

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

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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 HO<sub>2</sub>, 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 NO<sub>2</sub>). 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 NO<sub>2</sub> 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 HO<sub>2</sub> 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 HO<sub>2</sub> radicals in the condensed phase. Relative humidity had a strong impact on the HO<sub>2</sub> output, which shows a maximum value at intermediate humidity around 30%, likely due to different competing effects of dilution and reactant mobility. The observed NO<sub>2</sub>/HONO ratio was around 1.4 consistent with the secondary chemistry of HO<sub>2</sub> in presence of NO in the gas phase, indicating no additional direct release of OH to the gas phase nor direct conversion of NO<sub>2</sub> to HONO at the film surface. IC and BBA showed similar HO<sub>2</sub> production rates, while the HO<sub>2</sub> 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 NO<sub>2</sub> on solid organic compounds: a photochemical source of HONO?, *Faraday Discussions*, 130, 195, 2005.