Gas-phase products from nitrate radical oxidation of five monoterpenes: insights from free-jet flow-tube experiments

Jiangyi Zhang[1], Yi Zhang[1,2,3], Hannu Koskenvaara[1], Jian Zhao[1], and Mikael Ehn[1]

[1]Institute for Atmospheric and Earth System Research, Faculty of Science, University of Helsinki, Helsinki, 00014, Finland
[2]State Key Laboratory of Atmospheric Environment and Extreme Meteorology, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China
[3]College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

Correspondence to: Jiangyi Zhang (jiangyi.zhang@helsinki.fi) and Mikael Ehn (mikael.ehn@helsinki.fi)

Response to Referee #1

General comments:

The authors present an experimental study using a newly built free-jet flow-tube experimental setup that enables measurement of oxygenated organic compounds with close to no wall interaction. The specific setup aims to investigate the initial gas-phase oxidation stages with a short reaction time of 8.8s. In contrast to many other setups, this widely suppresses contribution of multi-generational oxidation as well as heterogeneous artefacts. In the presented work, the nitrate radical oxidation of 5 major monoterpene (MT) compounds are presented, which remains understudied compared to OH oxidation and ozonolysis. The results of this study are very helpful to improve our understanding of the formation of secondary organic aerosol precursor compounds in the atmosphere, linking structural differences to different HOM yields. The paper is well written and follows a clear logic. I have a few comments about the applied quantification and the interpretation of the results. I recommend publication once these comments have been addressed.

We thank the referee for taking the time to review our manuscript and for the positive and insightful comments. We will answer the specific comments point-by-point below. The referee's comments are in blue, and our answers are in black with updated content in **bold**.

Specific comments:

Comment #1:

I was surprised to see the comparatively high starting levels of MT, as the authors discuss the competition of bimolecular reaction and unimolecular termination or isomerization. The experimental setup seems to allow for lower concentrations and it seems to me, that compared to other studies, the instrumental limits of detection are

not as severe in this work. Is there a specific reason the authors chose the mixing ratios, which are high compared to typical atmospheric mixing ratios?

The referee is correct that our MT concentrations were 1-2 orders of magnitude higher than typical ambient concentrations. However, for the oxidation chemistry studied here, the absolute MT concentration is secondary, with the more relevant parameters being the oxidation rate and the concentration of RO_2 radicals. During the reaction time of 8.8 s within our flow-tube system, reacted MT amounts were 30-200 ppt and at the lowest concentrations, many low-yield products were barely distinguishable from the background. In other words, the high concentrations compensate for the longer reaction times in the atmosphere. In earlier flow-tube studies with reaction times of seconds, several tens of ppb of MT has commonly been used (Berndt et al., 2018; Berndt, 2021, 2022), making our results comparable to those studies.

Since many dimer signals were significant during our experiments also at the lowest concentrations used, especially $C_{20}H_{32}N_2O_8$ for BP, it would have been interesting to see how those signals behave at lower MT concentrations. Nevertheless, the aim of our study was to discern the distribution of radicals and closed-shell products from the reactions, rather than focusing on their kinetics. To improve clarity, we added the following sentence in Section 3.4: "**We did not explore the low levels of MTs where bimolecular reactions are negligible and RO_2 concentrations increase linearly with reacted [MT]. Because this study does not focus on kinetics, and since bimolecular reactions commonly occur in the atmosphere, we believe our experimental conditions provide an atmospherically relevant distribution of radicals and closed-shell products.**".

Comment #2:

More to that point, the presented DEA-CIMS spectra reach comparatively high normalized values, some signals appear to be as high as 0.15 ncps. At this level, the primary ion signal might decrease and the instrument signal might not show a linear correlation to the concentration anymore. Did the authors observe a drop in the primary ion signal?

This is the drawback of the broad sensitivity of the DEA-CIMS where even moderate concentrations can cause noticeable titration of the reagent ion. In our experiments, the drop in the primary ion was still considered to be low enough to not have a major impact on the linearity. Taking the α-pinene (AP) + NO_3 experiment as example, from the background stages to stage 8, the normalized signal of $C_{10}H_{16}O_2$ gradually increased to around 0.15, and the primary ion $C_4H_{12}N^+$ signals did decrease correspondingly. But it dropped by only roughly 20%, from

1.31×10^4 to 1.03×10^4 counts/seconds, which is below the empirically observed ~30% reduction threshold beyond which quantification becomes more strongly non-linear. Thus, the impact on measurement accuracy is expected to be small.

