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Atmospheric Chemistry and Physics
Discussions
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Interactive comment on **"Using GECKO-A to derive mechanistic understanding of SOA formation from the ubiquitous but understudied camphene"** *by* **Isaac Kwadjo Afreh et al.**

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1.1: The authors present a unique study in which a near-explicit chemical mechanism generator (GECKO-A) is used to consider the oxidation and SOA formation potential of camphene, a monoterpene of importance as a biomass burning emission, but that has received only limited attention in chamber studies. Comparisons are made with two well-studied species, a-pinene and limonene. The study is, in my opinion, very well conceived, thoroughly conducted and well written. I have some questions and comments below (mostly minor) that the author should consider prior to final publication in ACP.

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1.2: It looks to me as though some of the initial steps in the OH/a-pinene and maybe OH/limonene are specified (to match chamber data?), whereas camphene chemistry is presumably all derived from ‘free-running’ GECKO. If true, could this bias the results in any way?

Response: The initial rate constants (kOH, kO3, and kNO3) of α-pinene, camphene, and limonene were specified based on data from Atkinson and Arey, 2003. The initial branching ratios of α-pinene + OH were based on data from Peeters et al., 2001. Reaction products and rate constants of subsequent reaction steps of α-pinene, and the full camphene and limonene mechanisms were based on SARs. Therefore, we do not expect bias in the results due to differences in prescribed vs. free-running mechanism generation. To improve clarity, the following text has been added in lines 128-134: The monoterpene reaction schemes are generated by GECKO-A using established protocols, as described in Aumont et al. (2005). First, the mechanism generator analyzes the structure of the compound to determine the reactive sites and the plausible reaction pathways. Reaction products and initial branching ratios are based on experimental data when available. Otherwise, the reaction products and rate constants are estimated based on structure-activity relationships (SARs). The initial reaction rate constants of the monoterpenes with OH, O3, and NO3 were based on data from Atkinson and Arey (2003a). For α-pinene + OH, the initial branching ratios are based on data from Peeters et al. (2001). For subsequent reactions steps with α-pinene + OH and for the limonene and camphene mechanisms, reaction products and branching ratios are based on SARs.

1.3: Page 3, line 107: Can anything more be said to justify the selection of six generations of oxidation - e.g. were any of the previous studies alluded to conducted on monoterpenes?

Response: The selection of six generations of oxidation was based on previous studies on n-alkanes (Aumont et al., 2012). This has been clarified on line 112. In addition, we performed sensitivity studies early on that confirmed no significant change in the evolution of the gas and particle phase from 6 to 7 generations. We have added the following text on lines 112-113: “sensitivity studies performed in this work for α-pinene oxidation, where increasing the number of generations beyond six did not result in significant changes in the evolution of the gas and particle phases;”

1.4: Bottom right of Figure 3, the co-product should be acetone instead of formaldehyde

Response: Corrected.

1.5: Page 4, line 127: The peroxy radicals formed seem mostly to still contain the double ring structure of a-pinene (not just the 4-membered ring?).

Response: Agreed. Line 142 has been edited to clarify that it is the stable products, and not the peroxy radicals, which are predominantly four-membered ring species.

1.6: Page 4, line 135: I think the compound formed is camphenilone?

Response: Corrected.

1.7: Page 5, line 151: Did you mean acetylperoxy radical, rather than acetaldehyde?

Response: Yes. “Acetaldehyde” has been removed; the term “peroxy radicals” represents all peroxy radicals formed, including the acetylperoxy radical (lines 166-167). “…the alkoxy radicals either react with O2 or decompose to form formaldehyde and peroxy radicals.”

1.8: Page 5, line 154: camphenilone spelled incorrectly

Response: Corrected.

1.9: Page 5, line 155-157: You might mention here that an OH radical is also generated.

Response: We did not include inorganic species in the mechanism figures. The following sentence has been added to the text in lines 137-138: For figure clarity, inorganic species formed (including OH) are not shown.; and to the figure description (Figures 1, 2, 3, S1, S2, and S3) to clarify.

1.10: Page 6, line 220: What precursor(s) were studied by Shilling et al.?

Response: The sentence has been revised by adding "for α-pinene".

