Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-807-RC2, 2019

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Formation of highly oxygenated organic molecules from chlorine atom initiated oxidation of alpha-pinene" *by* Yonghong Wang et al.

Anonymous Referee #1

Received and published: 12 December 2019

General comments:

Wang et al. report results of laboratory chamber experiments of chlorine-atom-initiated oxidation of a-pinene in low and high NOx conditions. They conduct the experiments in a steady state chamber, varying the number of lights that are turned on to simulate different oxidation rates. They use published a-pinene+Cl reaction rates to calculate the concentration of Cl radicals in the chamber at different number of lights on, and report that the Cl concentrations are similar to atmospheric conditions. For low NOx conditions, new particle formation (based on number concentrations) is reported for all light intensities, but an increase in mass concentrations was only detected by the

AMS when 4 and 7 lights were on. Under high NOx conditions, dimer formation was suppressed and no SOA was detected; ozone was also formed which may have resulted in concurrent a-pinene ozonolysis reactions due to which the authors decided not to calculate HOM yields under high NOx conditions. HOM production yields from the low NOx conditions are calculated as 1.8% (within 0.8-4%), with high uncertainty due to a lack of calibration standards for HOM. Overall, the manuscript is well written, and describes results from experiments designed to address a scientific question not previously answered. I recommend publication of the manuscript after the comments below have been addressed.

Specific comments:

1) Experiments were conducted without the addition of water vapor, resulting (I assume) in an RH of $\sim$ 0% (please clarify in the manuscript if this is the case). As such RH is not a realistic condition, I request that the authors discuss how results (i.e. the formation of HOM and SOA) are expected to change under RH conditions that are more atmospherically relevant.

Section 1, Introduction:

2) Please provide references for: the studies that have focused on HOM formation from O3, OH and NO3; and for the concentration of Cl atoms being estimated as 1-10% of OH radicals.

3) It may be beneficial to discuss in which urban settings the reaction of a-pinene and Cl would be relevant, and express what range of RH would be encountered there.

Section 2.2, Instrumentation and analysis:

4) Please provide more information on how Ehn et al. (2014) obtained the HOM calibration factor, and whether or not it is expected to be instrument-specific. Why is the stated uncertainty range -50% to +100%? Could it be much larger, e.g. could the sensitivity differ by a factor of 10? If not, why not?

5) lines 220-221: Clarify why at high oxidation rates, autoxidation is thought to be inhibited compared to atmospheric conditions. Does this work support that conclusion, and if so, how?

6) lines 229-230 – please provide reference for 'earlier studies'

7) lines 264-266 - Wang and Hildebrandt Ruiz (2017) suggested that organochlorides may not flash vaporize efficiently, leading to an underestimation of the chloride content in the aerosol. While this earlier work was based on an aerosol chemical speciation monitor, the aerosol mass spectrometer used here uses the same vaporizer. I suggest the authors discuss this possibility and analyze the relative abundance of the Cl+ vs. the HCl+ signal in the particle spectra as suggested by Wang and Hildebrandt Ruiz.

Reference:

D. S. Wang and L. Hildebrandt Ruiz*. Secondary organic aerosol from chlorine-initiated oxidation of isoprene, Atmospheric Chemistry and Physics, 13491-13508, 17, 2017.

Section 3.2:

8) Are chlorinated organonitrates observed?

9) lines 293-295: How do the authors reach the conclusion that Cl oxidation (vs. ozonolysis) is the main loss mechanism for a-pinene? It should be possible to calculate this based on estimated Cl concentrations, measured O3 concentrations and published reaction rates, but this calculation is not mentioned in the manuscript.

10) lines 632-633: earlier in the manuscript the authors offer alternative explanations for the lack of Cl species in the HOM spectra. It is my understanding that the data presented here are not sufficient to conclude that H-abstraction is the dominant pathway. I suggest removing or modifying this sentence. Was HCl measured, and could its abundance point to the relative importance of H-abstraction vs. Cl- addition pathways?

Technical comments:

line 73: remove period after "organics"

line 78: "their" instead of "its"

line 101: et al. (instead of et.al)

line 110: remove "a" before laboratory

line 117: capitalize subtitle?

line 138: "this" instead of "such"

line 169: there are two sections 2.2

line 240: citation formatting

line 260: replace 'increased' with 'increase'

line 305: there are two sections 3.2

line 677-678: organic nitrates*

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