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Phototransformations of dinitropyrene isomers on models of the atmospheric particulate matter

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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 6hydroxy-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_2 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.

Keywords

surface phototransformations; dinitropyrenes; photodegradation rates; adsorbed; atmospheric chemistry

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_x . The high levels of morbidity and mortality of

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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 matter. Also, they can be secondary pollutant products of the photochemical reactions of parent PAHs with OH and NO_x radicals (Arey et al., 1986). Nitroarenes containing four or more fused aromatic rings, such as nitropyrenes, are almost entirely found in fine and ultrafine (<2.5µm) particles of ambient air (Schuetzle, 1983). Thus, significant attention has been directed to 1,6-dinitropyrene (1,6-DNP) and 1,8dinitropyrene (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, 1980) and have been detected in diesel exhaust particles (Hayakawa et al., 1994; Hayakawa et al., 1995; Hayakawa et al., 1995) and airborne particles in Japan (Hayakawa et al., 1995, Hayakawa et al., 1995; 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 and coworkers (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_2 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-NO₂pyrene, 8-OH-1-NO₂pyrene, and the pyrenediones were synthesized following the reported procedure by El-Bayoumi 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) of the samples. After equilibration for 30 minutes 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 4.45×10^{-3} W/cm² for the 1000 lamp and 2.33×10^{-3} W/cm² 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 minutes and centrifugation at 3500 rpm for 3 minutes 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 CH₃ CN/H₂O (70:30 v/v), while for the irradiated samples in acetonitrile a 60:40 v/v gradient was used. Samples were injected in triplicate (50µL) into a Jupiter C₁₈ 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,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 mm 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

 $10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The absorption spectra of the adsorbed DNP isomers are similar to those observed in acetonitrile (Fig. 1A,B). This indicates that adsorbed DNPs experienced a homogeneous environment as expected in untreated surfaces which are hydrated (de Mayo, 1982; James et al., 1985; Sotero and Arce, 2004). Nonetheless, major differences were a decrease of the vibronic structure in the red most absorption band of 1,6-DNP when adsorbed on silica, small shifts to the blue, and a slight broadening of the bands. These effects result from interactions between the π system of the DNP and the surface silanol groups (Fripiat and Uytterhoeven, 1962).

Isomers adsorbed at a loading of 10^{-7} mol/g (0.09% surface coverage) on acidic alumina presented a significant change in the UV absorption spectrum (Fig. 2, t=0). The band with maximum at around 292 nm (Fig. 1A), which corresponds to a short-axis polarized transition in the parent pyrene, seen in silica gel and in acetonitrile, almost disappears while the other bands are slightly red shifted. The intensity of the long-wavelength band, which has contributions from the NO₂ group absorption, was not affected on this surface. This unexpected behavior suggests a stronger interaction between the pyrene backbone π systems of the DNPs and surface active sites on the acidic alumina than with the silica surface.

Plots of the relative molar absorption coefficient for the isomers adsorbed on these surfaces (Fig. 1A), defined as $\varepsilon_i(\lambda) = f(R_{\infty,i}) - f(R_{\infty})$, where f(R) is the Kubelka-Munk function (Ciani et al., 2005) did not show additional bands or features when compared to regular absorbance plots (Fig. 1A).

The fluorescence emission spectra of the DNP isomers adsorbed on these surfaces resembled that observed in acetonitrile solutions (Fig. 3), depicting a broad emission band with maximum at 473 nm for 1,6-DNP and at 460 nm for 1,8-DNP (Fig. 4A,B, t=0). In general, emission spectra were much broader for the adsorbed samples (Fig. 4A,B, t=0), resulting from the hydrogen bonding interactions of the silanol hydrogen's with the NO₂ groups and the pyrene π system (Bauer et al., 1982;Bauer et al., 1984; Sotero and Arce, 2004). The type of solid and the average pore size affected to a greater degree the fluorescence emission than the absorption spectra. For 1,6-DNP adsorbed on acidic alumina three emission bands (λ_{max} at 500, 460, and 435 nm) where detected (Fig. 5) while for 1,8-DNP only one was seen (Fig. 4B), suggesting the formation of a surface-1,6-DNP emitting complex. Furthermore, in the silica of smaller pore size (2.5 nm), the emission intensity of 1,8-DNP was much smaller and broader than for the 6.0 nm pore diameter. Similar decreases in emission intensity with decreasing silica pore size have been observed for other PAHs (Sotero and Arce, 2004; Arce and Fioressi, 2005).

