

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-587

Anonymous Referee #2

Referee comment on "Secondary organic aerosol formation from camphene oxidation: measurements and modeling" by Qi Li et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-587-RC2>, 2021

In this work, the authors studied oxidation of camphene and the resulting secondary organic aerosol (SOA) formation. Most studies have shown that monoterpene SOA yields decrease with increasing NO_x, but this study shows the opposite for camphene. To understand this trend the authors combined chamber experiment results with detailed gas-phase (SAPRC) and aerosol formation (GECKO-A). They showed that NO increases the formation of radical intermediates that can isomerize rapidly to form highly oxygenated molecules (HOMs) which have very low volatilities. This study is beautifully done and provides an elegant explanation to a complex phenomenon. I am particularly impressed with how the authors integrated modeling with experimental results and provide a fundamental understanding of this system. I highly recommend publication, after addressing the following minor comments:

The only overall question that I have is how this can be generalized to other systems. What is unique about camphene that NO actually increases the formation of HOMs? We tend to think that NO and HO₂ promotes termination reactions, but in this case NO turns the radicals into an "isomerizable" form. Is this unique to camphene, or should we start looking for these pathways in other systems? Could this happen to, for example, sesquiterpenes, which may be an alternate explanation to the higher yields under higher NO_x?

Line-by-line comments:

Line 36: "14% of the total reactive VOC flux", is that 14% of the reactivity, or 14% of the mass emitted?

Section 1 Introduction: the literature review is concise and relevant. As a reader who does not think about camphene regularly, I would find some background information about camphene to be useful. For example, what is its OH rate constant, and how does its reactivity compare to other monoterpenes? Also I do not see its molecular structure until Figure 7. I personally like to visualize the molecule (its bicyclic structure, 1 C=C double bond) while reading the introduction so there is a better context.

Lines 70-84: given the results of this study showing the importance of HOM, it might be useful to mention the recent knowledge about RO₂ autoxidation as an important pathway for RO₂ radicals too (e.g. Crouse et al., J Phys Chem Lett, 2013 and many others).

Line 112: unnecessary space in citation

Table 1 footnote: "based on" instead of "base on"

Line 175: it is not clear why the experimental conditions cannot be used as initial conditions for GECKO-A?

Figure 1: it is difficult to compare the experimental camphene time trends with SAPRC model when they are in separate panels. I suggest overlaying them directly for easier comparison. Same goes for Figure S1.

Line 200-202 and Figure S1. It seems that simulated O₃ matches experimental levels in WO experiments, but the trend with increasing HC is inconsistent. SAPRC predicts lower O₃ as HC increases, but the experimental trend is more complex. The difference in measured O₃ seems quite big between 7ppb and 9ppb experiments, even though the experimental conditions are similar. Predicting O₃ in chamber experiments without added NO_x is notoriously difficult (e.g. unknown wall outgassing of NO_x), so I might be being nitpicky here, but I suggest toning down the sentence "For all parameters (camphene consumption, NO_x decay, O₃ formation, and OH levels), the SAPRC simulation results were generally in good agreement with the experimental data."

Figure 7 and Figure S4: After OH addition, the diagram shows that the alkyl radical with a resonance structure (the lone electron is spread over 3 carbons), but I don't think that is true. It is just a tertiary radical.

Table 4. VBS parameters: the c^* are presumably the c^* , not the log of c^* (which would be -1,0,1...) If that is the case, the 2nd row should be $c^* = 1 \text{ ug/m}^3$ (not 0)

Section 4.2 This is a really well written section that shows the most interesting results. It is also nice to see that the change in c^* can also be reflected in the VBS parameters. This might be coincidental, but one can see a single alpha of no added NO_x at c^* of 10 ug/m^3 , suggesting dominance of semivolatile material. With NO_x, there is a significant amount of nonvolatile material ($c^* = 0.1 \text{ug/m}^3$), and these trends are consistent with the predicted vapor pressures from GECKO-A.

Table 5. What is the definition of "first generation"? Some of these species go through multiple radical intermediates.

Lines 395-399: I am not sure if the argument is clear here. Why does the overall vapor pressure increase with HC0? It is not just partitioning (partitioning does not change the product distribution). Is it linked with RO2 chemistry? i.e. If HC0 increases, then RO2+RO2 increases and RO2+NO decreases, thus less HOMs?

Figure 10: It is interesting that GECKO-A predicts O/C as high as 1.3 at very low HC/NO_x, but the AMS did not measure O/C that high. If the authors have time, it would be really nice to see what O/C would look like at HC0/NO_x below 1. I do not believe I have ever seen O/C of chamber SOA measured to be 1. But not really a requirement here. Just curious.

Line 445: it will be really difficult to control beta values in experiments. Previous studies just use a very high NO, but that will shut off the RO2 isomerization channel.

References: The format for Odum 1996 appear to be incorrect.