Review on:

Hinks et al.: “Effect of Relative Humidity on the Composition of Secondary Organic Aerosol from Oxidation of Toluene”

General comments

The authors describe a laboratory study on the atmospheric oxidation and secondary organic aerosol formation from toluene oxidation under different relative humidity conditions. Humidity dependence of the SOA composition is reported for low NOx conditions. The chemical composition of SOA collected on filter samples was analyzed by offline nano desorption electrospray ionization coupled to a high resolution mass spectrometer (nano-DESI-HRMS) in both polarity modes. The mass concentration of the formed SOA was monitored for a different set of chamber experiments using a scanning mobility particle sizer (SMPS). The authors report different chemical composition at different RH, and hypothesize that oligomerization by condensation reactions in the condensed phase can explain the observation of enhanced SOA yield at low humidity. In agreement with earlier studies they see no humidity dependence of toluene SOA formation under high NOx conditions.

The work addresses the relevant scientific question of anthropogenic SOA formation, and therefore contributes to build a better mechanistic understanding on urban SOA burden under different atmospheric conditions. Therefore the paper certainly lies within the scope of “Atmospheric Chemistry and Physics”. It contributes with new experimental results on the SOA composition from toluene. As the authors state, toluene SOA yield experiments have already been described by others, but the linkage between SOA mass and composition has been missing. The scientific method of the SOA chamber experiment is clearly described and the measured SOA mass is corrected for chamber wall-losses. The offline analysis of Teflon filters is based on the established tool nano-DESI-HRMS, which provides the elemental composition of the condensed phase oxidation products as a basis for the hypothesis of different oligomerization efficiencies under different RH conditions.

I therefore recommend the article to be published in ACP, after the following specific comments and technical corrections have been addressed.

Specific comments

p.1 l.28: SOA formation mechanisms not only depend on solar irradiance, temperature and RH, but also on VOC precursor mixtures that ultimately govern RO2 radical concentration and on NOx levels which can affect branching and termination of oxidation pathways.

p.2 l.9: Another more recent publication (Zhao et al., 2017) that addresses a photochemical aqueous phase sink of dimers from VOC oxidation should be added.

p.3 l.16: A commonly known risk in offline analysis is (positive and negative) artefact formation on the filter, especially when reactive species, such as organic hydroperoxides (ROOH), organic peroxides (ROOR), peroxy acids etc., are sampled. This implies that the measured composition not necessarily reflects the composition and state of the aerosol in the chamber. Krapf et al. (2017) have shown that a significant fraction of highly oxidized and thermodynamically unstable products of VOC ozonolysis can decompose on the scale of minutes to a few hours. This brings me to the question of how the authors evaluated the effect of filter artefacts? How long and under which conditions were the filters stored until analysis by nano-DESI-MS? Was the aerosol in the high RH experiments dried before being sampled on the filter? How and by which solvent were the filters extracted during nano-DESI-MS analysis?

p.4 l.1: The authors use the term “SOA compounds” when discussing mass spectral patterns. How was the possibility of ion source cluster formation evaluated?

p.4 l.4: The fact that common major peaks were observed, suggests that these are the same products, however, the possibility exists that different isomers are formed. Whether this is the case can only be evaluated by a separation technique before mass spectrometry, and should be mentioned in this paragraph.

p.4. l.7: The authors argue that oligomer formation (in the condensed phase) is suppressed under high RH condition. Have the authors considered that oligomerization (especially dimerization) can also occur in the gas phase by RO2-RO2 recombination? Once the dimers that are formed in the gas phase partition to the condensed phase, they might undergo more rapidly hydrolysis reactions under high RH conditions, which in the end would result in a similar observation.

p.4 l.27: ESI sensitivity is not only driven by mass but also by functionality, solvent composition, polarizability and by the tendency of the analyte to interact with other matrix components. Therefore it is highly questionable that peak abundance is proportional to the observed mass fraction. The strongest argument against the proposed simplified relationship between sensitivity and molecular weight is actually given in figure 1: If the sensitivity would only be a function of molecular weight, why is the monomer-to-dimer ratio different between the positive and negative mode? Furthermore, we observed that ESI sensitivity between two very similar commercially available standards (pinonic acid and camphoric acid) can be different by orders of magnitude. Therefore, the authors should argue here more carefully and consider that different ionization efficiency can introduce a significant bias.

p.5, l.1: I agree that the signal in the lower volatility bin (Figure 3) is suppressed under high RH in the positive mode. However, for the negative mode this is not obvious. Did the authors try to normalize the figures on the base peak in the mass spectrum to present the relative changes more in detail?

p.6, l.22-24: Again: the authors should discuss the possibility of enhanced condensed phase hydrolysis reactions of dimers under high RH conditions. The enhanced viscosity of particles under low RH might suppress the rate of hydrolysis reactions.

p.13, Figure 3: The volatility distribution in (a) looks as it is cut on the high volatility end. How many products appear in the bins $\log_{10}(C_0)>6$? Can these products be summed up into one bin which contains all compounds of all bins with $\log_{10}(C_0)>6$?

Technical corrections

p.13, Figure 3: The figure caption contains (a) and (b) which is not shown in the figure. Also, the colour description in the caption is wrong: high RH should be “blue” and low RH “red”.

Literature

Krapf, M., El Haddad, I., Bruns, E. A., Molteni, U., Daellenbach, K. R., Prévôt, A. S. H., Baltensperger, U. and Dommen, J.: Labile Peroxides in Secondary Organic Aerosol, Chem, 1(4), 603–616, doi:10.1016/j.chempr.2016.09.007, 2017.

Zhao, R., Aljawhary, D., Lee, A. K. Y. and Abbatt, J. P. D.: Rapid Aqueous-Phase Photooxidation of Dimers in the α-Pinene Secondary Organic Aerosol, Environ. Sci. Technol. Lett., 4(6), 205–210, doi:10.1021/acs.estlett.7b00148, 2017.