Comment #3:

Did the authors test if some of the observed dimer signals can be formed during the ionization process and are actually artefacts from cluster formation of two monomers with DEA. There are some discrepancies between the nitrate-CIMS and the DEA dimer distribution in the spectra that might be affected by different primary ion concentrations. Furthermore, the authors describe limitations during the applications of a dilution tube, it would be interesting to see if all signals were affected similarly.

The possibility of dimer formation within the ionization process can be tested with a well-designed dilution tube. We agree that it would be interesting to see how different signals are affected after applying a dilution tube. Unfortunately, the dilution setup we used caused a significant drop in all signals, including the reagent ion, and was thus not useable, as discussed in the main text Section 3.4 as a limitation of the study. It is still a work in progress for us to develop a more suitable dilution tube, but unfortunately we could not provide unambiguous verification for the signals in this study. For the high yields of $C_{20}H_{32}N_2O_8$ from BP, we cannot rule out the possibility of ion-induced reactions during the ionization process. However, from earlier flow-tube studies (Berndt et al., 2018; Peräkylä et al., 2023), the ion-induced dimer formation was not significant for reacted AP up to 2×10^9 molecules/cm^3, which is comparable to the reacted MT concentrations in this study. Consequently, we do not expect this ion-induced process to be dominant under our experimental conditions. It remains an open question why the dimer signal is so high specifically for BP. We have added more discussion about this topic both in sections 3.2 and 3.4.

"**It remains unclear why BP in particular has such a high yield of this dimer. While we cannot rule out that this signal is impacted by some undesired chemical or instrumental effects, it is puzzling why such an effect would be so dramatic only for BP**".

"**However, as the levels of reacted [MT] in this study are comparable to earlier flow-tube studies where ion-induced dimer formation was found not to be significant (Berndt et al., 2018; Peräkylä et al., 2023), we do not expect such processes to be dominant in our experiments.**"

Comment #4:

The authors attempt a mass closure using both DEA and NO3 CIMS signals, both linked to calibration of the instrument with sulfuric acid. Considering that the calculated levels should be regarded as lower limits, which is stated by the authors, the results agree surprisingly well, but depending on the DEA primary ion signal behavior the strength of the presented mass closure might be doubtful. Small differences in the cluster stability might lead to large uncertainties.

Yes, using the calibration factor from sulfuric acid theoretically would give us lower-limit concentrations, considering that product species cluster with NO_3^- near the collision limit, similar to sulfuric acid. If DEA-detected species also form clusters near the collision limit, as assumed in Berndt's previous work (Berndt, 2022; Berndt et al., 2025), applying the same calibration factor largely accounts for ion–molecule reaction efficiency as flow profiles were identical for both detection modes. Also, the 20% drop of reagent ions at the highest concentrations is not a major issue for the quantification of DEA mode as explained in comments #2. While we note the lower-limit estimates, that account for e.g. less stable clusters of DEA with some less oxygenated organics, the mass-dependent transmission of the mass spectrometer may still compensate in the other direction as well, if the transmission at higher masses was much more efficient than in the reagent ion regions.

Due to the lack of oxygenated organic molecule standards, it remains challenging to directly determine calibration factors for organic peroxy radicals or closed-shell products. Another way of taking into account differences in the cluster stability would be doing voltage scans. We did voltage scans with the DEA mode, but with the voltages starting to differ, all signals started to decrease sharply, making it difficult to accurately fit a sigmoid curve for determining the relative cluster stabilities. At the end, we applied a universal calibration factor for both DEA and nitrate modes, the same way many early studies with multiple ionization schemes used to estimate lower-limit concentrations (Berndt, 2022; Berndt et al., 2025). Therefore, our results would still be comparable to early flow-tube studies. The agreement of the product closure results was seen for AP, limonene, and myrcene, though they have very different HOM yields. Note that we did include this as a limitation in Section 3.4: "Moreover, the lack of more specific standard calibration compounds than sulfuric acid (Section S2) limits our CIMS quantification for the larger organic compounds."

Comment #5:

During the experiments, a VOCUS PTR was monitoring the MT concentrations. Did the authors check for compounds with one or two oxygen atoms to support their hypothesis, that C10H16O contributes to the mass closure of some MT?

