

Interactive comment on “Halogenation processes of secondary organic aerosol and implications on halogen release mechanisms” by J. Ofner et al.

J. Ofner et al.

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We thank referee #1 for the careful consideration of our manuscript and the very detailed and helpful comments.

Referee #1 suggested that we should discuss the observations in view of specific chemical reactions/mechanisms in order to begin building a framework for understanding this chemistry - the major criticism of referee #2 as well. We follow these suggestions by adding a section with a detailed discussion of possibly occurring chemical reactions and mechanisms related to formation of halogenated species and transformation of functional groups to the discussion and to the conclusion. To avoid a duplication of our changes to the manuscript, please see our answer to referee #2 for this remark.

Answer to comment related to chapter 3.1: We did not study SOA formation from guaiacol in the absence of ozone. While this paper is focused on the heterogeneous interaction of RHS with preformed SOA or BBOA, further work on the homogeneous interactions is planned. We added (p. 2993,27): “Atomic chlorine induced hydrogen abstraction can explain the simultaneous formation of HCl and the decrease of $\nu(\text{C-H})$.” as a general remark. More experiments would be required to understand the observation of the second mode.

Answer to comment related to chapter 3.2 and 4.2: We changed the text at p. 2985,20-25 to introduce the normalization coefficients: “The single absorption spectra were normalized at 200 nm to an absorbance of 1 using the normalization coefficients λ , which changed the original absorption at 200 nm by about 5%. dA was calculated according to equation 1, where $\lambda^*F(R)^*$ is the normalized absorption spectrum of the aerosol after the reaction with RHS and $\lambda F(R)$ is the normalized absorption spectrum of the aerosol before the reaction.” p.2990,5-7: Change of text: “To achieve detailed changes in the diffuse-reflectance UV/VIS absorption spectra, the differential absorbance was calculated according to equation (1). The normalization coefficients at 200 nm are about 15% of the original values.”

We added the normalization coefficients to equation (1): See fig. 1 of the comment.

Following the suggestions of referee #1 we changed the figure and caption of Fig. 3: “Figure 3. Single absorption spectra (a) and change of the differential absorbance (dA) (b) in the UV/VIS spectra region due to the reaction of SOA with RHS formed from photolysis of molecular chlorine or bromine.” See fig. 2 of the comment.

We changed the figure and caption of Fig. 10: Figure 10. Single absorption spectra (a) and change of the differential absorbance (dA) (b) in the UV/VIS region due to the reaction of the organic aerosols with RHS released from the simulated salt pan, indicating a chlorination of the SOA. See fig. 3 of the comment.

Answer to comment related to chapter 3.3: Displaying the 30 minutes reaction spectra

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as transmissions was chosen because of several difficulties in quantifying the long-path absorption spectra. The path length of the infrared White cell was not stable and hence not fully quantified. The White cell was operated at the upper level of maximum reflections to enhance the detection threshold. With this configuration, small changes in temperature or vibrations can significantly change the path length. Furthermore, the long-path infrared spectra do not only contain gaseous species. There is a broad background of infrared absorption caused by the rather high amount of aerosol particles within the aerosol smog-chamber. Hence, automatic baseline correction procedures failed. Manual baseline correction was required for every single spectrum. Because of the unknown path length and aerosol background and the manual baseline correction, the authors have decided to indicate only qualitative changes of gaseous species, caused by the heterogeneous reaction. Furthermore, to avoid any quantitative interpretation, displaying transmission spectra was preferred to showing absorption spectra. Although the referee is right with his demand of a quantitative statement, we think that our dataset is currently too complex to perform a reliable quantitative interpretation. We added the following text to figure caption 4: “Due to the fact, that the represented spectra are transmission spectra, positive absorptions correspond to decreasing species, while negative absorptions indicate increasing species.”

Answer related to figure 5: We changed the figure and the caption and included reference spectra of unprocessed SOA samples as suggested by the referee. Figure 5. ATR-FTIR spectra of unprocessed SOA (Ofner, 2011) and SOA processed with RHS (L: SOA formed with simulated sunlight at 0% relative humidity; LW: SOA formed with simulated sunlight at 25% relative humidity). See fig. 4 of the comment.

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$$dA = \lambda^* \cdot F(R)^* - \lambda \cdot F(R) = -\lg \frac{I^*}{I_0} + \lg \frac{I}{I_0} = \lg \frac{I}{I^*}$$

Fig. 1.