3.2 Photochemical transformations on models of the atmospheric particulate matter

3.2.1 1,6- DNP—Irradiation of adsorbed, 1,6-DNP onto silica gel 6.0 nm average pore diameter or in acidic alumina surfaces resulted in a decrease in the absorption bands, an increase in absorbance in the region of 425 to 700 nm, and formation of isosbestic points as the irradiation proceeded (Fig. 6). This indicated that photodegradation of 1,6-DNP and formation of photoproducts on the surface were occurring. Similar spectral changes were observed in the presence of N₂ or O₂. An interesting observation is that the increase in absorbance in the 300–330 nm wavelength interval was more pronounced when 1,6-DNP was irradiated in acetonitrile than on the silica surface, suggesting a different distribution of products in those two media as discussed below. The low intensity fluorescence band of adsorbed 1,6-DNP decreased as a function of irradiation time while a broad emission band with maxima at 516 nm (in a N₂ atmosphere) (Fig. 4A) and at 530 nm (O₂) grew in intensity with time, demonstrating the formation of different fluorescent products under the different gaseous atmospheres. A 38% fluorescence quenching of 1,6-DNP adsorbed onto acidic alumina by O₂ was observed in unirradiated samples, not seen on silica gel surfaces or in

acetonitrile. This points out to the fact that because alumina is not a porous surface, the adsorbed 1,6-DNP molecules are more exposed to the O_2 molecules increasing the possibility of collisional quenching processes. Upon irradiation on this surface, a broad emission band with maximum at 564 nm increases in intensity with irradiation time as the 1,6-DNP emission bands decreased. The product's emission band was more intense under a N_2 atmosphere, although its formation rate was greater under O_2 . In acetonitrile, the emission band of the products (not shown) presented a maximum at 550 nm; red shifted in comparison to the emission by the adsorbed products on silica gel (O_2), while blue shifted to those emitting on alumina (564 nm). Thus, suggesting different photodegradation pathways depending on the environment.

Photodegradation rate constants for DNPs, valid under the stated irradiation conditions, were determined by fitting the HPLC chromatographic peak area of the unreacted DNP as a function of the irradiation time to a first-order photoprocess rate equation (Table 1). It is important to consider that the magnitude of the rate constant in the different media cannot be directly compared due to differences in the amount of light absorbed by each sample, even when the incident intensities are similar. However, the relative magnitudes of the rate constants for solution and adsorbed samples provide important information on the effect of the microenvironment on the photoreactivity of these pollutants. For example, in the case of 1,6-DNP (Table 1) the results show that on the acidic alumina surface this isomer is more photostable than in silica, while on this surface there is a slight increase in the photoegradation rate in the presence of oxygen in comparison to other environments.

More significant differences were observed in the distribution and relative yields of the identified photoproducts (Table 2). Photodegradation of 1,6-DNP on silica gel 6.0 nm resulted in 1,6-pyrenedione (16% relative yield) and 6-OH-1-NO₂pyrene (34%) as the principal products. No significant differences in the number of products or in their relative yields were observed under an O_2 or N_2 atmosphere. Nonetheless, the photodegradation on acidic alumina resulted in five different additional products not detected in irradiations on silica gel or in acetonitrile solutions. Furthermore pyrenediones were not observed. The large increase in the relative yield of the hydroxynitropyrene product (80%) in acidic alumina is explained in terms of a larger availability of hydrogen atoms on the surface which can be abstracted by the nitropyrenoxy radical (Arce et al., 2008). The acidic environment will favor the enolic form of the intermediate over (scheme 1) the carbonyl (pyrenediones). This could explain the absence of pyrenediones in this environment.

