

Ozonolysis of shikimic acid particles caught in the act

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It has been shown that organic compounds may become solid or semi-solid under atmospheric conditions (Virtanen et al., 2010). It is therefore important to understand how the physical state of aerosol components might affect chemical ageing and thus their environmental impact (Shiraiwa et al., 2011). Shikimic acid is a plant metabolite, which has been found to be present in biomass burning aerosol (Medeiros et al., 2008), and which has convenient physical properties at low relative humidity for the purpose of the present experiment. Here, we studied the chemical ageing of individual submicron shikimic acid particles on a substrate as a function of size and humidity in situ using scanning transmission X-ray microscopy (STXM) and near edge X-ray absorption fine structure spectroscopy (NEXAFS).

Shikimic acid particles were generated by ultrasonic nebulisation of solution, dried with a diffusion drier, size-selected by a differential mobility analyzer (DMA) and then impacted on a silicon nitride membrane. A temperature controlled environmental micro reactor (Huthwelker et al., 2010; Zelenay et al., 2011) was used to adjust relative humidity during the experiment (13%-83% RH) and facilitate in situ exposure to ozone. All STXM and NEXAFS experiments were conducted at the Pollux beamline at the Swiss Light Source.

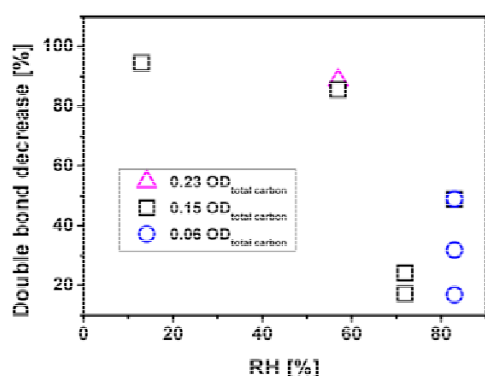


Figure 1. Humidity dependence of oxidation after 211 min exposure to 2.5 ppm ozone. Different symbols mark particles of different total carbon optical density, which is a measure of particle thickness.

Upon oxidation, the carbon K-edge spectra for shikimic acid particles show a clear decrease of the optical density (OD) at 284.5 eV, where resonant

absorption occurs due to the carbon-carbon double bond of shikimic acid. Figure 1 demonstrates the increasing degree of oxidation with increasing humidity. It is likely due to water acting as a plasticizer for shikimic acid, which leads to a decrease in viscosity and thus increase in diffusivity of reactants. Detailed analysis shows that no gradient is observed within the particles. Combined with the size dependence of the oxidation shown in figure 2, this points to either a shallow gradient or a surface limited process.

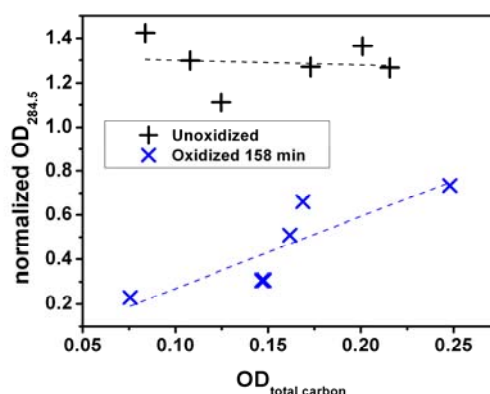


Figure 2. Double bond peak height at 284.5 eV before (black +) and after (blue x) oxidation with 2.5 ppm ozone as a function of particle size, expressed as optical density of total carbon (310-320 eV).

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