

Imaging and Product Generation in Highly Viscous Organic Aerosol Particles

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Heavy aerosol loading threatens human health across the globe and is typically related to photochemical processing associated with emission of organic, inorganic and trace metal compounds [1]. Aerosol particles dominated by organic solutes may attain a high or ultra-high viscosity ($>10^{12}$ Pa s) becoming solid-like in cold and dry air, limiting diffusion of organic and reactive molecules through the particle volume, thus slowing chemistry. In contrast, illumination and thus photochemistry to produce radicals may occur through the bulk of light absorbing particles irrespective of diffusion limitations, but its efficiency is not well constrained. We investigated iron oxidation state changes in particles containing various concentrations of citric acid and iron(III) citrate using environmental X-ray spectromicroscopy and coated wall flow tube experiments. Chemical images of aerosol particles with resolution currently as low as 35x35nm were acquired in a humidified microreactor revealing spatial gradients in the concentration of iron(II) and iron(III) compounds [2]. We have also quantified the release of volatile products, such as acetic acid, acetaldehyde and acetone, due to radical reactions and decarboxylation subsequent to ligand to metal charge transfer [3] using proton transfer reaction mass spectrometry. Condensed phase products, such as compounds with 6-11 carbon atoms were determined from HPLC-MS analysis implying functionalization, oligomerization and possibly radical-radical recombination reactions occurred during photochemical cycling. We have found striking evidence that particles and films quickly became anoxic due to reactions with organic radical species, despite being in an O₂ atmosphere, which may explain our vast molecular product distribution in terms of carbon number. Our results are highly important for the accurate prediction of aerosol phase radical generation and chemical loss of oxygenated organic aerosol dominated by carboxyl functionalities [4]. These findings are important for other photochemically active species commonly found in the atmosphere, implying a ubiquity of persistent radicals in airborne particles.

[1] H. Tong et al. Faraday Discuss. **200**, 251-270 (2017).

[2] P. A. Alpert et al. Phys. Chem. Chem. Phys. **21**, 20613-20627 (2019).

[3] J. Dou et al. J. Phys. Chem. Lett. **10**, 4484-4489 (2019).

[4] A. Laskin et al. *Annu. Rev. Anal. Chem.* **9**, 117-143 (2017).