

**Photochemical degradation of 1,6- and 1,8-dinitropyrene in solution**Maria Morel<sup>1</sup>, Rafael Arce<sup>1</sup><sup>1</sup>University Of Puerto Rico-rio Piedras Campus

Nitrated polycyclic hydrocarbons (NPAHs) are environmental pollutants that originate from either the direct combustion of petrochemical fuels or other organic matter, or from the atmospheric photochemical reactions of PAHs with hydroxyl radicals and NO<sub>x</sub> radicals. In particular, significant attention has been directed to 1,3-dinitropyrene (DNP), 1,6-DNP and 1,8-DNP because these are the strongest bacterial mutagens so far reported in the literature, and have exhibited carcinogenicity in experimental animals. Thus, it is important to understand their environmental fate. However, little has been done in terms of understanding their phototransformation mechanisms. Irradiation of 1,6- and 1,8-DNP in acetonitrile showed a decrease in their characteristic absorption bands in the presence of O<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O, and an increase in a new band with maximum at 450 nm as irradiation time increases, demonstrating their photodegradation and transformation into products. These photoproducts are highly fluorescent, presenting a broad emission band around 520-540 nm. In presence of the different additives, 1,6-DNP photodegraded 10 times faster than 1,8-DNP. Both DNPs present similar initial photodegradation rates in acetonitrile solutions saturated with N<sub>2</sub> or O<sub>2</sub>. This implies that oxygen reactive species are not involved in major photodegradation routes. In water containing solutions the 1,8-DNP photodegradation rate increases by a factor of two compared to 1,6-DNP and a new major photoproduct with relative yield of 34.1% was observed. This suggests a larger extent of participation of water in the intermediates steps of the 1,8-DNP degradation. Transient absorption spectra in acetonitrile for 1,6-DNP depict an absorption band at 580 nm and for 1,8-DNP at 520 nm. These bands decay with a first order rate constant of  $7.6 \times 10^{-5} \text{ s}^{-1}$  and  $1.5 \times 10^{-6} \text{ s}^{-1}$  in the presence of N<sub>2</sub> for 1,6-DNP and 1,8-DNP respectively. Possibly a triplet intermediate is responsible for these absorption bands since the presence of O<sub>2</sub> increased the decay rate constants. HPLC reverse phase was used to separate and tentatively identify the photoproducts formed from the irradiation of both DNPs in acetonitrile in the presence of different additives found in the environment. Two chromatographic fractions were separated and tentatively identified as 1,6-pyrenedione and 6-hydroxy-1-nitropyrene for 1,6-DNP as well as 1,8-pyrenedione and 8-hydroxy-1-nitropyrene for 1,8-DNP. Their relative yields of formation in acetonitrile, expressed as the ratio of the chromatographic area of the product to the area of the photodegraded DNP are: for 1,6-pyrenedione 5.34% (N<sub>2</sub>), 5.19% (O<sub>2</sub>) and 14.84% (H<sub>2</sub>O); for 6-hydroxy-1-nitropyrene 3.99% (N<sub>2</sub>), 4.50% (O<sub>2</sub>) and 11.30% (H<sub>2</sub>O); for 1,8-pyrenedione 5.4% (O<sub>2</sub>) and 33.0% (H<sub>2</sub>O) and for 8-hydroxy-1-nitropyrene 37.2% (O<sub>2</sub>) and 17.9% (H<sub>2</sub>O). Other chromatographic fractions are still to be identified. The incorporation of similar oxygen functionalities in the photodegradation of other nitro aromatics have been reported thus suggesting that the proposed nitro-nitrite rearrangement could also occur as a major route for the photodecomposition of dinitropyrenes. The financial support by NIH SCoRE (grant 55066M08102) and RISE (grant 5R25GM061151) is gratefully acknowledged.