Moreover, the possibility of an H atom abstraction reaction by the DNP triplet excited state, observed in acetonitrile for the mononitropyrene (Arce et al., 2008), is enhanced yielding a protonated radical, $Py(NO_2)(NO_2H)$, which is expected to form a hydroxynitropyrene derivative (Scheme 2).

Another major difference is that the strong interactions of 1,6-DNP with the acidic alumina surface provides photodestruction pathways in which the loss of the nitro group and of π,π^* bands associated with the pyrene skeleton are evident (Table 2, products PI,PII). Based on the absorption spectrum features, these products are different to those unidentified products detected in pure acetonitrile or in 5.6 M H₂O acetonitrile. Moreover, the relative yield of 6-OH-1-NO₂pyrene is higher on this surface than in solution. These results suggest that it is not the presence of co-adsorbed water, but the interaction of this DNP with the active sites which causes the difference in reaction pathways.

3.2.2 1,8-dinitropyrene—This isomer was irradiated adsorbed onto silica gel 2.5 and 6.0 nm average pore diameters to study the effect of this surface's physical property on the photochemistry, on acidic alumina, and in acetonitrile. Irradiation in these different

microenvironments resulted in a similar behavior as that observed for the 1,6-DNP isomer; a decrease in the 1,8-DNP absorption bands, the formation of isosbestic points, and an increase in absorbance above 450 nm (Fig.7), once again demonstrating the photodegradation and formation of adsorbed products. Likewise, the fluorescence emission band of 1,8-DNP (Fig.4B) decreased with irradiation time, while a broad emission ($\lambda_{max} = 520$ nm on silica 6.0 nm, 518 nm silica 2.5 nm) grew.

The 1,8-DNP isomer is three times more photoreactive than the 1,6-DNP when adsorbed onto silica surfaces, while in solution the reverse was observed (Table 1). Thus, surface interactions can enhance the photodegradation of 1,8-DNP to a larger extent than a polar solvent environment. Similar to the 1, 6 DNP isomer, the reactivity of 1,8-DNP decreased on alumina in comparison to the silica surfaces, while the isomers presented similar photoreactivities on acidic alumina. Thus, not only structural differences are important factors in determining differences in photoreactivity, but the influence of the environment (solution versus surface) is very significant.

No effect on the photodegradation rate constants was observed when 1,8-DNP was irradiated on silica of different average pore diameter (Table 1) although differences in the type of the photoproduct and relative yields were observed. Pyrenediones and 8-hydroxy-1nitropyrene were observed when 1,8-DNP adsorbed on silica 6.0 nm was irradiated in the presence of O2 (Table 3) but not under an N2 atmosphere. Interestingly, photolysis of this isomer in the smaller pores in the presence of O_2 did not result in the formation of these products (Table 3). The formation of pyrenediones and hydroxynitropyrene in the larger pore diameter silica in the presence of O_2 suggests that inside these pores, as well as, in acetonitrile the DNP molecules are not restricted to experience changes in the torsional angle of the NO2 group at the excited singlet state (Crespo-Hernández et al., 2008) or for the formation of the oxaziridine ring prior to the nitro-nitrite rearrangement. The fact that these products are not seen under a N₂ atmosphere suggest that even if the pyrenoxy radical ((NO₂)PyO•) is formed due to the mobility constrains imposed by the dimensions of the pore, if the O_2 molecule is not inside the pore, as is the case in the 2.5 nm silica, no further oxidation of this intermediate will occur to lead to the formation of pyrenediones. Likewise, the absence of a dinitrohydroxypyrene product seen in acetonitrile, but not in samples adsorbed onto models of atmospheric particulate matter, implies that inside the pores or on the surfaces the mobility of the NO radical (Scheme 3) is restricted and recombines back with its geminate radical.

