

Interactive comment on “Oligomerization Reactions of Criegee Intermediates with Hydroxyalkyl Hydroperoxides: Mechanism, Kinetics, and Structure-Reactivity Relationship” by Long Chen et al.

Anonymous Referee #1

Received and published: 4 January 2019

This manuscript describes the gas phase reactions of Criegee intermediates (CI) formed from ozonolysis with hydroxyalkyl hydroperoxides (HHP) to determine the feasibility of these reactions in the formation of oligomeric species in atmospheric ozonolysis. The authors complete this task thoroughly with a number of different CI and HHP. The consecutive reactions for oligomer formation are clearly feasible thermodynamically and kinetically when considered in and of themselves. All the reactions studied proceed via exothermic formation of a pre-reactive complex and have reaction barriers of 4.5-13 kcal/mol. The authors have studied important reactions for the understanding

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of new particle formation from ozonolysis, but the exact context in terms of overall CI reactivity is not discussed clearly and the context of their results needs to be clarified. As an overall loss process for CI, the reactions studied are minor, with the apparent lifetimes of nearly 2 hours, while unimolecular loss alone will be much faster (less than 1 second for the dimethyl CI). The investigated reactions may play a role in the processes of SOA and/or new particle formation, as these biomolecular reactions of CI with other organic compounds form material with very low volatility. This is a good contribution to the field. I recommend this manuscript for publication following minor revisions to the text and a substantial increase of the data presented in the supplemental material.

General Comments:

The sentence on lines 45-48 is plagiarized from Donahue et al.(1) I do not have the resources to fully vet the rest of this manuscript, but all text must be in your own words. You cannot copy such fine sentences as if they were your own. ALL instances of copied text must be removed and replaced with text you produce.

Please make clear throughout that the reactions studied are minor loss processes for CI. Your lifetime of 6000 seconds is quite long compared to other CI reactions. In addition, make explicitly clear that you calculate the lifetime with respect to only reaction with HHP. You often speak of just “lifetime” and do not specify reaction with HHP.

The products formed may be subject to other loss processes than thermal unimolecular decay, such as photolysis and reaction with more abundant reaction partners (e.g. OH). The authors need to place the chemistry studied here in a broader context and discuss (even if briefly) other loss processes.

As the major importance of this work relates to formation of secondary organic aerosol, the authors should make a better attempt to compare the possible influence of this specific chemistry on SOA formation and observed SOA formation from ozonolysis experiments, such as that in Ehn et al.(2) Further it should be clearly stated early on in the manuscript that the reactions studied are gas phase. A reaction with HHP might

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suggest to many that this chemistry occurs within the particle phase where HHP could have a higher concentration.

All optimized geometries of the stationary points must be added to supplementary material. Pictures are not sufficient, z-matrices must be included. Also The imaginary frequencies which are used in your Eckart calculations should be included.

Be very careful about referring to SOAs as individual aerosols. As this work may relate to new particle formation this may technically be correct, but this usage is often problematic. Line 26 has the INCORRECT usage, it should be “secondary organic aerosol (SOA)”, because the general term refers to mass added to existing aerosol due to condensation of material onto existing particles.

You state the importance of entropy in the free energy barriers, but you do not discuss its origin. Please comment on key vibrational modes that contribute to entropic factors.

Specific Comments:

Did the authors look for cyclic products? For example products where both dashed bonds in IM1a becoming full covalent bonds?

Do you rely solely on free energy estimate outputs? Are other methods such as SCTST too costly?

In sections 3.3 and 3.4, the discussion of loss processes for CI is flawed. Unimolecular decay is always a significant loss process. You seem to misinterpret the references you cite, both Drozd et al. and Long et al. find short thermal lifetimes for the CI formed in ozonolysis.(3,4) The authors must revise their statements to make clear that CI generally have significant unimolecular decay.

The energy labels in the supplement are confusing. The italics/non-italics energies are not always in same vertical order. Change the figure labels to make the non-italics energy the upper number in all cases. Do this for the main manuscript figures as well.

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There are a number of awkward sentences/phrases, missing words, or grammatically confusing sentences. Carefully check over this document. I have listed a number of these below.

Line 27 change to “influence”

Line 43 Add Guenther et al as a reference for alkene emissions.5

Line 119 change to “is the dominant..”

132 change to “reactions occur during the. . .”

147 change to “there is little known of the reactivity. . .”

167 change to “represents”

168 change to “needs”

238 change to “possess OH and OOH”

246 change to “particularly”

267 – It is confusing to see a negative energy of stability, re-word this, and other instances, to be clearer.

315-317 You have an error the citations to Kroll et al. The year should be 2001.(6,7)

(1) Donahue, N. M.; Drozd, G. T.; Epstein, S. A.; Presto, A. A.; Kroll, J. H. Adventures in Ozoneland: Down the Rabbit-Hole. *Phys. Chem. Chem. Phys.* 2011, 13 (23), 10848–10857. (2) Ehn, M.; Thornton, J. A.; Kleist, E.; Sipila, M.; Junninen, H.; Pullinen, I.; Springer, M.; Rubach, F.; Tillmann, R.; Lee, B.; et al. A Large Source of Low-Volatility Secondary Organic Aerosol. *Nature* 2014, 506, 476–479. (3) Long, B.; Bao, J. L.; Truhlar, D. G. Unimolecular Reaction of Acetone Oxide and Its Reaction with Water in the Atmosphere. *Proc. Natl. Acad. Sci.* 2018, 115 (24), 6135–6140. (4) Drozd, G. T.; Kurtén, T.; Donahue, N. M.; Lester, M. I. Unimolecular Decay of the Dimethyl-Substituted Criegee Intermediate in Alkene Ozonolysis: Decay Time Scales

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and the Importance of Tunneling. *J. Phys. Chem. A* 2017, 121 (32), 6036–6045. (5) Guenther, A.; Geron, C.; Pierce, T.; Lamb, B.; Harley, P.; Fall, R. Natural Emissions of Non-Methane Volatile Organic Compounds, Carbon Monoxide, and Oxides of Nitrogen from North America. 2000, 34. (6) Kroll, J. H.; Clarke, J. S.; Donahue, N. M.; Anderson, J. G.; Demerjian, K. L. Mechanism of HO Formation in the Gas-Phase Ozone – Alkene Reaction. 1. Direct, Pressure-Dependent Measurements of Prompt OH Yields Pressure-Dependent Measurements of Prompt OH Yields †. 2001. (7) Kroll, J. H.; Hancox, T. F.; Donahue, N. M.; Demerjian, K. L.; Anderson, J. G. Accurate, Direct Measurements of OH Yields from Gas-Phase Ozone-Alkene Reactions Using an In Situ LIF Instrument. *Geophys. Res. Lett.* 2001, 28 (20), 3863–3866.

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