

Influence of Physical State on Shikimic Acid Ozonolysis

S.S. STEIMER^{1,2*}, U.K. KRIEGER², M. LAMPIMÄKI¹,
T. PETER² AND M. AMMANN¹

¹Laboratory of Radiochemistry and Environmental Chemistry,
Paul Scherrer Institute, 5232 Villigen, Switzerland
(*correspondence: sarah.steimer@psi.ch)

²Institute for Atmospheric and Climate Science, ETH Zurich,
8092 Zurich, Switzerland

Introduction

Atmospheric aerosols undergo continuous transformation, changing their physical and chemical properties. Secondary organic aerosol particles (SOA) can form amorphous solids and semi-solids under atmospheric conditions [1]. Since such physical states are highly viscous, diffusivity decreases which in turn could slow down chemical reactions. First indications of such behaviour were e.g. shown for reaction of protein films [2] and SOA-coated benzo[a]pyrene [3] with O₃. Here we investigated the influence of physical state on the ozonolysis of shikimic acid, a proxy for reactive oxygenated organics. Its viscosity was adjusted by varying humidity between 0% and 92%. 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 O₃ is measured via loss from the gas phase and in situ X-ray microspectroscopy on single particles, where oxidation of the bulk interior can be directly observed.

Discussion of Results

EDB measurements showed clear evidence of humidity dependent glass formation and correlation of water content and water diffusivity. Dependence of the ozonolysis on relative humidity was observed with both flow tube and microspectroscopy measurements. The 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. Microspectroscopy showed that shikimic acid degradation is both humidity and size dependent which points to a reacto-diffusion limited process. 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.

[1] Virtanen *et al* (2010) *Nature* **467**, 824-827. [2] Shiraiwa *et al* (2011) *Proc. Natl. Acad. Sci. USA*. **108**, 11003-11008. [3] Zhou *et al* (2013) *Faraday Discuss.* **165**, 391-406.