



## Influence of physical state on the ozonolysis of shikimic acid

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Atmospheric aerosols are an important focus of environmental research due to their effect on climate, air quality and human health. They undergo continuous transformation, changing their physical and chemical properties. Recent findings show that secondary organic aerosol (SOA) particles can form amorphous solids and semi-solids under atmospheric conditions [1]. Since such physical states are highly viscous, diffusivity within the bulk decreases. The decrease in mass transport could slow down chemical reactions, thereby increasing the lifetime of the organic compounds involved. First indications of such behavior were recently shown for reaction of thin protein films with ozone [2], formation of organonitrogen from ammonia uptake to  $\alpha$ -pinene secondary organic material [3] and reaction of SOA-coated benzo[a]pyrene with ozone [4].

In this study, we investigated the influence of physical state on the ozonolysis of shikimic acid. Said carboxylic acid is a constituent of biomass burning aerosols and used here as a proxy for oxygenated organic material. Its viscosity was adjusted by varying the humidity of the system between 0% and 92% RH, assuming correlation between the two parameters since water acts as a plasticizer. The system was probed with three complementary techniques: an electrodynamic balance (EDB), measuring the response of single particles to changes in humidity, coated wall flow tube measurements, where uptake of ozone is measured via loss from the gas phase and in situ X-ray microspectroscopy on single particles, where oxidation of the bulk can be observed. Additionally, a kinetic model was used to facilitate data analysis.

EDB measurements showed clear evidence of humidity dependent glass formation and correlation of water content and water diffusivity. The dependence of the ozonolysis on relative humidity was observed with both flow tube and microspectroscopy measurements. The coated wall flow tube experiments showed a long term, gradually changing ozone uptake over more than 15 hours, the magnitude of which varied over nearly two orders between lowest and highest humidity. It was possible to separate the uptake into two distinct kinetic regimes, the first of which displayed a Langmuir-Hinshelwood type behavior regarding the ozone gas phase concentration. Microspectroscopy showed that the speed at which the characteristic double bond peak of shikimic acid disappeared was humidity dependent.

The measured dependence of the reaction kinetics on humidity supports the hypothesis that the uptake coefficient is highly dependent on the diffusion coefficients of ozone and/or shikimic acid in the organic film.

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[4] Zhou, S., et al., Kinetic limitations in gas-particle reactions arising from slow diffusion in secondary organic aerosol. *Faraday Discussions*, 2013. 165: p. 391-406.