Unfortunately, the VOCUS PTR was not measuring from the flow-tube system during the actual experiments in July 2025, since it was deployed elsewhere. However, in Feb 2025 when we did test experiments, we used the VOCUS PTR and it confirmed that our syringe pump system for MT injection was accurate (discussed in Supplement Section S2). But during the test experiments, we did not use the external reactor to produce NO_3 and N_2O_5, resulting in the ozonolysis-dominated spectra. We checked that the $C_{10}H_{16}O$ peak showed up in the spectra but attributing its origin is extremely difficult. Overall, the VOCUS PTR mentioned in the Section 2.3 was only used for the validation of the syringe pump system. Therefore, we discussed the possible unseen products containing one O-atom as a limitation in Section 3.4: "The formation of these unseen products can be investigated by future studies using instruments with better selectivity."

We noticed that what we originally wrote in the last paragraph of Section 2.3 could be misleading and make readers think we connected VOCUS PTR during the actual flow-tube experiments. We removed "monitor VOC concentrations and", and now the updated sentence is **"A Vocus proton-transfer-reaction time-of-flight mass spectrometer (Vocus PTR-TOF, Tofwerk AG) was used to validate the syringe pump system (see Section S2 for details)".**

Also, to make it clearer and reduce confusion, in the second to the last paragraph of supplementary Section S2, we added: **"Note that the Vocus PTR was only used during test experiments in Feb 2025 and was absent for actual experiments in July 2025 due to its unavailability. During test experiments…"**, and modified the last sentence: "**This syringe pump system was also used to inject other four MTs and TME at specific rates, based on the density and molecular mass of each compound and the target concentrations.**".

Comment #6:

The nitrate radical is commonly assumed to initiate the reaction with AP by adding to the double bond. However, there is some work that suggests the contribution of H-abstraction pathways to AP degradation.

Vereecken, L.; Peeters, J. Theoretical Study of the Formation of Acetone in the OH-Initiated Atmospheric Oxidation of α-Pinene. J Phys Chem A 2000, 104 (47), 11140–11146. https://doi.org/10.1021/jp0025173

Shen, H.; Vereecken, L.; Kang, S.; Pullinen, I.; Fuchs, H.; Zhao, D.; Mentel, T. F. Unexpected Significance of a Minor Reaction Pathway in Daytime Formation of Biogenic Highly Oxygenated Organic Compounds. Sci Adv 2024, 8 (42), eabp8702. https://doi.org/10.1126/sciadv.abp8702

The authors observed the formation of C10H16O2 during the oxidation of AP and carene and suggest the contribution of C10H16O. I suggest including a discussion about previously discussed H-abstraction pathways as well.

It's a good point that like OH radical, NO_3 radical could theoretically initiate the reaction with MTs by undergoing H-abstraction pathways. The H-abstraction would first result in alkyl radical $C_{10}H_{15}$ and then the peroxy radical $C_{10}H_{15}O_2$ following a O_2 addition. The following bimolecular reactions and autoxidation steps would result in a sequence of radicals $C_{10}H_{15}O_x$. However, we did not see any noticeable amount of radical $C_{10}H_{15}O_x$ that could be attributed to NO_3 oxidation, meaning that the possible H-abstraction pathways were negligible in our flow-tube experiments. For example, although we saw the presence of $C_{10}H_{15}O_4$ and $C_{10}H_{15}O_6$ for AP and carene, respectively, their behavior during our experiments (Figs. 2 and S3) suggest that they were from O_3/OH oxidation instead of NO_3 oxidation (details on distinguishing O_3/OH oxidation products from NO_3 oxidation ones can be found in the second paragraph of Section 3.1).

We added the following discussions at the end of fourth paragraph of Section 3.1: **"It is worth noting that a minor oxidation pathway of H-abstraction by OH radical was previously reported (Shen et al., 2022; Vereecken and Peeters, 2000), producing a sequence of radicals such as $C_{10}H_{15}O_{2,3,4}$. However, we did not see any noticeable amount of radical $C_{10}H_{15}O_x$ that could be attributed to NO_3 oxidation, meaning that its possible H-abstraction pathways were negligible in our flow-tube experiments.".**

Comment #7:

A 0-D box model was used to calculate the oxidant levels at the start of the reaction based on gas-phase reactions. It seems like upon dilution after the reaction chamber as well as upon mixing in the flow tube itself, a major fraction of the nitrate radicals is derived from N2O5, as the dilution of the NO3 level would result in much lower mixing ratios. Did the authors estimate the loss fraction of N2O5 to surfaces and how much that could influence the oxidant levels in the setup?

