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Reply on RC2

Axel Fouqueau et al.

Author comment on "An experimental study of the reactivity of terpinolene and β -caryophyllene with the nitrate radical" by Axel Fouqueau et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-1011-AC2>, 2022

First of all, 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 its recommendations. Answers have also been provided for all comments and changes have been performed accordingly. Please find below the answers to the comments:

General Comments

This manuscript describes an experimental study of the reactions of a monoterpene and sesquiterpene with NO₃ radicals. Rate constants were measured in a glass chamber using absolute and relative rate methods. Product and mechanism studies were conducted in a stainless-steel chamber and gas-phase products were analyzed online using a proton transfer reaction-mass spectrometer with a H₂O⁺ and NO⁺ ion source. Gas and aerosol products were analyzed by infrared spectroscopy to quantify nitrate compounds. Particle size and volume concentrations were monitored with a scanning mobility particle sizer. The study is relevant to understanding the nighttime formation of organic nitrates from VOC oxidation, which can impact SOA and ozone formation. The measured rate constants generally agree with those measured previously, thereby giving confidence to the reported values. The study also provides new yields of acetone, organic nitrates, and SOA; and the reaction mechanisms proposed for each compound seem to explain the observed products quite well. Overall, I think the measurements were well done, the interpretation of the data is accurate, and the paper is clearly and concisely written. I think the manuscript is publishable in ACP, and I have only a few minor comments.

Specific Comments

Line 95: Please define IBBCEAS.

The acronym IBBCEAS has been previously define in the introduction of "2 Experimental section" (line 82).

Line 215: Can't you use ion-molecule reaction rate theory to estimate rate constants for ionization and then quantify products?

The application of ion-molecule reaction rate theory for estimating rate constants for ionization in the frame of a PTR-MS has been mainly developed for H_3O^+ ionization (and in a minor extent for O_2^+ and NH_4^+ , Bhatia et al., 2020; Strekowski et al., 2019). To our knowledge, it has never been used in a NO^+ oxidation study.

The study of Sekimoto and Koss, 2021 shows that calculated ion-molecule rate constants for $\text{H}_3\text{O}^+ + \text{VOC}$ may have an accuracy of 10 % in comparison to the measured ones. These constants are used in a frame of PTR-MS VOC sensitivity calculation, which can be estimated with an accuracy of 20-50 % without direct standard calibration, depending on the physical conditions in the drift tube. These sensitivities can be significantly worst for some compounds, and particularly if their fragmentation is unknown. In the case of our study, the composition of the analyzed mixtures is complex and the fragmentation behavior of the products is not completely understood due to the high quantity of peaks and the similar structure of the products (which have similar fragments). In this context, the quantification would have been associated to a high uncertainty.

Also, the use NO^+ as ionization agent, which is still not investigated with this technique, lead to different ionization pathways (as explained L. 132-136), and consequently to very complex rate constant estimations. The application of this theory is thus a major challenge in this technique.

Considering these limitations, we preferred to not use this method to quantify the products, and mainly use the PTR-MS as a qualitative technics.

Line 220: What products do you mean? Acetone? On line 215 you state that you can't quantify products because of the lack of standards.

In this sentence, "products" was referring to the products that are measured by FTIR, which allow their quantification, i.e. total organic nitrates and acetone. The sentence has been modified to: **"When products can be quantified by FTIR concentration is measurable by FTIR, product their formation yields were calculated by plotting their molecular concentration of product against the reacted BVOC molecular concentration and by calculating the slope at the origin."** (L.224-225).

Line 355: Stating that the SOA yields are below 90% is not very useful, since that means they could be anywhere from 0 to 89%. I suggest giving the actual range of yields.

The sentence has been changed to **"between 50% and 90%"** (L. 357).

Line 376: Since you know the VOC-NO3 rate constant and approximate NO3 radical concentration, it seems that you can calculate the reaction lifetime and compare that to the mixing timescale. That would be useful support for the explanation given here.

