

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.

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First, the authors would like to thank the anonymous referee for this discussion and its constructive comments, corrections and suggestions that ensued. We have carefully replied to all its comments and the paper has been improved following his recommendations. All technical corrections suggested by the referee have been carefully performed. Answers have also been provided for all comments and changes have been performed accordingly. Please find below the answers to the comments:

Specific comments:

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First, to facilitate a discussion of the proposed mechanisms the authors show only two radicals (line 440). I would have benefited 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.

The mechanisms of the two other radicals for α -terpinene and γ -terpinene have been added in the supporting information (Figures S4 & S5). Sentences have been added L. 456 (“The mechanism of the two other alkyl radicals is presented in Fig. S4.”) and L. 538 (“The mechanism of the other two alkyl radicals is presented in Fig. S5.”).

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.

We indeed focused the discussion on ring opening fragmentation for the alkoxy radical. Using the SAR of Vereecken and Peeters (2009) the energy for the loss of the isopropyl or methyl group is calculated to be 10.2 kcal mol⁻¹. It is the same for all the non-ring opening fragmentations, because the local configuration around the alkoxy group is the

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same. As a reminder, the energy for the ring opening fragmentation is 6.0 and 6.5 kcal mol⁻¹. A difference of 4 kcal mol⁻¹ is significant enough to predict that this is a minor pathway. For γ -terpinene, no acetone formation has been detected and for α -terpinene the acetone yield is very low, suggesting that the loss of the isopropyl group is a minor pathway, in good agreement with the SAR result. The loss of the methyl group leads to the formation of formaldehyde, which is not specific product. We decided not to discuss about.

Sentences have been added to complete the discussion: L. 476: “The SAR developed by Vereecken and Peeters, 2009 which is based on DFT calculations, has been used to estimate the energy barriers of the various reaction pathways of the alkoxy radicals. Energy barriers for reactions 7 and 8 appear to be similar (Eb,7 = 6.0 kcal mol⁻¹ et Eb,8 = 6.5 kcal mol⁻¹, with an error estimated by the authors of 0.5 kcal mol⁻¹), leading to similar branching ratios for the two possible ring openings. The loss of methyl or isopropyl group presents an energy barrier significantly higher (10.2 kcal mol⁻¹) whatever the alkoxy radical considered. These pathways appear minor compared to the ring opening and this is in good agreement with the fact that acetone was not detected during the experiments.” L. 558: “The SAR proposed by Vereecken and Peeters, 2009 allowed estimating the energy barriers of the different evolution pathways of alkoxy radicals. It suggests that ring openings (reactions 7 and 8) are the two most likely pathways with similar energy barriers (respectively 6.0 and 6.5 kcal mol⁻¹). As for γ -terpinene, reaction 7' corresponding to the loss of the isopropyl group appears to be less favorable with an energy barrier of 10.2 kcal mol⁻¹.”

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

The “highly soluble” sentence refers to miscibility both in aqueous phase and in polar organic phase. This has been clarified in the manuscript: “both in aqueous phase and organic aerosol (Picquet-Varrault et al., 2019)” (L. 46). The following citations were added to references: Picquet-Varrault, B., Suarez, R., Duncianu, M., Cazaunau

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M., Pangui, E., David, M. and Doussin, J.-F.; Photolysis and oxidation by OH radicals of two carbonyl nitrates: 4 nitrooxy-2-butanone and 5-nitrooxy 2-pentanone, Atmos. Chem. Phys., 20, 487–498, 2020.

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.

The referee is right when saying that the low purity of α -terpinene may affect the organic nitrates and SOA yields. At the time the experiments were carried out, no higher purity sample was commercially available. We have contacted the company in order to have information about impurities but it was not able to provide it. Nevertheless, prior to each α -terpinene injection, a purification stage was performed by pumping the sample in the vacuum line. This stage may contribute to remove high volatility impurities. For low volatility impurities, it is expected that they will remain in the sample (condensed phase). For yield calculations, it was therefore considered that only terpinene was introduced into the chamber. However, because these impurities remain unknown, we cannot state with certainty that this purification stage is 100% efficient. Therefore, it should be considered that this may generate additional uncertainty on yields which may be slightly underestimated. This has been explained in the manuscript L.86, L.341 and L. 411.

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

The Palas Welas used is a Welas digital 2000. It has been used in the case of α -terpinene in order to complete the distribution when the distribution measured by the SMPS was out of the measurement range. Information have been added in the article L. 154 (“conducted on α -terpinene”) and L. 155 (“Welas Digital 2000”).

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

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We agree that this hypothesis is debatable and we have removed it from the text. Following sentences have been removed: L. 469: “However, if one hypothesizes that the products have similar responses, one can consider that signal intensities provide information on major products and that a product which has a strong signal is largely formed.” L463: “In both modes, the dicarbonyl compound coming from the decomposition of the RO radical by reaction 7 has an intense signal, suggesting a high formation yield.” L.467: “The signal of the trifunctional compound formed by reaction 8 (m/z 230) is weak and can be explained by its low volatility which suggests a partition in favor of the aerosol phase.”

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.

It is true the branching ratios are unitless and that we were referring to activation energies. It has been corrected L. 560.

Technical Corrections 56. The statement “trees emissions” should be “tree emissions” It has been corrected.

133. The sentence containing “allowing to propose” is incomplete. Maybe allowing “us” to propose? It has been corrected by “allowing the authors to propose”.

193. There is a typo in the parentheses in this sentence “products, RO₂ radicals,...)” It has been corrected.

248. It should be Raoult’s Law. It has been corrected.

890. The citation is missing page numbers. It has been corrected.

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

Figure 7 and 8: The two different shades of gray used to differentiate Primary and

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Secondary Products are almost indistinguishable in my copy.

The mechanisms are not made with two different shades of gray used to differentiate Primary and Secondary Products but in pink and blue squares. These figures have been made to be seen with colors.

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