1.11: Page 7: line 228: This is maybe not be a fully addressable question at this point, but would the presence of OH scavengers likely have a major effect on the results?

Response: Sensitivity simulations were performed using CO as an OH scavenger. The differences in calculated O/C ratios for both alpha-pinene and limonene were small, and insufficient to explain the differences between the model simulations and observations. Though this is not an exhaustive study of the potential effects of an OH scrubber on composition, given the results of the sensitivity simulations we have removed the suggestion that this may explain model-measurement discrepancy.

1.12: Page 7, line 232: It might be worth emphasizing that these top-ten lists presumably evolve with reaction time.

Response: The sentence has been revised to note that these are the top 10 products at the end of the simulation.

1.13: Some of the structures in Figures 5 and 6 look a little bit strange (with overlapping or extended bonds). Can these be cleaned up a bit?

Response: Yes. Corrected. Thank you for the suggestion.

1.14: Figure 9b: Converting the x-axis units to ppb would be useful, I think, since these are the units used throughout the text.

Response: The units on the x-axis in Figure 9b have been changed to ppb.

1.15: Page 9, near line 305: Could the high SOA yield from limonene (and its by-products) be in part driven by its shorter lifetime (hence giving more time in the simulations for C2 oxidation of products?).

Response: Yes. The lower volatility products formed from limonene oxidation are expected to be in part a result of the shorter lifetime of limonene and its oxidation products. This behavior is also expected to be influenced by (i) the relative contribution of gaseous oxidants (here mainly OH, but also O3 for a-pinene and limonene) and (ii) the structure of the formed alkoxy radicals, and thus their chemical evolution by fragmentation/functionalization (e.g. Camredon et al., 2007). The following sentence has been added in lines 324 – 326 “The shorter lifetime and the chemical structure, including presence of two double bonds, contribute to the relatively high SOA yield of limonene.”

Please also note the supplement to this comment:
https://acp.copernicus.org/preprints/acp-2020-829/acp-2020-829-AC1-supplement.pdf

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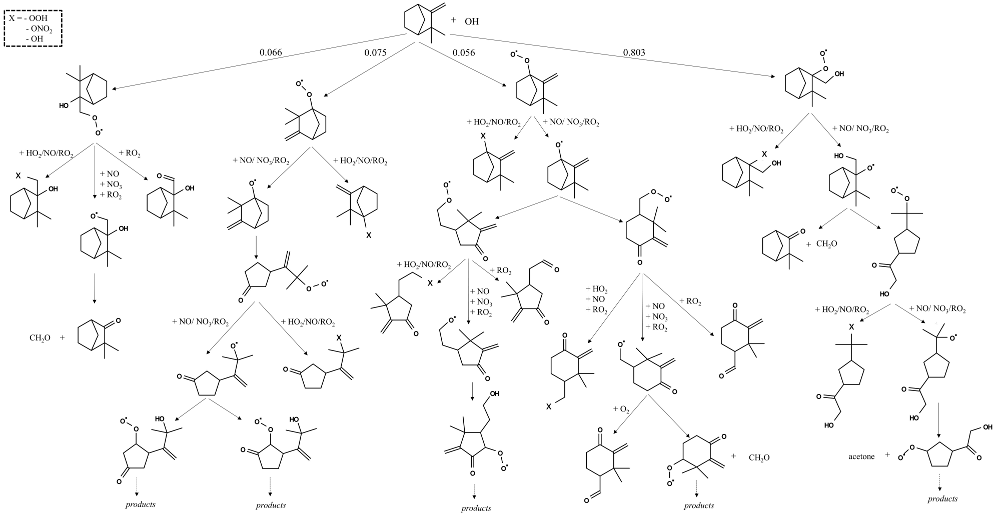

Fig. 1. Figure 3: Initial oxidation pathways of camphene oxidation with OH as represented in GECKO-A (inorganic products are not shown).

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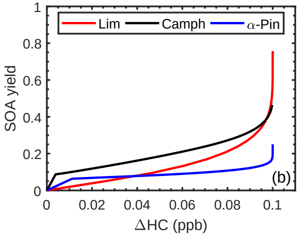

Fig. 2. Fig9b:simulated SOA yield as a function of reacted hydrocarbon concentration (ïĄĎHC) during controlled reactivity simulation