Responses to Reviewers (acp-2020-829)

Manuscript: "Using GECKO-A to derive mechanistic understanding of SOA formation from the ubiquitous but understudied camphene"

We thank the reviewers and the editor for their comments on our revised submission. We believe we have addressed the outstanding concerns. Responses are in italics, modified text in red, and the line numbers refer to the "track changes" version of the revised manuscript.

Reviewer Report #1:

No response needed.

Reviewer Report #3:

I share the same concern as the Reviewer #2 pointed out that the modeling results are likely not representative of the actual atmosphere scenarios without carefully accounting for the autooxidation chemistry of peroxy radicals and their self/cross-reactions as a widespread source of highly oxidized monomeric and dimeric products (HOMs) that significantly contribute to the SOA formation in the monoterpene system. Recent kinetic studies have demonstrated that this autooxidation pathway could effectively operate and affect the product distributions from the ozonolysis of a-pinene at relatively short RO2 bimolecular lifetimes, e.g., in the presence of ~ppb levels of NO (Lyer et al. Nature Communications 2021). This level of NOx as an upper bound below which the RO2 isomerization outcompete their bimolecular reactions with NO/RO2/HO2 is relevant to the conditions vastly encountered in most regions of the U.S. and also those conditions measured in fire plumes.

One of the major objectives of this work was to better understand the chemistry of camphene; particularly in comparison to more well-studied monoterpenes, alpha-pinene and limonene. The controlled reactivity simulations were designed to facilitate comparison of these three terpenes in a buffered system, in which the gas-phase oxidant levels were controlled and the RO_2 radicals reacted equally with HO_2 and NO. We recognize that this does not cover the suite of chemical conditions in the ambient atmosphere, including those in which unimolecular RO_2 reactions play a critical role in forming SOA and defining SOA composition and properties. We believe that the interesting results of this first chemically-detailed modeling study will encourage more complete characterization of camphene gas-phase chemistry and SOA formation under a range of atmospherically relevant conditions. To further emphasize these points, the following edits have been made:

line 22: added "and peroxy radical reacted equally with HO2 and NO".

line 33-34: revised to read "This first detailed modeling study of the gas-phase oxidation of camphene and subsequent SOA formation highlights opportunities for future measurement-model comparisons and lays a foundation for developing chemical mechanisms and SOA parameterizations for camphene that are suitable for air quality modeling."

lines 437-440: To the closing sentence, "Further modeling and/or experimental studies are needed to develop and test a suitable SOA parameterization for representing camphene in air quality models", we added the clause: "including a robust assessment of the role of gas-phase HOM formation via RO_2 autoxidation, and condensed-phase accretion reactions, on SOA composition and yields under a range of atmospherically relevant conditions."

We agree with the reviewer that the understanding of the conditions under which unimolecular RO_2 reactions can occur in the ambient atmosphere is expanding, and that accounting for HOM formation by unimolecular RO_2 reactions, and subsequent dimerization, will be critical for accurate predictions of SOA formation and composition in the ambient atmosphere. We note that while such reactions are not considered in this work, given the recent availability of SARs to predict the rate coefficients of RO_2 H-shifts, the product distributions presented in the mechanism schematics may be useful for understanding the relative or potential importance of such reactions in the systems studied.

While I understand, as the authors stated, that full consideration of HOM formation/dimerization is not possible at this time, I suggest, however, a number of sensitivity tests need to be at least performed to evaluate the uncertainties arising from this missing chemical mechanism in the simulations. My understanding that such tests are feasible based on previous published GECKO-A studies, see a couple of examples below.

One of the strengths of a near-explicit chemical mechanism model is that parameterized representations of key reactions are not necessary, provided relevant data and/or SARS exist. Given the recent availability of the referenced SAR by Vereecken and Noziere, we believe that a more rigorous assessment and greater contribution can be made by incorporating a version of that SAR into GECKO-A and running camphene simulations under a range of atmospherically relevant scenarios. We have added text throughout the manuscript to more clearly acknowledge the lack of HOM monomer formation via RO_2 autoxidation, and the implications for the results and conclusions presented.

line 103-109: revised to read: "Autoxidation, leading to the formation of highly oxygenated molecules (HOM) in the gas phase (e.g., Bianchi et al., 2019; Ehn et al., 2014), is not currently represented in GECKO-A. A SAR to predict the rate coefficients of peroxy radical (RO_2) H migration reactions (H-shifts) that lead to the formation of HOM was recently published by Vereecken and Nozière (2020). The straight implementation of this SAR into GECKO-A would lead to a non-manageable number of species and reactions. Therefore, reduction protocols are currently under development to consider the autoxidation reactions in subsequent model versions. For the application presented herein, limitations and implications of the absence of HOM formation via RO_2 autoxidation are discussed where relevant."

