

Imaging and modelling trace metal photochemistry 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. 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, iron(III)-citrate, copper(II)-citrate and copper(II) salts using environmental X-ray spectromicroscopy with control of relative humidity, RH, and temperature, T. Chemical images of single aerosol particles with resolution currently as low as 35×35 nm² were acquired in a humidified microreactor revealing spatial gradients in the concentration of iron(II), iron(III), copper(I) and copper(II) compounds. We have also quantified the CO₂ formation from coated wall flowtube experiments due to decarboxylation subsequent to ligand to metal charge transfer and the condensed and gas phase products using proton-transfer reaction mass spectrometry to characterize the complex chemical reaction scheme. We observed that iron was largely reduced in particles despite being in an oxygen atmosphere immediately after exposure to atmospherically relevant UV light exposure i.e. using 375 nm LED and a measured intensity of 3 W m^{-2} for 15 min. This implies that oxygen uptake, diffusion, reactive oxygen species generation and metal reoxidation reactions were slow compared to photochemical reduction. When relative humidity, $\text{RH} < 50\%$, there was significant oxidation only near the surface of particles extending over scales of tens of nanometers. At higher RH, particles became more homogeneously oxidized. We concluded that O₂ reaction and diffusion is limited and results in organic radical persistence in particles. In the presence of copper, iron was immediately oxidized after UV exposure, which is in sharp contrast to particles without copper. If oxygen is limited, and therefore cannot quickly reoxidize iron, then copper oxidation reactions or cross iron-copper redox reactions must generate more radicals than expected. We aim to improve the kinetic treatment of radical production from copper and iron, which can affect redox cycling in organic aerosol. Such information is necessary for the accurate prediction of aerosol phase radical generation, chemical loss of oxygenated organic aerosol dominated by carboxyl functionalities and identifying diffusion limitations leading to the preservation of reactive oxygen species and free radicals.