On silica of smaller pore diameter, the HPLC chromatogram depicted at least 5 products of which 3 present complete loss of the nitro group and pyrene π aromatic ring absorption bands (Table 2, products PA, PB, PC). None of those products resembled pyrene which should be expected as result of NO₂ loss. Only one of the unidentified products (Table 2A, PD) showed three bands (220, 352, 460 nm) with the longest wavelength band in a region that could suggest the incorporation of electron donating groups. On silica gel 6.0 nm, a series of unidentified photoproducts with absorptions in the 250–375mm region were detected. According to spectroscopical data reported by El-Bayoumy and Hetch (1983) for 4,5-dihydroxy-1-nitropyrene, it is possible that this type of compound could be one of the products observed on silica gel. In comparison to the 1,6-DNP isomer irradiated on 6.0 nm silica under an O₂ atmosphere, the 1,8-DNP product's relative yields for the hydroxynitropyrene and the pyrenediones are significantly smaller, close to 50% less, thus demonstrating structural effects on the photoreactivity on the surfaces (Tables 2,3). The absorption spectra of the major photoproducts detected for irradiated 1,8-DNP (or for 1,6-DNP) adsorbed on the silica surfaces were different to those observed in irradiations in acetonitrile solutions in absence or presence of water. In acetonitrile the products show bands with maxima at 560 nm (tentatively assigned to dinitrohydroxypyrene), not observed

for the powdered samples. Thus, this difference cannot be accounted for by reactions of intermediates with adsorbed water molecules on the solid surface. Products from irradiated samples of 1,8-DNP on acidic alumina were not extracted.

4. Conclusions

Aerosols are complex systems in which nitro-PAHs can be found in diverse microenvironments (McDow et al., 1994). Depending of their source, nitro-PAHs can be associated to an organic liquid like layer or solid-air interface of inorganic oxides. Photodegradation of nitro-PAHs in the atmospheric particulate matter and diesel exhaust particles is one of the principal transformation channels of these contaminants (Fan et al., 1995; Fan et al., 1996; Yu, 2002; Kameda et al., 2011). In terms of the atmospheric chemistry implications, our results demonstrate that the phototransformation routes of the dinitropyrenes depend on the microenvironment in which these are encountered. It must be emphasized that not only the chemical properties of the surface (silica versus acidic alumina) but also the average pore diameter and the presence or absence of oxygen resulted in significant changes in the distribution, type of product and photodegradation rates. In an organic liquid-like region of an aerosol 1,8-DNP is expected to show shorter lifetimes, compared to when adsorbed onto inorganic oxides, in contrast to the behavior observed for 1,6-DNP. DNP isomers phototransform into hydroxynitropyrenes, pyrenediones, and other low yield unidentified products except in regions of limited mobility such as small pores. The photochemical formation of hydroxynitropyrene isomers from 1-nitropyrene in diesel exhaust and airborne particles has been recently reported (Kameda et al., 2011). Most hydroxynitropyrene isomers as well as the diones (Benson et al., 1985) show lower mutagenicity (Manabe et al., 1985; Ball et al., 1984; Kameda et al., 2008) than the parent nitropyrene. Thus, the present results indicate that during the atmospheric transport of the DNPs, these strong bacterial mutagens can be phototransform into less biologically active intermediates. When adsorbed onto the inorganic oxides, some of the products lack the absorption features related to the nitro group which can be associated to products of lower mutagenicity. The photodegradation of dinitropyrenes located on acidic surfaces proceeded at a lower rate. Longer residence lifetimes in acidic particulate matter should be observed as well as an increase in the hydroxynitropyrenes levels. Because the hydroxynitropyrenes and pyrenediones present strong absorption bands in the visible region, these could phototransform into products for which their biological activity must be investigated.

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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.



Figure1.

A. Absorption spectra of 1,6–DNP on models of atmospheric aerosols \Box , 2.4 × 10⁻⁵ M acetonitrile; O, adsorbed on SiO₂ 6.0 nm, loading 1×10⁻⁶ mol/g; Δ , relative molar absorption coefficient; **B.** absorption spectra of 1,8–DNP on models of atmospheric aerosols, Δ , 9.2 × 10⁻⁶ M acetonitrile; \Box , SiO₂ loading 1×10⁻⁷ mol/g.

Wavelength (nm)



Figure 2.

