Radical production from photosensitization of imidazoles, benzophenone and 4-BBA

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The condensed phase of aerosol particle can host indirect photochemical processes, initiated by photosensitizers, which are among the light absorbing organic compounds (brown carbon (Laskin *et al.* 2015)). The excited triplet states of these sensitizers initiate condensed phase radical production at wavelengths in the UVA and visible range (George *et al.*, 2015). Here, we compare the effect of the sensitizers imidazole-2-carboxaldehyde (IC), benzophenone (BPh) and 4-Benzoylbenzoic acid (4-BBA) on the rate of HO_2 production from the reaction of their triplets with citric acid (CA), a proxy for secondary organic aerosol material. These or similar sensitizers are expected to be widely abundant in atmospheric particles from multiphase chemical processes.

Experiments were performed by means of coated wall (CWFT) and aerosol flow tube (AFT) experiments. In both cases, mixtures of the sensitizers and CA were exposed to UVA light in presence of an excess of NO as a scavenger for HO_2. The loss of NO over the films of the CWFT or in presence of aerosol in the AFT was measured by a chemiluminescence detector (CLD), also configured for the distinction of the products (HONO or NO_2). The dependence of the NO loss on the initial NO concentration, the photosensitizer concentration in the condensed phase, relative humidity, light intensity, oxygen molar fraction were investigated as well as the HONO and NO_2 yields.

We found the HO_2 production to be a clear function of the molar ratio of photosensitizer to CA (Fig. 1) and of 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_2 radicals, which are released to the gas phase. Therefore, in absence of other gas phase oxidants, the loss of NO in the gas phase could be related to the production of HO_2 radicals in the condensed phase. IC and 4-BBA showed similar HO_2 production rates, while the HO_2 yield with benzophenone was around 50 times higher. The differences may be understood in terms of differing sensitizer excitation rates due to different overlaps between spectral absorbance and lamp emission spectrum, in terms of different rate constants of the triplets with CA and in terms of the physical state of the films.

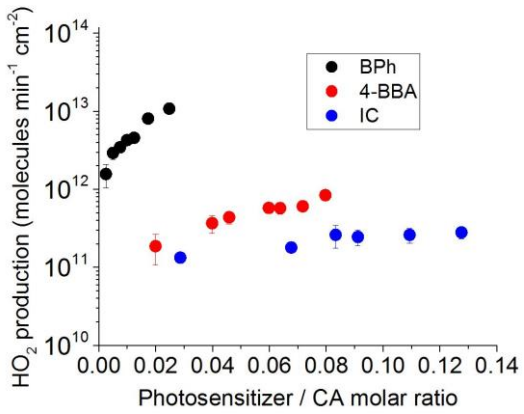

Figure 1. HO_2 production as a function of the molar ratio of the sensitizer to CA in the film of the CWFT.

Figure 2 shows some raw data of results from AFT experiments, showing the response of NO to switching on lights in absence of particles (black) (blank effects due to the AFT walls), in presence of CA aerosol (green) and in presence of CA aerosol with 0.5 mole ratio of IC (red), clearly demonstrating the HO_2 yield from the particles initiated by the sensitizer. Preliminary analysis shows that the yield from the aerosol particles is about an order of magnitude higher than from films of the same composition in the CWFT, likely due to more efficient release of HO_2 out of the condense phase.

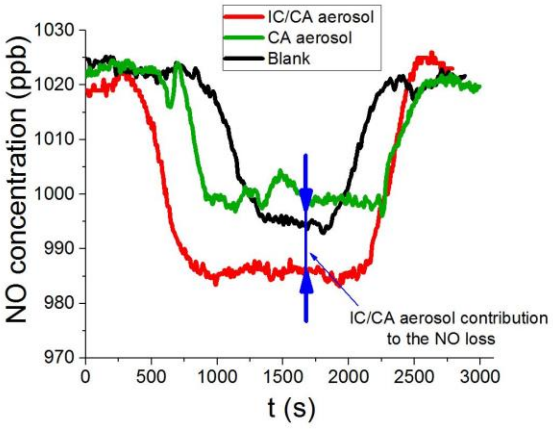

Figure 2. IC/CA aerosol contribution to the NO loss

George, C., Ammann, M., D'Anna, B., Donaldson, D. J., and Nizkorodov, S. A., (2015) *Heterogeneous photochemistry in the atmosphere*, Chemical reviews.

Laskin, A., Laskin, J. and Nizkorodov, S. A., (2015) *Chemistry of Atmospherc Brown Carbon*, Chemical reviews