

Interactive comment on “Chlorine-initiated oxidation of n-alkanes under high NO_x conditions: Insights into secondary organic aerosol composition and volatility using a FIGAERO-CIMS” by Dongyu S. Wang and Lea Hildebrandt Ruiz

Anonymous Referee #1

Received and published: 10 July 2018

General Comments

This paper reports results of a laboratory study of secondary organic aerosol (SOA) formation from the oxidation of a series of n-alkanes with Cl atoms in the presence of NO_x in a smog chamber. The gas-phase composition of products and SOA was analyzed using a FIGAERO-CIMS to obtain information on product molecular formulas and thermal desorption profiles, and an ACMS and SEMS were used as well. The

Printer-friendly version

Discussion paper



results were then interpreted in terms of the reasonably well-established mechanism for alkane oxidation by OH radicals, with the addition of possible oligomer-forming reactions. Interesting observations are reported on chlorine-containing products, organic nitrates, other multi-generation oxygenated products, and a new 2-D format is used to present composition and thermal data. The results provide a nice comparison to OH oxidation and the molecular and thermal characterization of products may be useful for future development and testing of models for these reactions. The experiments are very well done, and the introduction, data analysis, and interpretation are thorough and clearly written. Cl oxidation of VOCs has not been well studied, and as shown here its products can differ in significant ways from OH oxidation. There is thus plenty more to be done, but this paper is a good starting point for detailed SOA chemistry studies. I think the paper can be published in ACP after the following comments are addressed.

Specific Comments

1. In a study of the aging of pentadecane by OH/NO_x that was not cited here (Aimanant and Ziemann, AS&T, 2013), evidence was presented based on thermal desorption profiles for the presence of acetal dimers formed from cyclic hemiacetals. These would likely be very stable and so probably desorb intact. Do the authors see any evidence for such oligomers?
2. Can the composition data be used to estimate average molecular weights for the SOA analyzed by the FIGAERO-CIMS? It would be useful to use these values to convert the mass yields of SOA to molar yields of SOA, since this gives a better indication of the efficiency of SOA formation. Otherwise the large mass yields (due in large part to the extensive oxidation) give the impression that a large fraction of the alkane is converted to SOA, which is not really true.
3. Is there any indication for chemistry occurring between Cl, O₂, and NO_x? Would this be expected?
4. Structure-activity relationships for the reactions of alkanes with Cl atoms indicate

[Printer-friendly version](#)[Discussion paper](#)

that the ratio of rate constants for abstraction of primary/secondary H-atoms is significantly smaller than for OH reactions, indicating that more reaction occurs at the ends of the alkanes with Cl than with OH. Have the authors considered what the consequences of this might be with regards to the products being formed?

5. Have the authors considered comparing vapor pressures estimated from the measured desorption temperatures with those predicted from proposed molecular structures and the SIMPOL group contribution method?

6. It would be useful to provide a little more detailed speculation on the proposed nature of the thermal decomposition products. Are these thought to be formed by simple reversible dissociation of hemiacetals, for instance, or by cleavage of strong C-C or C-O bonds? Or might they just be compounds that are “trapped” in a solid SOA matrix that cannot escape until the SOA melts?

7. I did not see a quoted density for calculating SOA yields from SEMS data. This value and its source should be noted.

Technical Comments

None.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-443>, 2018.

Printer-friendly version

Discussion paper

