



# Phototransformations of dinitropyrene isomers on models of the atmospheric particulate matter



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## HIGHLIGHTS

- Photodegradation rates of 1,6 and 1,8-dinitropyrenes.
- Photoproducts adsorbed onto models of the atmospheric particulate.
- Structural differences and the environment affect the photoreactivity of dinitropyrenes.
- Formation of hydroxynitropyrenes and pyrenediones principal products.
- The photochemistry of adsorbed dinitropyrenes is compared to that in acetonitrile.

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## ABSTRACT

The 1,6 and 1,8-dinitropyrenes (DNP) isomers are strong mutagens and carcinogens encountered in diesel exhaust and airborne particles. Relative photodegradation rates were determined and some products were characterized when these isomers were irradiated adsorbed onto models of the atmospheric matter. These are compared to their photochemical behavior in a polar nonprotic solvent. The 1,8-DNP isomer is three times more reactive than the 1,6-DNP when irradiated adsorbed onto silica gel surfaces, while the reverse order is observed in solution, demonstrating the influence of structural differences and environmental effects on the photoreactivity. Oxygen is a key factor in the formation of pyrenediones from 1,8-DNP in solution and on silica gel which is not the case for 1,6-DNP. The average pore diameter (2.5 versus 6.0 nm) of the silica surfaces induces a significant change in the product distribution and relative yields of 1,8-DNP because pyrenediones or 8-hydroxy-1-nitropyrene are not produced in the smaller pore silica. A 6-hydroxy-1-nitropyrene product is observed both in acidic alumina and silica (6.0 nm) surfaces. On acidic alumina the rates of phototransformation of the isomers are equal, a significant increase in the relative yield of the hydroxynitropyrene product is observed compared to the silica and unidentified products in which the absence of NO<sub>2</sub> and pyrene absorption bands were observed, demonstrating the surface effect on the photodegradation. Overall, the presence of some products indicates the occurrence of a nitro-nitrite rearrangement on the surface with the participation of a pyrenoxy radical as their precursor.

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## 1. Introduction

In the atmosphere pollutants are in the gas phase or adsorbed onto particulate matter, where thermal and photochemical reactions are the major degradation pathways. The atmospheric particulate matter is a complex matrix of directly and indirectly emitted pollutants. The latter are formed from the reaction or interaction of primary pollutants with other components of the

atmosphere such as OH radicals and NO<sub>x</sub>. The high levels of morbidity and mortality of people exposed to high concentrations of the atmospheric particulate matter has made it a primary pollutant (Cohen, 2000). These detrimental health effects are mainly related to the presence of respirable mutagens and carcinogens.

The observed direct mutagenic activity of particulate organic matter cannot be only attributed to the presence of polycyclic aromatic hydrocarbons (PAHS), but also to the nitropolycyclic aromatic hydrocarbons (NPAHS) (Tokiwa et al., 1987; Finlayson-Pitts and Pitts, 1997). These can be primary pollutants that originate from the incomplete combustion of fossil fuels and other organic

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matter. Also, they can be secondary pollutant products of the photochemical reactions of parent PAHs with OH and NO<sub>x</sub> radicals (Arey et al., 1986). Nitroarenes containing four or more fused aromatic rings, such as nitropyrenes, are almost entirely found in fine and ultrafine (<2.5 μm) particles of ambient air (Schuetzle, 1983). Thus, significant attention has been directed to 1,6-dinitropyrene (1,6-DNP) and 1,8-dinitropyrene (1,8-DNP) because these compounds are among the strongest bacterial mutagens so far reported in the literature and have shown to be carcinogenic in experimental animals. These dinitropyrenes were first found in Xerox toners (Rosenkranz et al., 1980) and have been detected in diesel exhaust particles (Hayakawa et al., 1994, 1995a,b) and airborne particles in Japan (Hayakawa et al., 1995a,b; Kuo and Chen, 2000), as well as in precipitation, and soil indicating their persistence in the environment in different matrices. Although their atmospheric concentration is much lower than those of their parent PAH, their contributions to the total mutagenicity and carcinogenicity of the atmospheric particulate matter are significant.

It is known that these DNPs reach the atmosphere and interact with sunlight, although limited work has been done in terms of understanding the phototransformation mechanisms of DNPs. Work done has focused mainly on their separation and identification from diesel exhaust emissions and atmospheric particulate samples (Watanabe et al., 1999; Kuo and Chen, 2000; Murahashi et al., 2001). Holloway et al. (1987) studied the photochemical behavior of 1,8-DNP in DMSO and coated onto silica. Irradiation of 1,8-DNP with wavelengths larger than 310 nm resulted in a half-life of 0.7 days in DMSO and a half-life of 5.7 days when coated onto silica, showing greater photostability when adsorbed on a surface. The principal photodecomposition product of 1,8-DNP was identified as 1-nitropyrene-8-ol based on HPLC retention times, UV, and MS spectra. More recently, results from our laboratory on the photochemistry of 1,6-DNP and 1,8-DNP in acetonitrile demonstrated that structural differences influence their photochemical behavior because 1,6-DNP was four times more photochemically reactive than 1,8-DNP and also influenced the product distribution (Morel et al., 2006).

