

Radical production from photosensitization of imidazoles

PABLO CORRAL-ARROYO^{1,2}, LAURA GONZÁLEZ³, SARAH STEIMER¹, RAINER VOLKAMER^{3,4},
THORSTEN BARTELS-RAUSCH¹, MARKUS AMMANN¹

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

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) using NO as a probe molecule for HO₂, by means of coated wall flow tube experiments. IC, which acts as a photosensitizer, originates from secondary chemistry of glyoxal in the aerosol phase in the atmosphere (KAMPF 2012). 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 IC 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 IC/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 IC 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, the loss of NO in the gas phase could be related to the production of HO₂ radicals. Relative humidity had a strong impact on the HO₂ output, which shows a maximum value at intermediate humidities 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. 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

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