

Interactive
Comment

Interactive comment on “The influence of physical state on shikimic acid ozonolysis: a case for in situ microspectroscopy” by S. S. Steimer et al.

Anonymous Referee #1

Received and published: 22 April 2014

This manuscript describes the measurement of ozone uptake rates to probe the properties of shikimic acid particles under different humidity conditions in a controlled chamber. Linearized rate expressions for diffusion-limited and volume-limited consumption are fitted to apparent degradation rates of aromatic bonds lost through oxidation by ozone to determine the dominant mechanism for ozone uptake at high and low RH regimes. The decreased rate of uptake and lack of degradation in bulk-phase aromatic bonds at lower RH despite competing processes - increasing organic molecule concentration and higher solubility of ozone in organic than aqueous phase - are used to infer increased viscosity of the solution at low RH. This manuscript presents a novel application of a reactor coupled with STXM to semi-quantitatively study uptake mechanisms which elucidate particle-phase properties under high and low RH regimes. It is

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carefully written and presents a contribution to aerosol instrumentation and our understanding of organic-water aerosol mixtures; it is therefore recommended for publication in *Atmospheric Chemistry and Physics*. Comments are included below.

General comments:

Is another possible interpretation that an oxidized layer rapidly forms (e.g., Renbaum and Smith, *PCCP*, 11, 2441-2451, 2009) and reduces the uptake of the ozone at the surface in the low RH case rather than reducing the viscosity through the solution? The ozone mass accommodation coefficient and gas-phase diffusion resistance may additionally enter consideration if the uptake is then not primarily limited by viscosity.

Is there any qualitative information regarding the increase in oxidized bonds in time/space that can be simultaneously reported by this technique? How frequent/constant is the contamination, and how is it distributed over a image stack? Over what regions are the spectra in Fig. S1 averaged (are the black and gray lines for the same sample?), and can any information be extracted by averaging over a larger number of pixels/lines? Can the authors overlay a difference spectrum between the black and gray to show a correlation with I0?

Figure S3. The nature of the contamination and what is shown in the figure is not entirely clear, though the message seems to be that the analytical technique should be able to identify absorbance gradients larger than 100 nm, so the fraction of aromatic bonds oxidized during reacto-diffusive uptake reside in regions smaller than this distance from the surface (should be clarified in the manuscript). STXM has indeed previously been demonstrated to reveal the presence of layers/gradients on the order of 100 nm from spatial analysis of STXM images (Takahama et al., *JGR*, 115, D01202, 2010).

Minor comments:

In absorbance figures, "Intensity [a.u.]" (y-axis label) is missing the second period.

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Many of the calculations depend on the determination of $[Y]_{b,0}$ but is not documented in any detail in the manuscript.

The loss rate of ozone to the reactor chamber (and corrections, if any) was not mentioned.

Would the solubility of ozone be higher (p.7367, top) as the aerosol approaches the composition of pure shikimic acid? At these temperatures the shikimic acid should be in solid phase rather than liquid.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 7355, 2014.

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