Diffuse reflectance spectra of 1,6-DNP at different irradiation times adsorbed on acidic alumina 1.0×10^{-7} mol/g in the presence of O₂, \Box , t=0 min; O, t=10 min; , t=30 min.



Figure 3. Fluorescence emission spectra of dinitropyrene isomers 3.0×10^{-5} M in ACN; λ_{ex} : 396 nm (\Box , 1,8-DNP) and 378 nm (Δ , 1,6-DNP).





Figure 4.

A. Fluorescence emission spectra of 1,6-DNP adsorbed on SiO₂ 6.0 nm, 1.06×10^{-6} mol/g, N₂ (ex. 403 nm) as a function of irradiation time. \Box , t=0 min; Δ , t=3 min; , t=10 min; O, t=30 min; **B.** Changes in the fluorescence emission spectra of 1,8-DNP adsorbed on SiO₂ 6.0 nm 1.0×10^{-7} mol/g (ex. 397 nm) as a function of irradiation time in the presence of O₂, \Box , t=0 min; Δ , t=40 min; O, t=60 min; , t=90 min.





Fluorescence emission spectra of 1,6-DNP adsorbed on acidic alumina, N₂ 1.0×10^{-7} mol/g (ex. 411 nm), \Box , t=0 min; O, t=10 min; Δ , t=20 min; , t=40 min.



Figure 6.

Diffuse reflectance spectra of 1,6-DNP adsorbed on silica gel 6.0 nm as function of irradiation time Loading: $1.0 \times 10^{-6} \text{ mol/g}$; O_2 . \blacksquare , t=0 min; \Box , t=3 min; , t=10 min; Δ , t=40 min.



Figure 7.

Time dependent diffuse reflectance spectra of 1,8-DNP adsorbed on silica gel 6.0 nm, loading: 1.0×10^{-7} mol/g; O₂. \blacksquare , t=0 min; \Box , t=20 min; O, t=60 min; , t=110 min; Δ , t=150 min.

$$\begin{array}{l} \mathsf{Py}(\mathsf{NO}_2)_2 \xrightarrow{hw} \mathsf{Py}(\mathsf{NO}_2)_2 \ (\mathsf{S}_1(\pi,\pi^*)) \xrightarrow{isc} \mathsf{Py}(\mathsf{NO}_2)_2 \ (\mathsf{T}_1(n,\pi^*)) \\ \\ \mathsf{Py}(\mathsf{NO}_2)_2 \ (\mathsf{S}_1(\pi,\pi^*)) \ \text{or} \ \mathsf{Py}(\mathsf{NO}_2)_2 \ (\mathsf{T}_1(n,\pi^*)) \xrightarrow{\textit{nitro-nitrits}} \ (\mathsf{NO}_2)\mathsf{Py}\mathsf{ONO} \longrightarrow \end{array}$$



Scheme 1.

$$\begin{split} &\mathsf{Py}(\mathsf{NO}_2)_2 + \mathsf{hv} \to \mathsf{Py}(\mathsf{NO}_2)_2 \, (\mathsf{S}_1(\pi, \pi^*)) \\ &\mathsf{Py}(\mathsf{NO}_2)_2 \, (\mathsf{S}_1(\pi, \pi^*) \xrightarrow{i \, \mathrm{sc}} \, \mathsf{Py}(\mathsf{NO}_2)_2 \, (\mathsf{T}_1(n, \pi^*)) \to \mathsf{Py}(\mathsf{NO}_2)_2 \, (\mathsf{T}_1(\pi, \pi^*)) \\ &\mathsf{Py}(\mathsf{NO}_2)_2 \, (\mathsf{T}_1(\pi, \pi^*)) + \mathsf{HO}\text{-surface} \to (\mathsf{NO}_2)\mathsf{Py}(\mathsf{NO}_2\mathsf{H})^{\bullet} + \bullet \mathsf{O}\text{-surface} \end{split}$$

Scheme 2.

