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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A comparative and experimental study of the reactivity with nitrate radical of two terpenes: α-terpinene and γ-terpinene" *by* Axel Fouqueau et al.

Anonymous Referee #1

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General Comments

Fouqueau et. al. presents the results from a series of gas-phase reactions of the two monoterpenes α-terpinene and γ-terpinene with the nitrate radical. They report rate constants obtained from absolute and relative methods as well as measurements of SOA and organic nitrate yields. While organonitrate yields were similar for each, γ-terpinene yielded significantly more SOA than α-terpinene. Tentative product identifications using PTR-MS facilitated a discussion of potential reaction mechanisms for each system. The two monoterpenes are structurally similar, however, α-terpinene possesses a conjugated system which gives rise to a radical mobility that is believed

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to impact reactivity and contribute to suppression of SOA yields relative to γ-terpinene. Overall, the authors do a good job highlighting how a small change in chemical structure can have dramatic implications on chemical reactivity which need to be accounted for in modeling efforts.

The measurements and their discussion are appropriate for Atmospheric Chemistry and Physics and I recommend that it be accepted with minor revisions. I believe the data to be of high quality and an important contribution to the community's understanding of monoterpene oxidation reactions.

Specific Comments

I have two comments concerning the proposed mechanisms.

First, to facilitate a discussion of the proposed mechanisms the authors show only two radicals (line 440). I would have benefitted from seeing all four "options" drawn out for each species, even if the remaining two for each terpene were presented in the SI. The structures that formed are not necessarily identical. For example, γ -terpinene oxidation (Figure 7, reaction 1, right branch), the authors show nitrate radical addition to the tertiary carbon which generates a secondary alkyl radical, when addition to the secondary carbon would yield a more stable tertiary radical. I appreciate that this is a complex mechanism and that the authors want to keep the figure as clean as possible, but something is missing by not showing all options.

Second, the alkoxy radical that would form on the tertiary carbon by the pathway described above would have a non-ring opening fragmentation pathway similar to what is shown in Figure 8, reaction 7' for α-terpinene. On line 549 the authors discuss that ring openings are the most likely pathways based on the Vereecken and Peeters (2009) SAR and provide information on the energy, but ignore any discussion of the non-ring opening pathway. It would be helpful here to have some information on what the difference in energies and the expected branching ratios would be if the formation of the isopropyl radical were included. How different are the energies and would this lead

to the branching change at all? Their observations of relatively low concentrations of acetone are supported by this claim, but a discussion of why this might be the case would be helpful.

46. It is unclear if “highly soluble” refers to miscibility in the organic aerosol or aqueous phase.

85. The α -terpinene is only 85% pure and it is unclear if this factored into the any calculations, especially given the low SOA yields for this species.

151 What is the model of the Palas Welas used in this study? How was this data used in this study?

460. It is a personal preference to not suggest that signal intensity provide information on concentrations in the absence of the appropriate standards.

551. Branching ratios are unitless quantities but the sentence “with similar branching ratios (differing of 0.6 kcal/mole)” suggests that it has units of molar energy. If this is an activation energy, maybe state that.

Technical Corrections

56. The statement “trees emissions” should be “tree emissions”

133. The sentence containing “allowing to propose” is incomplete. Maybe allowing “us” to propose?

193. There is a typo in the parentheses in this sentence “products, RO2 radicals, . . .)"

248. It should be Raoult’s Law.

890. The citation is missing page numbers.

900. The title has a typo. It reads “reaction barrier heightsw” but should be “heights”.

Figure 7 and 8: The two different shades of gray used to differentiate Primary and Secondary Products are almost indistinguishable in my copy.

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