Yes, after the 5 LPM injector flow carrying NO_3/N_2O_5 diluted into the 95 LPM main flow within the flow-tube, the much smaller decrease of NO_3 compared to other precursors was due to decomposition of N_2O_5. We did estimate the wall loss rates of both NO_3 and N_2O_5 (see Table S1) within the pre-reactor (inner diameter: 40 mm) and the injector (inner diameter: 8 mm), based on a previous study (Lambe et al., 2020). Since the free-jet flow-tube has negligible wall interactions, we did not consider any wall loss within the flow-tube. As the referee noticed, a major part of NO_3 in the flow-tube is from N_2O_5 decomposition within the flow-tube, since the NO_3 loss rates are so high in the injector tube. Only if the loss rates of NO_3 would be considerably decreased would they have a noticeable effect on oxidant and oxidation product levels. However, if varying the N_2O_5 wall loss rates, the oxidant levels would change. For example, doubling N_2O_5 wall loss rates would result in roughly one fourth of the oxidant levels while halving the loss rates would result in doubled oxidant levels. The current

estimated wall loss rates for NO_3 and N_2O_5 used in the box model are based on previous research, and thus should provide reasonable results, but we do note the inherent uncertainties in Section 3.3: "Considering the inherent uncertainties stemming mainly from the calibration factor applied to CIMS quantification (Section S2) and the estimated coefficients of NO_3 and N_2O_5 wall losses within the box model (Table S1), it is possible that we were able to observe almost all the products."

We added the following discussion about limitation of the box model in Section 3.4: "**It is notable that the box model used for estimating concentrations of reacted MTs does not capture turbulent mixing, and thus an instantaneous dilution of the injector flow into the main flow was assumed. However, the experimentally determined reaction times theoretically account for turbulent mixing. Nevertheless, some uncertainties may arise from different relative concentrations of oxidants and reactants.**".

Comment #8:

Could a heterogeneous reaction of N_2O_5 explain nitrate formation? What was the humidity level reached during the experiments?

The flow-tube experiments were conducted under dry conditions as mentioned in Section 2.1: "The experiments (temperature: 298 ± 2 K; pressure: 1 atm; dry conditions: relative humidity < 1 %) were carried out in a newly constructed free-jet flow-tube system…". Thus, the heterogeneous reaction of N_2O_5 with water forming HNO_3 should be negligible. By doing tests with only NO_2 flow from an NO_2 cylinder going into the flow-tube system, we saw a large amount of HNO_3 depleting DEA primary ion ($C_4H_{12}N^+$). Moreover, during the actual experiments, by adding a HEPA filter after the NO_2 cylinder, the HNO_3 was mostly removed, confirming that the majority of HNO_3 was directly from the NO_2 cylinder.

Comment #9:

Mainly in Figure 4 but also in S9, there are more arrows than corresponding formulas, which makes it quite hard to read the plot, I suggest to remove 'empty arrows'.

These are not "empty arrows", and the reason why multiple arrows sometimes point to a single formula is because they point from different masses, owing to the fact that one molecule can be charged by clustering with both labeled (e.g., $^{15}NO_3^-$) and non-labeled primary ions (e.g., NO_3^-). This caused two (or three if the ion contained a reagent ion dimer) adjacent mass-to-charge ratios to correspond to the same molecule. In Figure 4, the primary ions are omitted for simplicity and the detailed charging schemes are shown in fig. S9, as mentioned in the caption of Fig. 4. To reduce confusion, we added the following explanation in the captions of figs. 4 and S9:

"Note that, in some cases, multiple arrows point to a single formula from different m/z because one molecule can cluster with both ^{15}N-labeled primary ions and non-labeled ones, resulting in two or three adjacent mass-to-charge ratios corresponding to the same molecule.".

We also noticed and corrected a few errors in the formulas within figs. 4 and S9.

Comment #10:

The first part of the 'Implications' section actually reads very similar to a conclusions section. Maybe the authors could emphasize more the implications for SOA formations, that these results might comprise. Can we expect the SOA formation to change between night and daytime using the presented results?