$$\begin{array}{l} \mathsf{Py}(\mathsf{NO}_2)_2 \xrightarrow{\mathsf{hv}} \mathsf{Py}(\mathsf{NO}_2)_2 \left(\mathsf{S}_1(\pi,\pi^*)\right) \xrightarrow{\mathsf{isc}} \mathsf{Py}(\mathsf{NO}_2)_2 \left(\mathsf{T}_1(n,\pi^*)\right) \\ \\ \mathsf{Py}(\mathsf{NO}_2)_2 \left(\mathsf{S}_1(\pi,\pi^*)\right) \text{ or } \mathsf{Py}[(\mathsf{NO}_2)_2 \left(\mathsf{T}_1(n,\pi^*)\right) \xrightarrow{\mathsf{nitro-nitrite}} (\mathsf{NO}_2)\mathsf{PyONO}) \leftrightarrow (\mathsf{NO}_2)\mathsf{PyO}\bullet+\mathsf{NO} \\ \\ (\mathsf{NO}_2\mathsf{PyO})\bullet + \mathsf{HO}\text{-surface} \rightarrow \mathsf{NO}_2\mathsf{PyOH} + \bullet \mathsf{O}\text{-surface} \\ \\ (\mathsf{NO}_2\mathsf{PyO})\bullet \rightarrow \mathsf{PyO}_2(\mathsf{pyrenediones}) \end{array}$$

Scheme 3.

Table 1

Photodegradation rate constants for 1,6-DNP and 1,8-DNP on models of atmospheric aerosols

| | | SiO ₂ | Acidic Al ₂ O ₃ | Acetonitrile |
|-------------------------------------|----------------|--------------------------------------|---|---|
| | | $k_{photo}\times 10^{-2}~(min^{-1})$ | $k_{photo} \times 10^{-2} \ (min^{-1})$ | $k_{photo} \times 10^{-2} \ (min^{-1})$ |
| NO 2 | N_2 | $0.68 \pm 0.01 \; (6.0 \; nm)$ | 0.49 ± 0.02 | 2.7 ± 0.7 |
| NO ₂ | O ₂ | 0.85 ± 0.01 (6.0 nm) | 0.53± 0.03 | 2.9 ± 0.5 |
| Loading: 1.0×10^{-6} mol/g | | | | |
| NO ₂ | N ₂ | 2.3 ± 0.3 (6.0 nm) | 0.44 ± 0.01 | 0.74 ± 0.04 |
| 0 ₂ N | | $2.3\pm0.2~(2.5~\text{nm})$ | | |
| | O ₂ | $2.1 \pm 0.1 \ (6.0 \ nm)$ | 0.51 ± 0.02 | 0.62 ± 0.03 |
| | | $2.2 \pm 0.1 \ (2.5 \text{ nm})$ | | |
| Loading: 1×10^{-7} mol/g | | | | |
| | | | | |

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Table 2

Photoproducts formed during photolysis of 1,6-DNP on models of atmospheric aerosol.

| Additive | t _r (min) | UV-Vis, λ _{max} (nm) | Compound | Relative yield ^(a) (%) | | |
|-------------------|-------------------------|----------------------------------|-------------------------|--------------------------------------|--|--|
| Silica gel 6.0 nm | | | | | | |
| | 4.120 | 239, 308, 405, 450 | pyrenediones | 16.32 | | |
| N_2 | 5.756 | 238, 300, 445 | 6-hydroxy-1-nitropyrene | 33.72 | | |
| | 8.740 | 245, 285, 376, 411 | 1,6-DNP | 65.90 ^(b) | | |
| O ₂ | 4.128 | 239, 308, 405, 450 | pyrenediones | 17.42 | | |
| | 5.628 | 238, 300, 445 | 6-hydroxy-1-nitropyrene | 30.04 | | |
| | 8.740 | 245, 285, 376, 411 | 1,6-DNP | 67.13 <i>(b)</i> | | |
| | | Acidic alı | ımina | | | |
| | 3.652 | 210 | PI | 9.03 | | |
| | 3.916 | 215, 250 | PII | 9.72 | | |
| N_2 | 4.896 | 210, 235, 295, 420 | PIII | 10.25 | | |
| | 5.784 | 238, 300, 445 | 6-hydroxy-1-nitropyrene | 4.11 | | |
| | 8.742 | 245, 285, 376, 411 | 1,6-DNP | 58.00 <i>(b)</i> | | |
| | 3.648 | 210 | PI | 8.47 | | |
| 0 | 3.936 | 215, 250 | PII | 5.90 | | |
| O_2 | 4.128 | 210, 425 | PIV | 3.65 | | |
| | 4.412 | 210, 300, 425 | PV | 7.25 | | |
| | 5.780 | 238, 300, 445 | 6-hydroxy-1-nitropyrene | 82.00 | | |
| | 8.742 | 245, 285, 376, 411 | 1,6-DNP | 62.00 ^(b) | | |
| | | Acetoni | trile | | | |
| | 1.76 | 291, 594 | | 6.9 | | |
| N_2 | 3.02 | 231, 249, 194, 547 | Dinitrohydroxypyrene | 35.0 | | |
| | 4.75 | 208, 238, 308, 405, 450 | 1,6-pyrendiones | 8.5 | | |
| | 8.364 | 238, 300, 445 | 6-hydroxy-1-nitropyrene | 3.99 | | |
| H ₂ O | 8.204 | 238, 300, 445 | 6-hydroxy-1-nitropyrene | 11.30 | | |

