Photo-Induced OH Reactions of Naphthalene and Its Oxidation Products on SiO₂

Claire Brusso¹,², Matthew Duane¹, Patrick Carlier², Dimitrios Kotzias¹

¹Joint Research Centre, European Commission, TP 290, I-21020 Ispra (VA), Italy
²LISA, Université Paris VII, bat 44-45, 2 place Jussieu, F-75251 Paris cedex 05, France

Abstract

The photo-induced degradation of naphthalene, 1,4-naphthoquinone, 1-naphthol and 1-NO₂ naphthalene, adsorbed on silica gel, and with the addition of nitrogenous air pollutants e.g. NO₂ (as KNO₂) was investigated. Results indicate that compounds adsorbed onto a solid carrier are degraded when irradiated with UV light (λ > 290 nm) in the presence of nitrites. The key species initiating the naphthalene degradation is the OH-radical which is generated through the photolysis of NO₂. Reaction products identified were 2-formyl-cinnamaldehyde, 1,4-naphthoquinone, nitronaphthol, o-phthaldialdehyde, phthalide and nitronaphthalene. A mass balance between 40 - 50% was achieved.

Under the same irradiation conditions, 1-NO₂ naphthalene is mainly degraded by direct photolysis while degradation of 1-naphthol and 1,4-naphthoquinone proceeds via the reaction with OH-radicals. Identified products were hydroxy- nitro- nitroso- and quinones compounds.

Keywords: 1-naphthol; 1-NO₂ naphthalene; heterogeneous reactions; naphthalene; nitrite; silica gel

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants in urban and remote atmospheres. They are formed by the combustion of almost any fuel under oxygen-deficient conditions and may be transported through the atmosphere in the vapour phase and/or adsorbed on particulate matter. When adsorbed on particulate matter, and through interaction with the active centres of the solid carrier, PAHs are subjected to changes in their physicochemical properties. In the presence of other atmospheric constituents (e.g. NO₂, NOₓ salts) adsorbed on the solid carrier, additional reactions can take place which finally lead to the degradation of PAHs and the formation of PAH oxidation products with different toxicological properties from those of the parent compounds.

In this work, the photo-induced reaction of naphthalene adsorbed on silica gel and with the addition of nitrite salts (as KNO₂) was investigated. Silica gel was used as a model solid carrier, while NO₂ (as KNO₂) was selected as a representative of the nitrogenous air pollutants. Naphthalene was chosen as a model compound because of its high abundance in the atmosphere. Even if naphthalene due to its volatility remains to a high extent, heterogeneous reactions of it on the surface of particles in the polluted urban atmosphere are possible, once emitted in the vapour phase. The derivatives of naphthalene (1-naphthol, 1,4-naphthoquinone and 1-NO₂ naphthalene) were irradiated under the same conditions applied to naphthalene as well, in order to acquire additional information on the degradation pathway of PAHs adsorbed on particulate matter.

2 Experimental Section

The compounds adsorbed on the silica gel at levels of approximately 100 to 150 mg compound/g substrate were irradiated in a double chamber photo-reactor made of Pyrex glass [1]. In the first chamber, the compounds were irradiated in the presence of water only (130 mg H₂O/g SiO₂). In the second chamber, about 11 mg of KNO₂ were dissolved in water and added to the compound/silica gel mixture. The UV light, generated by a Philips HPK 125W mercury lamp, was filtered through a Pyrex coolfinger (λ > 290 nm). Irradiation times were 2 and 5 hours.

In the presence of water and UV light, KNO₂ generates OH radicals through the photolysis of NO₂ according to reaction (1):

\[ \text{NO}_2 + \text{H}_2\text{O} + \text{hv} \rightarrow \text{NO} + \cdot \text{OH} + \text{OH} \] (1)

At the end of the irradiation process, the silica gel/compound mixture was extracted consecutively with 50 ml CH₂Cl₂ and 50 ml of ether using an ultrasonic bath. The extracts were concentrated to 2 ml and a GC/MS analysis was performed. Samples were then evaporated to dryness and dissolved in 2 ml methanol. An LC/MS analysis was performed subsequently.