In this work 1,6 and 1,8-DNP were used as model compounds to study their photochemical properties on models of the atmospheric particulate matter to determine their possible degradation pathways. For this purpose, we have determined photodegradation rates and characterized some photoproducts of these isomers when irradiated on silica gel of two different average pore diameters and acidic alumina, in the presence and absence of O<sub>2</sub> and compare these results to those in acetonitrile solutions. This study can contribute to a better understanding of the behavior of these atmospheric contaminants and helps to establish a more realistic evaluation of the toxicity and risk of these isomers.

## 2. Experimental

### 2.1. Reagents and sample preparation

1,6 and 1,8-dinitropyrene, both 98% pure were obtained from Sigma–Aldrich or from AccuStandard. 6-OH-1-NO<sub>2</sub>pyrene, 8-OH-1-NO<sub>2</sub>pyrene, and the pyrenediones were synthesized following the reported procedure by El-Bayoumy and Hecht (1983) and used as standards for the identification of the photoproducts. Silica gel (pore size 2.5 nm, 100–250 mesh, pore size 6.0 nm, 130–270 mesh) and acidic alumina (60–325 mesh) were obtained from Sigma Chemical Co. and used inactivated as models of the atmosphere particulate. Acetonitrile (Optima), ethyl acetate and tert-butyl methylether were purchased from Fisher Scientific.

The adsorbed samples were prepared by adding a measured amount of a stock solution of 1,6-DNP in ethyl acetate or 1,8-DNP

in tert-butylmethylether. These solvents were selected because they were easy to remove by rotatory evaporation. An aliquot of the stock solution was added to a weighted amount of the adsorbent to obtain the desired loading (mol g<sup>-1</sup>) of the samples. After equilibration for 30 min in the dark, the solvent was then evaporated by roto-evaporation. Diffuse reflectance spectra of the powder samples were recorded to verify the adsorption of the DNP onto the surface. The reproducibility of sample preparation and of the loading procedure was established from the initial diffuse reflectance and fluorescence emission intensities recorded at 45° from the excitation and emission monochromators for solid samples using a Cary 1E double beam spectrophotometer with an integrating sphere and a Varian Cary Eclipse fluorometer, respectively.

### 2.2. Irradiations

The samples were irradiated with either a 300 W or a 1000 W Xe (Hg) Oriel short arc lamps. The irradiation system consisted of the lamp housing with lenses, a water filter, a band pass filter (7–59 Corning Glass, 300–500 nm range) to simulate the solar radiation and a sample holder. The irradiance after the filter in front of the sample was  $4.45 \times 10^{-3} \text{ W cm}^{-2}$  for the 1000 lamp and  $2.33 \times 10^{-3} \text{ W cm}^{-2}$  for the 300 W. For powder samples a rotatory cell was used (Natush et al., 1980; Behymer and Hites, 1988).

### 2.3. Extraction and high performance liquid chromatographic analysis

Irradiated samples were extracted using four portions of 5.0 mL of acetonitrile followed by sonication for 3 min and centrifugation at 3500 rpm for 3 min for each portion. The collected supernatant was concentrated to a final volume of 1.0 mL for HPLC analysis.

Chromatographic separations were done using a Shimadzu HPLC system equipped with two model LC10AD high-pressure pumps and a photodiode array UV–visible detector SPD-M10A and a fluorescence detector, RF-10A × 1. The extracts were analyzed using a separation gradient CH<sub>3</sub>CN/H<sub>2</sub>O (70:30 v/v), while for the irradiated samples in acetonitrile a 60:40 v/v gradient was used. Samples were injected in triplicate (50 μL) into a Jupiter C<sub>18</sub> column (Phenomenex) using an auto-sampler. Standards were used for the characterization of some of the products by comparing their retention times and UV–Visible and fluorescence spectra with those of the photoproducts. The dinitrohydroxypyrene was identified from its MS spectrum (Agilent HPLC/MS–W-TOF).

## 3. Results and discussion

### 3.1. Absorption and fluorescence properties

The 1,6 and 1,8 DNP isomers present three major absorption bands in the 200–450 nm wavelength region which facilitate their atmospheric photochemistry (Fig. 1A and B). The structured bands in the UV region are assigned to π,π\* transitions of the extended system of conjugated double bonds of the pyrene backbone. The long-wavelength band of the isomers that extends from 320 to 460 nm is a common feature of nitroaromatics such as mononitropyrenes (Arce et al., 2008), and has contributions of π,π\* transitions from the pyrene skeleton and the nitro group (Crespo-Hernández et al., 2008). In acetonitrile, these isomers show high absorption capacities with molar absorption coefficients of the order of 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>. The absorption spectra of the adsorbed DNP isomers are similar to those observed in acetonitrile (Fig. 1A and B). This indicates that adsorbed DNPs experienced a homogeneous

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