(a) Relative yield = (product peak area / photodestroyed DNP area) × 100;

(b)% photodegradation of DNP (3hr)

Table 3

Photoproducts formed during photolysis of 1,8-DNP on models of atmospheric aerosols.

| Additive | t _r (min) | UV-Vis, λ _{max} (nm) | Compound | Relative yield ^(a) (%) |
|----------------|-------------------------|----------------------------------|-------------------------|--------------------------------------|
| | | Silica g | el 2.5 nm | |
| | 1.796 | 220, 336 | РА | 12.42 |
| | 1.900 | 223 | PB | 5.70 |
| N_2 | 3.884 | 215 | PC | 5.59 |
| | 4.124 | 220, 352, 460 | PD | 9.39 |
| | 4.568 | 247, 277 | PE | 10.30 |
| | 7.912 | 245, 284, 396 | 1,8-DNP | 88.32 <i>(b)</i> |
| | 1.804 | 220, 336 | РА | 19.73 |
| | 3.908 | 215 | PC | 6.64 |
| O ₂ | 4.116 | 220, 352, 460 | PD | 12.07 |
| | 4.568 | 247, 277 | PE | 19.91 |
| | 7.912 | 245, 284, 396 | 1,8-DNP | 80.71 <i>(b)</i> |
| | | Silica g | el 6.0 nm | |
| | 1.792 | 220, 270, 340 | РА | 22.00 |
| N | 3.896 | 220, 255 | PC | 7.50 |
| 1 N 2 | 4.112 | 220, 352, 460 | PD | 17.07 |
| | 5.160 | 255 | PF | 37.86 |
| | 7.912 | 245, 284, 396 | 1,8-DNP | 85.43 <i>(b)</i> |
| | 1.732 | 210, 338 | РА | 8.46 |
| | 3.100 | 222, 540 | PG | 7.12 |
| | 4.124 | 220, 352, 460 | PD | 25.14 |
| O ₂ | 4.632 | 210, 275, 352, 440 | pyrenediones | 9.50 |
| | 5.168 | 255 | PF | 44.44 |
| | 5.496 | 238, 295, 445 | 8-hydroxy-1-nitropyrene | 18.18 |
| | 7.912 | 245, 284, 396 | 1,8-DNP | 79.67 <i>(b)</i> |
| | | Aceto | onitrile | |
| | 1.78 | 280, 342, 561 | | 2.70 |
| N_2 | 3.38 | 231, 297, 570 | hydroxydinitropyrene | 15.7 |
| | 4.79 | 236, 295, 351, 513 | | 23.6 |
| | 8.16 | 237, 294, 378, 416 | 8-hydroxy-1-nitropyrene | 5.9 |

^(a)Relative yield = (product peak area / photodestroyed DNP area) \times 100;

(b) photodegradation of DNP after 1hr

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