

Radical production from photosensitization of imidazoles, benzophenone and 4-benzoylbenzoic acid

Pablo Corral Arroyo (1,2), Laura González (3), Sarah Steimer (1), Rainer Volkamer (3,4), Christian George (5), Thorsten Bartels-Rausch (1), and Markus Ammann (1)

(1) Laboratory of Radiochemistry and Environmental Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland, (2) Department of Chemistry and Biochemistry, University of Bern, 2012 Bern, Switzerland, (3) Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA, (4) CIRES – Cooperative Institute for Research in Environmental Sciences, Boulder, CO, USA, (5) IRCELYON – Institute of Researches on Catalysis and Environment, Lyon, France

Reactions promoted by light are key in atmospheric chemistry. Some of them occur in the condensed phase of aerosols which may contain light absorbing organic compounds that provoke photochemical reactions such as humic like material (GEORGE 2005). Our aim is to understand the role these reactions play in atmospheric photochemistry. This work explores the radical reactions initiated by UV light in mixtures of citric acid (CA) and imidazole-2-carboxaldehyde (IC), benzophenone and 4-Benzoylbenzoic acid (BBA) using NO as a probe molecule for HO₂, by means of coated wall flow tube experiments. The loss of NO was measured by a chemiluminescence detector (CLD), also configured for the distinction of the products (HONO or NO₂). The dependence of the NO loss on the initial NO concentration, the photosensitizer concentration in the film, relative humidity, light intensity, oxygen molar fraction were investigated as well as the HONO and NO₂ yields. We found a clear correlation between the loss of NO above the film and the molar ratio of photosensitizer/CA, and also between the NO loss and the light intensity. The variation of the observed NO loss with oxygen corroborates a mechanism, in which the triplet excited state of the photosensitizer is reduced likely by the predominant donor in the system, citric acid, to a reduced ketyl radical. This reactive species is transferring an electron to molecular oxygen, which in turn leads to production of HO₂ radicals, which are released to the gas phase. Therefore, in absence of gas phase oxidants, the loss of NO in the gas phase could be related to the production of HO₂ radicals in the condensed phase. Relative humidity had a strong impact on the HO₂ output, which shows a maximum value at intermediate humidity around 30%, likely due to different competing effects of dilution and reactant mobility. The observed NO₂/HONO ratio was around 1.4 consistent with the secondary chemistry of HO₂ in presence of NO in the gas phase, indicating no additional direct release of OH to the gas phase nor direct conversion of NO₂ to HONO at the film surface. IC and BBA showed similar HO₂ production rates, while the HO₂ yield with benzophenone was around 50 times higher. We could preliminary quantify for the first time the contribution of these processes to the oxidative capacity in the atmosphere and conclude that their role is significant for aerosol aging.

References

George, C., Strekowski, R. S., Kleffmann, J., Stemmler, K., and Ammann, M.: Photoenhanced uptake of gaseous NO₂ on solid organic compounds: a photochemical source of HONO?, *Faraday Discussions*, 130, 195, 2005.