lines 190-192: Added, "It is noted that the simulations are unable to capture HOM formation via RO_2 autoxidation and subsequent dimerization (Ehn et al., 2014), that may have occurred in the chamber studies, particularly under DO conditions."

lines 232-243: Added, "Overall, the model simulations agree well with the observed trends in SOA yield as a function of SOA mass. The largest discrepancies are for α-pinene ozonolysis, in which SOA mass is underpredicted relative to the observations. The contribution of HOM formation from RO_2 autoxidation is expected to be more important under such conditions, when the lifetime of RO_2 is sufficiently long for autoxidation to compete with biomolecular reactions and monoterpene oxidation by O_3 is greater than by OH leading to higher HOM yields (Ehn et al., 2014; Jokinen et al., 2015). The inclusion of HOM formation and subsequent dimerization would lead to an increase in predicted SOA mass in both the α-pinene and limonene ozonolysis simulations. An increase in SOA mass due to HOM formation and subsequent dimerization would improve the measurement-model agreement for α-pinene, but would also lead to an overprediction of SOA mass for limonene. In addition, a non-negligible contribution of HOM monomers and dimers to the particle phase would increase the calculated O/C ratio, and increase the measurement-model discrepancy further discussed below. McVay et al. (2016) reported similar conclusions for α-pinene photolysis experiments; a parameterized representation of RO_2 autoxidation in GECKO-A increased predicted SOA mass for low UV conditions, improving measurement-model agreement at the end of the experiment; and resulted in no change for high UV conditions."

lines 332-334: Added, "The calculated lifetime of RO_2 with HO_2/NO was < 60 s, and thus it is assumed that these biomolecular RO_2 reactions would be dominant, and the absence of HOM formation via RO_2 autoxidation in GECKO-A did not significantly impact the results and conclusions derived from these simulations."

1. The authors could refer to McVay et al. ACP (2015) in terms of adding the RO2 isomerization channel to the original GECKO mechanism. Recent published RO2 isomerization kinetics in a-pinene ozonolysis (e.g., Kurteń et al., JPCA, 2015; Zhao et al., PNAS, 2018) could be adapted to assess the relevance of the autooxidation chemistry under conditions simulated in this study and how this chemistry could change the product distribution and consequently the SOA yields and composition.

In McVay et al., HOM formation via autooxidation was represented by adding a single product from the alpha-pinene + O_3 reaction with a molar yield of 7%. The results of this representation were variable in the context of improving measurement-model agreement. This study has now been explicitly referenced in the context of including a parameterized representation of HOM formation in GECKO-A (see red text above).

2. La et al. ACP (2016) incorporated a heterogeneous reaction pathway in the GECKO simulations of the SOA formation from photooxidation along-chain alkanes. For this study, it is important to test how the particle-phase dimerization such as the peroxyhemiacetal formation from the poly-peroxides that are largely present in the HOMs molecules (see kinetics in e.g., Bakker-Arkema and Zimemann 2020) could alter the SOA mass and composition.

In the manuscript, we differentiate HOM formation via gas phase RO_2 autoxidation (as defined by Bianchi et al. 2019) from accretion product formation via heterogeneous or condensed-phase reactions. Highly-oxygenated (6+ O) gas-phase products are formed in the GECKO-A modeling simulations, but as noted in the manuscript and reviewer responses, RO_2 autoxidation and condensed-phase reactions are not represented. We agree with the reviewer that accretion product formation is important, and we acknowledge in the manuscript that such reactions are likely occurring in the chamber studies. We have added text throughout the manuscript to more clearly acknowledge the lack of condensed-phase reaction chemistry, and the implications for the results and conclusions presented.

line 125: Revised to read, "Condensed-phase reactions are not currently represented in GECKO-A; the limitations and implications of which are discussed where relevant."

lines 377-380: Revised to read, "Product volatility distributions can be influenced by gas-phase RO_2 autoxidation, and condensed-phase reactions, which were not considered here. While HOM formation likely played a minor role in these controlled reactivity simulations, the monomer building blocks of known accretion reactions were predicted for all monoterpenes studied. Thus, it is expected that accretion product formation could occur under these conditions, leading to changes in the simulated volatility distributions."

lines 430-431: Added, "The predicted SOA yields do not account for condensed-phase accretion reactions, which could occur under the simulation conditions."