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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Secondary organic aerosol from chlorine-initiated oxidation of isoprene" *by* Dongyu S. Wang and Lea Hildebrandt Ruiz

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We thank the referee for the suggestions and recommendations. Below are our responses to the comments.

(a) Reviewer: Introduction: The authors should add a Paragraph to the introduction about natural and anthropogenic halogen sources and sinks in the atmosphere to introduce this topic to the readers; e.g. by: Simpson et al., Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts, Chem. Reviews, 2015. Roland von Glasow, Wider role for airborne chlorine, nature, 464, 2010. Finlayson-Pitts, Halogens in the Troposphere, Anal. Chem., 82, 770-776, 2010. Buxmann et al., Consumption of re-

active halogen species from sea-salt aerosol by secondary organic aerosol: slowing down the bromine explosion, Environ. Chem., 12, 476-488, 2015.

Response: We have added a discussion on natural and anthropogenic halogen sources and sinks to the introduction of the revised manuscript as suggested by the reviewer.

(b) Reviewer: p2 line 30: Please add the characteristics of the UVA light source: actinic flux, quantified UV/VIS spectrum.

Response: We have included additional information on the UV light source.

Manuscript changes in Section 2.1: "The UV spectrum is similar to other blacklight sources reported in literature (Carter et al., 2005). The NO2 photolysis rate is used to characterize UV intensity and was determined to be 0.5 min-1, similar to ambient levels (e.g. 0.53 min-1 at 0 degrees zenith angle, Carter et al., 2005)

(c) Reviewer: P3 line 31 "loss of organic vapors to Teflon surfaces" Teflon films, used for aerosol smog-chambers, are known to store various gaseous species, especially NOx, which is released from the Teflon film by UV radiation and increased temperatures. Has this been observed or taken into account? Please add a related statement to the manuscript.

Response: We have added a discussion on wall emissions and conducted chamber modeling to estimate the background contribution to secondary OH chemistry. Overall, chlorine-isoprene chemistry dominates gas-phase chemistry and secondary HOx production.

Manuscript changes in Section 2.1: "Between experiments, "blank experiments" were conducted in which seed particles, ozone, and chlorine gas (Cl2 Airgas, 106 ppm in N2) were injected into the chamber at high concentrations and UV lights were turned on to remove any residual organics that are released from the Teflon® chamber under UV. Background effects were estimated using the SAPRC chamber modeling soft-

ware (http://www.engr.ucr.edu/∼carter/SAPRC/) in combination with the Carbon Bond 6 (CB6r2) chemical mechanism which was modified to include basic gas phase inorganic chlorine chemistry in addition to Cl2 and ClNO2 photolysis (Sarwar, Simon, Bhave, & Yarwood, 2012; Yarwood et al., 2010). Wall effects are represented within the model by a constant emission of nitrous acid (HONO) from the chamber walls on the order of 0.1 ppb min-1, which was determined separately in chamber characterization experiments (Carter et al., 2005)."

Manuscript changes in Section 3.4: "The SAPRC chamber model results indicate that more than 99% of the isoprene reacts with Cl; secondary OH chemistry is therefore only a very minor pathway in these experiments. Model results also show that HO2 production is dominated by isoprene-chlorine chemistry, whereas wall effects dominate HO2 production (>60 %) after all isoprene has been consumed. It is worth noting that the model does not explicitly represent Cl-initiated oxidation of reaction products, which can produce additional HOx radicals. Therefore, we expect the actual secondary OH chemistry to be more important than the current model estimation."

References

Carter, W. P. L., Cocker, D. R., Fitz, D. R., Malkina, I. L., Bumiller, K., Sauer, C. G., Pisano, J. T., Bufalino, C. and Song, C.: A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation, Atmos. Environ., 39, 7768–7788, 2005

Sarwar, G., Simon, H., Bhave, P., & Yarwood, G. (2012). Examining the impact of heterogeneous nitryl chloride production on air quality across the United States. Atmospheric Chemistry and Physics, 12(14), 6455–6473. doi:10.5194/acp-12-6455-2012

Yarwood, G., Jung, J., Whitten, G. Z., Heo, G., Mellberg, J., & Estes, M. (2010). Updates to the Carbon Bond Mechanism for Version 6 (CB6). In Presented at the 9th Annual CMAS Conference, Chapel Hill, NC, October 11-13 (Vol. 6, pp. 1–4).

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