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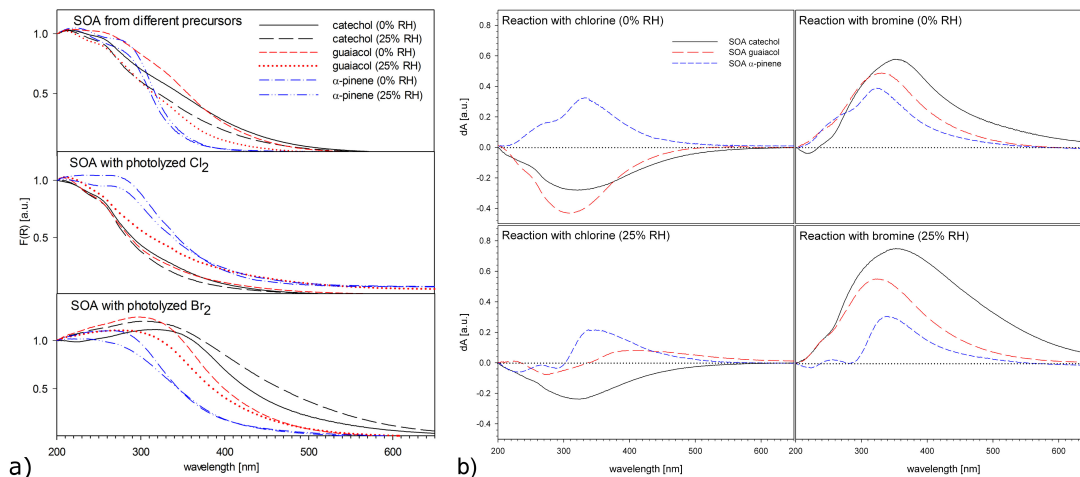
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Fig. 2.

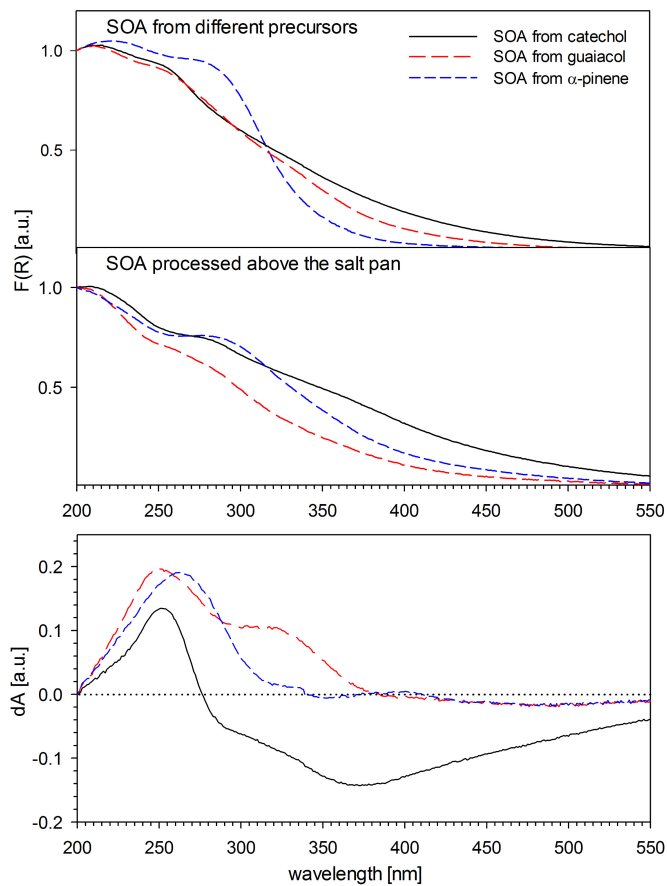
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Fig. 3.

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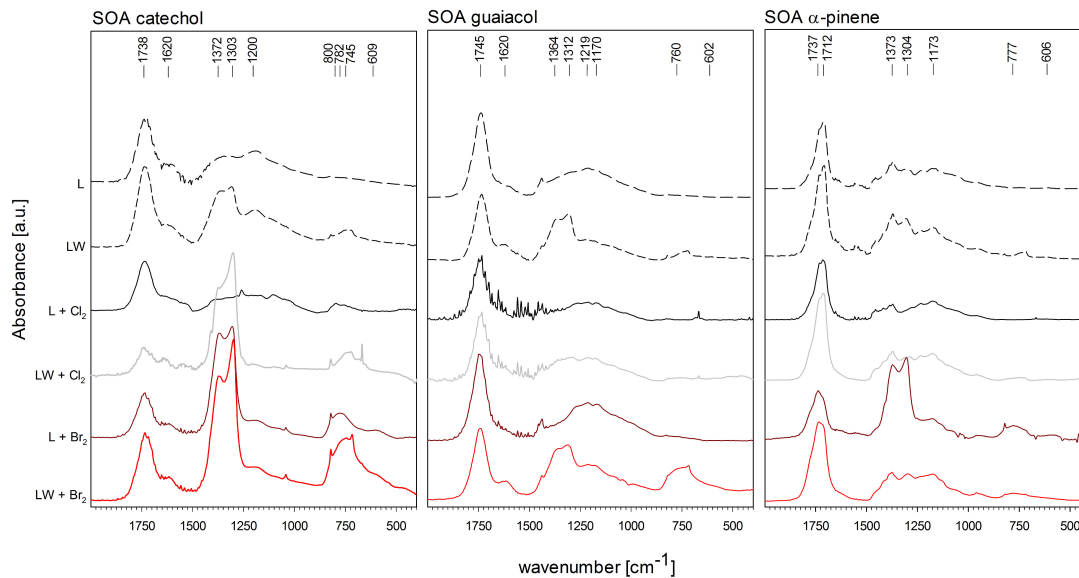
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Fig. 4.

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