For the GC/MS analysis, the following procedures were used: 1 µl of the extracted was on-column injected into a HP5890 GC equipped with SE-54 column (50 m x i.d. 0.32 mm, 0.4 mm). The temperature was programmed from 40°C (3 min) to 220°C (10 min) with a rate of 5° min⁻¹. The MS detector (HP5972), equipped by a Electron Impact source,
was operated in scan mode from m/z 60 to 300. For LC/MS analysis, aliquots (50 μL) of the solution were loop injected into a Thermo Separation HPLC coupled to a Finnigan Mat LCQ ion-trap mass spectrometer. The HPLC, equipped with a Nova-pak C18 column (Waters, 30 cm x 3.9 mm), ran in the gradient mode (CH3OH/H2O at 0.8 ml/min) programmed from 30% to 95% CH3OH in 35 min. For hydroxy-compound analysis, the outlet of the HPLC was split (3:1) to the ESI interface in a negative mode. For the analysis of nitrogenous and oxygenated derivatives, the HPLC was interfaced to the ion-trap through an atmospheric pressure chemical ionisation (APCI) source in a positive mode. Additional details regarding the LCQ conditions are given elsewhere [2].

3 Results and Discussion

Naphthalene

Direct photolysis of naphthalene constitutes a minor degradation pathway; even after 5 hours of irradiation, no degradation was observed (→ Table 1). In the presence of KNO2, approximately 15% of naphthalene reacted to form mainly three compounds: 2-formyl-cinnamaldehyde, nitronaphthol, and 1,4-naphthoquinone. Others products such as 1-naphthol, NO2-naphthalenes, o-phthaldialdehyde and phthalide were detected at lower levels. A mass balance of 40-50% was achieved (→ Fig. 1). Part of these compounds were also described in the work of Guillard et al. [3]. They were produced by the photodegradation of naphthalene adsorbed on TiO2, Fe2O3, muscovite and fly ash using UV light > 340 nm. Under the conditions used in the studies of Guillard et al. [3], direct photolysis of the adsorbed naphthalene was excluded. In our study, the initial step of the naphthalene degradation on silica gel is mainly the OH radical attack. The products formed were also identified in the gas phase reaction of naphthalene with OH radicals [4,5]. However, it seems that more 1,4-naphthoquinone and 2-NO2-1-naphthol are produced by naphthalene reaction on surfaces compared to the gas phase reaction [5,6].

1-naphthol, 1,4-naphthoquinone and 1-NO2 naphthalene

Irradiation of 1-naphthol, 1,4-naphthoquinone and 1-NO2 naphthalene adsorbed on silica gel in the presence of water leads to degradation rates which, after 2 hours of irradiation, ranged from a few percent for 1-NO2 naphthalene to 15% for 1-naphthol and 1,4-naphthoquinone (→ Table 1). The 1-naphthol reaction yielded mainly to 1,4-naphthoquinone (approx. 50%) and the 1-NO2 naphthalene reaction produced low concentrations (less than 6%) of 1,4-naphthoquinone, nitro naphthol and 2-naphthol. No 1,4-naphthoquinone reaction product was identified.

1-naphthol and 1,4 naphthoquinone are partly subject to direct photolysis which explains their degradation without KNO2 conditions. The degradation rates of 1-naphthol and 1,4-naphthoquinone, however, significantly increased when KNO2 was added to the system, leading to the formation of nitrated derivatives for 1-naphthol (→ Fig. 2). Although no additional 1-NO2 naphthalene degradation was noticed, a new product tentatively identified as a dinitro-naphthol was detected at high levels in the presence of KNO2.

Table 1: Degradation rate (in %) of adsorbed naphthalene, 1-NO2 naphthalene, 1-naphthol and 1,4-naphthoquinone on silica gel and irradiated with and without KNO2

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<thead>
<tr>
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<th>2 h irradiation</th>
<th>5 h irradiation</th>
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<tr>
<td></td>
<td>hv</td>
<td>hv + KNO2</td>
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<td></td>
<td></td>
<td>hv</td>
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<tr>
<td>naphthalene</td>
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<tr>
<td>1-naphthol</td>
<td>15</td>
<td>75</td>
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<tr>
<td>1-NO2 naphthalene</td>
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<td>&lt; 5</td>
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<tr>
<td>1,4-naphthoquinone</td>
<td>15</td>
<td>30</td>
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Fig. 1: Products observed and their formation yields from the photoinduced OH reaction of naphthalene in an absorbed phase (in the presence of KNO2)

Fig. 2: Reaction products of 1-naphthol and 1-NO2 naphthalene adsorbed on silica gel