybenzophenone can be efficiently quenched by phenols and substituted phenols (Canonica et al., 2000). It is therefore assumed that the same mechanism might occur on the surface or in the bulk of the atmospheric aerosols. Hence, the degradation processes of phenols and substituted phenols that hardly absorb light above 290 nm could be efficiently mediated by photosensitizers. The efficiency of such reactions depends on the number of reactive species produced by excitation

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of the photosensitizers as well as on the ability of these compounds to interact with the phenolic substances (George et al., 2005; Kahan et al., 2006; Jammoul et al., 2008; Nieto-Gligorovski et al., 2008).

A number of studies have been devoted on the photochemical reactions that could possibly lead to the formation of macromolecular substances (humic-like substances, HULIS) (see the reviews of Rudich, 2003 and Vione et al., 2006 with the references therein). The molecular masses of such compounds range between 300 and 700 Da similarly to the HULIS extracted from atmospheric aerosols collected during field measurements (Havers et al., 1998; Kiss et al., 2005; Hoffer et al., 2005). Moreover, HULIS are known to absorb solar radiation in the visible range and consequently influence the climate on a regional and a global scale.

In a previous paper (Nieto-Gligorovski et al., 2008), it was reported that heterogeneous reactions of ozone and 4-PP in presence of 4-CB as a photosensitizer efficiently lead to the formation of hydrophobic molecular structures which were associated to the HULIS substances. This work is a continuation of our effort to increase the knowledge on photosensitized reactions which take place on the aerosol surfaces.

Spectra were taken before and after the simultaneous ozone and light exposure of the organic coatings which were either 4-phenoxyphenol or mixtures of 4-phenoxyphenol/4-carboxybenzophenone. These spectra were obtained using gas chromatography–mass spectrometry (GC–MS) coupled to a derivatization analytical technique. A number of secondary products have been identified and, in many cases, the identifications were confirmed with the corresponding standards. Proton transfer reaction-mass spectrometry (PTR-MS) was used for the analysis of the gas-phase products in those photosensitized heterogeneous reactions. In addition, density functional theory (DFT) calculations were performed to provide additional insights into the photosensitized heterogeneous chemistry. The reaction mechanism was proposed and discussed in detail.

In fact, the reaction system proposed in this work can both contribute to the formation of small secondary organic products and serve as alternative pathway for the formation of HULIS. This original mechanism is of atmospheric relevance in the sunny and dry, ozone polluted regions that are impacted by biomass burning. Although not well characterized, it is now clear that the variation of the adsorbed organic material on aerosol surfaces is dramatically altered upon the ageing processes. These variations of the organics on the aerosol surfaces play an important role in many issues, such as the direct and indirect climate changes, adverse health effects from inhaled particles, effects on cloud droplet chemistry, and ozone production.

2. Materials

In this study, AEROSIL®R812 (Evonik, France) was used with purity ≥99.8%, average size of 7 nm and specific surface of $260 \pm 30\ \mathrm{m^2\,g^{-1}}$.

The standards for the identification of the following compounds: 4-carboxybenzophenone, 4-phenoxyphenol, phenol, hydroquinone, catechol, 4-hydroxybenzoic acid, benzoic acid, fumaric acid, terephthalic acid, maleic acid, 1,2,4-trihydroxybenzene and 4,4′-oxydiphenol were provided from Sigma–Aldrich with purity ≥99%.

3. Experimental setup

3.1. Coating preparation and experimental procedure

The heterogeneous processing takes place in a rotary photoreactor where the particles of any size can be rotated in a bulb which is transversally irradiated by the light source.

In general AEROSIL is a fine, white, light and amorphous powder consisting of primary particles in the nanometer range (7–16 nm), resulting in a very large specific surface area (from 100 to $260\ \mathrm{m^2\,g^{-1}}$). The primary particles are not isolated but are fused together in relatively stable chain-like aggregates, which in turn form larger agglomerates in the micrometer range. The average specific surface of this silica particle is much higher than the values generally measured for natural mineral particles. Underwood et al. (2001) have reported surface specific values of 3.1 and 11.0 $[\mathrm{m^2\,g^{-1}}]$ which correspond to the sand particles of the Sahara and dust of Gobi Desert, respectively. However, the highly polar surfaces of commercial silica particles such as AEROSIL®R812 may simulate to a first approximation, inorganic oxide aerosols found in the environment (Barbas et al., 1996).

A stock solution of 4-phenoxyphenol (99%, Sigma–Aldrich, Germany) and 4-carboxybenzophenone (99%, Sigma–Aldrich, Germany) at 1:1 molar ratio with a total concentration of $\approx 1\ [\mathrm{mg\,ml^{-1}}]$ in dichloromethane (99,9% HPLC grade, Sigma–Aldrich, Germany) was prepared in advance. Ten milliliter of this solution was mixed with 1 g of Silica particles Aerosil®R812, in a pyrex bulb with a volume of $500\ \mathrm{cm^3}$. This bulb was wrapped with the aluminum foil and attached to a rotary evaporator where the particles were dried about 40 min at 40 °C and 850 mbar, obtaining surface concentrations of 4-PP and 4-CB of $\approx 2\ [\mathrm{ng\,cm^{-2}}]$ for the experiments. An initial coating of 1% (w/w) (mass fraction of organics compared to the carrier) from fused silica particles Aerosil®R812 of both compounds, the reactant and the photosensitizer, was achieved.

The dried coated solid particles were then exposed to the simulated sunlight emitted from a broadband continuous light source such as a xenon lamp (300 W) at distance of 10 cm from the bulb. The rotation of the bulb ensured a homogeneous irradiation of the particles during the whole experiment. Simultaneously, an ozone flux with mixing ratios ranging between 250 ppb and 6 ppm in air flowed throughout the bulb. The production of ozone was achieved via commercial ozone generator (UVP, LLC Upland, UK). This ozone generator is based on O_2 photolysis by mercury penray lamp which is inserted into the radiation housing. The increase of ozone mixing ratio up to 6 ppm was essential to obtain a significant ozonolysis of 4-PP and 4-CB in the time frame of the experiment, which enabled us to clearly identify the reaction products.

3.2. GC–MS analysis

After a reaction time ranging between 2 and 12 h, the particles were solvent extracted in dichloromethane for 15 min by sonication (Branson 3510, USA). The obtained extracts were filtered with iso-disc filters (Sigma–Aldrich, France). Finally, the clear solutions were analyzed by GC–MS using electron impact ionization (70 eV) according to the following parameters: column: THERMO TR-5MS (internal diameter 0.25 mm, length 30 m, film thickness 0.25 μm), injection volume: 1 μl, inlet temperature: 250 °C, interface temperature: 330 °C, with the following temperature program: hold 1 min at 80 °C; increase temperature to 220 °C at a rate of 15 °C/min; increase temperature to 300 °C at 25 °C/min; hold 15 min at 300 °C. The samples were injected in the splitless injection mode. The injector was switched to split mode 1 min after an injection was made.

3.3. Derivatization technique associated with GC–MS

The reactant 4-PP and the photosensitizer 4-CB along with the reaction products contain various mono- and poly-functional groups. It is therefore very difficult to identify them directly by GC–MS analysis.

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