

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

Anonymous Referee #1

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Wang and Hildebrandt Ruiz present a laboratory study of secondary organic aerosol (SOA) formation from chlorine-initiated oxidation of isoprene in chamber experiments under low relative humidity and low NOx conditions. They report maximum SOA yields from two different types of experiments, the initial injection of chlorine, and the continuous injection of chlorine. In both cases, prompt SOA formation was observed. In the light of recent observations of unexpectedly high reactive chlorine concentrations in the atmosphere, this study contributes important findings for a better evaluation of the role of chlorine-initiated oxidation reactions of organic compounds in the atmosphere. The supplement gives comprehensive additional information, e.g. a valuable discussion of quantification issues of particulate chloride with the ACSM/AMS. In my opinion, the

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study is highly topical and deserves publication in ACP after taking into account the following comments:

- a) p.5, line 1: The limitations of estimating O:C, H:C, and the oxidation state of carbon from f44 based on empirical correlations should be briefly discussed. For example, equation S-1 in section S2 may underestimate O:C values substantially in environments dominated by NOx-free isoprene chemistry (Canagaratna et al., 2015). Also, the presence of heteroatoms may introduce deviations from equation S-3 in section S2 when estimating the oxidation state of carbon (Kroll et al., 2011).
- b) p.5, line 13: The separation of experiments A1-A5 and experiments H1/H2 seems to be somewhat arbitrary. In my opinion, experiment H1 should be experiment A6, and the much higher maximum yield of this experiment should be part of the discussion of section 3.3. Experiment H2 is a technical experiment to "...explore the ability of the ACSM to detect organic chloride" (supplement, section S4). I was confused to find information about H2 in Table 1, and I recommend to remove it from the table and just explain the character of this experiment in the supplement.
- c) p.5, line 21: Chlorinated organic compounds have also been identified in ambient aerosol samples from Western Australia by ion cyclotron mass spectrometry (Kamilli et al., 2016), with a higher abundance of chlorinated organic compounds in daytime samples when photochemistry is active.
- d) p.7, line 19: The VOC:Cl2 ratios may be expected to be much higher under atmospheric conditions than in the presented experiments. Do the authors have some insight, or could they speculate about how the yields may change for larger isoprene:Cl2 ratios? Also, when presenting the highest observed SOA yields, why do the authors exclude experiment A1 for the average yield of the initial injection experiments?
- e) p.8, line 8: When discussing secondary OH chemistry, the authors mention potentially unidentified HOx production pathways other than HO2 production during formation of CMBO. It would be extremely interesting to have at least a semi-quantitative

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estimate of the contributions of chlorine-initiated secondary OH chemistry vs. OH chemistry from other sources, potentially also due to chamber wall effects.

Technical comments:

in manuscript: p.2, line 16 and p.7, line.27: When referring to isomers of CMBO, these should be isomers of chloromethylbutenone, e.g. 1-chloro-3-methyl-3-butene-2-one, not "isomers of 3-methyl-3-butene-2-one". p.3, line 23: Change "relatively ionization efficiencies" to "relative ionization efficiencies". p.4, line 10: The reference should read "Odum et al., 1996". p.9, line 4: Change "produced form" to "produced from". p.9, line 6: Change "chlorine-initiation oxidation" to "chlorine-initiated oxidation". p.18, Table 1: I don't understand the value of the VOC:Cl2 ratio in experiment H2.

in supplement: p.3, line 7: Change "number of water cluster" to "number of water clusters". p.4, line 7: Remove "greater than" before "44 % overestimation could be expected".

References

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