We considered doing such a calculation, however NO_3 was not monitored during mechanistic experiments and N_2O_5 concentration was below the detection limit preventing

from estimating NO₃ concentration. Therefore, the calculation of reaction lifetime is impossible.

Figure 8. I think NO₃ addition occurs preferentially to form the tertiary alkyl radical, so wouldn't it be better to show that reaction pathway?

We agree that the formation of the tertiary radical is expected to be the major pathway. However, because the formation of hydroxy-nitrate was observed and can only be explained by the formation of the secondary radical, we decided to show this pathway, not as the major one but just to allow explaining the hydroxy-nitrate formation.

In conclusion, if the tertiary alkyl radical coming from the addition on the endocyclic radical is shown, the figure will not contain the formation of hydroxy-nitrate compound, which is a key product in this study.

Neither Figure 8 nor Figure 9 consider possible isomerization of alkoxy radicals, and assume instead only reaction with O₂ or decomposition. This assumption might be supported using SAR calculations of Vereecken & Peeters, PCCP, 2009 & 2010, although results from Aschmann et al. JPCA 2011 for cycloalkoxy radicals indicate that for β-caryophyllene some isomerization should occur.

This was an omission but we agree that we have to discuss this point. The reason of this omission was that no compounds coming from isomerization were detected, and it was considered minor by Vereecken & Peeters, 2009 & 2010 SAR. On Figure 8 and 9, only the products that were detected are shown. Products coming from this pathway were searched but none was found. Nevertheless, this reaction lead to the formation of heavy functionalized products that can be difficult to measure with PTR-MS for two reasons: (i) it cannot measure too heavy products, which is probably the case for isomerization products of β-caryophyllene, and (ii) these compounds can be probably found largely in particle phase. No analysis at the molecular scale was conducted in the particle phase during our experiments. Indeed, in this study we only measure the total organic nitrates in the aerosol phase from their IR absorption band. Nitrates formed by this pathway will thus not be differenced. The occurrence of this pathway is thus not in disagreement with the observation of high SOA formation.

The following text has been added L. 655-664: **"Products coming from isomerization were not detected in this study. Even though it is considered as minor pathway by Vereecken and Peters, 2009 calculation, it was proved to be possible in Aschmann et al., 2012 for cycloalkoxy radicals. Isomerization could thus occur for β-caryophyllene. Products coming from this pathway were searched but none was found. Nevertheless, this reaction lead to the formation of heavy functionalized products that can be difficult to measure with PTR-MS for two reasons: (i) it cannot measure too heavy products, which is probably the case for isomerization products of β-caryophyllene, and (ii) these compounds can be found largely in particle phase. No analysis at the molecular scale was conducted in the particle phase during our experiments. Indeed, in this study we only measure the total organic nitrates in the aerosol phase from their IR absorption band. Nitrates formed by this pathway will not be differenced with other ones. The occurrence of this pathways is thus not in disagreement with the observation of high SOA formation."**

In addition, the following citation has been added:

"Aschmann, S. M., Arey, J., and Atkinson, R.: Kinetics and Products of the Reactions of OH Radicals with Cyclohexene, 1-Methyl-1-cyclohexene, cis-Cyclooctene, and cis-Cyclodecene, <https://doi.org/10.1021/jp307217m>, 2012."

Line 588: Similar to Comment 3, it is not very useful to state that SOA yields are <100%.

It has been corrected to **"between 50 and 90 % and not 100 %"** (L. 606-607).

References

Bhatia, M., Biasioli, F., Cappellin, L., Piseri, P., and Manini, N.: Ab initio calculation of the proton transfer reaction rate coefficients to volatile organic compounds related to cork taint in wine, 55, e4592, <https://doi.org/10.1002/jms.4592>, 2020.

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Strekowski, R. S., Alvarez, C., Petrov-Stojanović, J., Hagebaum-Reignier, D., and Wortham, H.: Theoretical chemical ionization rate constants of the concurrent reactions of hydronium ions (H_3O^+) and oxygen ions (O_2^+) with selected organic iodides, J Mass Spectrom, 54, 422–428, <https://doi.org/10.1002/jms.4349>, 2019.