**Atmospheric
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Discussions

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

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R: 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.

A: We do know from EDB measurements that shikimic acid forms a glass at low humidities. We also know from the chemical maps that the reaction product still diffuses freely at 52% RH, which precludes that a non-diffusing oxidized layer has formed down to this humidity. It is possible that formation of an oxidized layer (of a thickness below

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resolution of the STXM) is an additional effect at very low humidities. This cannot be determined from the available data. However it is not necessary to invoke an additional barrier for transport. We can estimate diffusion coefficients from structurally similar compounds such as sucrose, or from measurements of water diffusivity in shikimic acid (Steimer et al., manuscript in preparation). For the drier conditions employed in the present experiment, these diffusion coefficients get low enough for both reactants, so that they do not move over sufficient distances (100nm) within the time scale of the experiment. This point will be strengthened more in sections 3.3 and 3.4.

R: Is there any qualitative information regarding the increase in oxidized bonds in time/space that can be simultaneously reported by this technique?

A: Yes, an example of this can be seen in Fig. 2. As mentioned on p.7363, line 1-4, both the appearance of the peak at 286.4 eV and the change at 288.2 eV should be due to an increase in oxidized bonds. The text will be adapted to make this clearer.

R: How frequent/constant is the contamination, and how is it distributed over an image stack?

A: If this is about the first section of the Supplement (Carbon contamination and spectral distortion): carbon contamination of the beamline varies between beamtimes, but usually stays constant during a specific beamtime and thus from measurement to measurement. As it arises from contamination of the optical elements and windows of the beamline itself, the effect manifests all over the sample. If this is about the third section of the supplement (Chemical mapping): carbonaceous impurities of an unknown nature where found only during measurement of the 12% RH sample in 3 out of 33 measured particles.

R: 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?

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A: The spectra are averaged over single particles. The two particles were from different samples and measured at beamtimes more than one year apart. This will be added to the text. While it would be possible to make a difference spectrum, we do not think this adds anything as the correlation between the difference in absorption and low I0 is already directly obvious from the current graph.

R: 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).

A: Yes, this is indeed the reason why we added this information (illustration of the spatial resolution in chemical mapping). We will add your suggestions to the supplemental information to make this clearer.

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

A: Will be changed

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

A: As written on p. 7365, l. 6-9 the initial concentrations at the various humidities were determined with an electrodynamic balance. A manuscript containing the exact procedure is currently being written and should already be submitted to AMTD at the time of final revisions of this paper. The appropriate citation will be added.

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

A: We measured ozone only after the reactor and did therefore not measure the loss rate explicitly. Given the small amount of shikimic acid in one sample (less than picogram), it should be below detection limit.

R: 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.

A: As the solid shikimic acid is in glassy form, it is still amorphous, with only a small difference in free energy compared to the liquid. Thermodynamic properties such as solubility should therefore not be strongly affected. Apparent changes to solubility are due to kinetic effects which are explicitly considered in our evaluation via the diffusion coefficient.

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