



Diffusion and reaction impeded iron carboxylate complex photochemistry

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Iron-carboxylate-complex photochemistry is an important sink of carboxylic acids in the troposphere and an important source of OH radicals in the aerosol phase. Using Fe(III) containing citric acid as proxy for secondary organic aerosol material, we examined feedbacks between microphysical conditions in terms of liquid phase viscosity and the photochemical oxidation of Fe(III). Experiments were performed in a scanning transmission X-ray microscope, a coated wall flow tube and an electrodynamic balance. In an unprecedented manner, we observed spatially resolved Fe oxidation state inside the particle, radical and OVOC production, and mass loss, respectively, determined as a function of relative humidity and visible and UV irradiation applicable to the Earth's surface. These online observables were complemented by offline analysis of oxidation products by high resolution HPLC-MS. Data analysis was supported by depth-resolved modelling of diffusive transport in the liquid, photolysis and chemistry. The results clearly show that at room temperature, the liquid phase solubility and diffusivity of molecular oxygen becomes a major limiting factor for relative humidity below about 50%, leading to a delay of reoxidation of Fe(II), production of functionalization and fragmentation products, production of accretion reactions likely from radical recombination, and finally a corresponding delayed mass loss.