We now removed some summarizing sentences from the beginning of the Implications section to make it sound less like the Conclusions. Now the updated first part is: "**Our findings validate the previous observations that small structural differences among MTs strongly influence the product distributions during oxidation, and demonstrate that the HOM yield of an individual MT from NO_3 oxidation can differ significantly from that by O_3/OH oxidation. Still,…**"

We did not initially discuss much about SOA formation based on our results, mainly because in our short-reaction-time flow-tube experiments, there were no particles formed. Also, the HOM yields could not be directly linked to SOA yields, and the differences were discussed in the Implications section, wherefore we suggested a future study to help us understand to which extent HOMs are able to explain SOA formation at the end of the conclusions section.

However, as we discussed in the Implication part that HOM yields of different oxidants would differ, we believe that the SOA formation would change between night and daytime. Thus, we added the discussion regarding this in the Implication section 3.4: **"Since HOMs are a large source of SOA (Ehn et al., 2014), the SOA formation is expected to vary between day and night, depending on the VOC distribution and the dominant oxidant (e.g., OH vs NO_3). For instance, if limonene is the key precursor driving SOA formation during the day, its role would diminish at night because the rapid reaction limonene + NO_3 yields far fewer HOMs and more of the volatile compound $C_{10}H_{16}O_2$. The correlation between HOM formation and SOA mass is most evident at low OA mass concentrations, where extremely low-volatile HOM species dominate new particle formation and early growth. In more polluted environments with higher pre-existing OA mass, however, low-volatile and semi-volatile (i.e., non-HOM) oxidation products can contribute substantially to SOA mass. Therefore, HOM and SOA yields are not always closely related, and their relationship can vary**

significantly across different chemical regimes and environments (with differences in VOC composition, oxidant conditions, and background OA loadings).".

Minor comments:

Comment #1:

I would suggest to use a different color for the two data points with the same NO2 concentration in figures 6 and S8 to make it easier to read and understand the plots.

Our preference would be to retain the original colors, as we hope that readers would compare these two points at the same NO_2 concentration and find that there was no large change between the two conditions. To help avoid misunderstandings, we added the following explanation in the caption of the fig. 6: **"Note that stages 5 and 8 have the same $[NO_2]_0$ = 32.5 ppb, but the stage 8 has a higher O_3 level thus a higher reacted [MT] by NO_3."** For the caption of fig. S8, we added **"Note that stages 5 and 8 have the same $[NO_2]_0$ = 32.5 ppb."**

Comment #2 – #6:

L193: should read "we used the following criteria"

L 289: should read "than its corresponding RO2 C10H16NO5"

L247: should read "the comparatively low signals"

L275: I think the RO2 radical should be the corresponding C10H16NO5

L282: should read "It is present even…"

Thanks for noticing the mistakes. We revised the first three accordingly in the main text. For the L275, the RO_2 radical here should be $C_{10}H_{16}NO_6$ instead of $C_{10}H_{16}NO_5$, because it was considering bimolecular reactions RO_2 + $R'O_2$ forming ROH and R'C=O. In this case, the closed-shell monomer $C_{10}H_{17}NO_5$ comes from $C_{10}H_{16}NO_6$. For the L282, "Its presence" is the subject for the sentence, the main structure of which is "Its presence rules out…".

Response to Referee #2

General comments:

This study presents early-stage HOMs products and their yields from NO3 + five monoterpenes using flow-tube experiments. The authors were able to distinguish NO3 products from O3/OH oxidation products, derived individual product yields and constrained total HOMs yields from NO3 oxidation of different monoterpenes. By using two ionization schemes, they were able to detect a wide range of close-shell compounds and RO2 that provided insights into the reaction mechanisms. Overall this manuscript is well written and is suitable for ACP. I only have a few comments.

We thank the referee for taking the time to review our manuscript and for the positive and insightful comments. We will answer the specific comments point-by-point below. The referee's comments are in blue, and our answers are in black with updated content in **bold**.

Specific comments:

Comment #1:

Line 131, regarding CIMS calibrations, was the DEA mode also calibrated using sulfuric acid and was the sensitivity factor applied universally to the wide range of species detected? How large was the uncertainty in sensitivity?

Sulfuric acid calibration was performed for the nitrate mode, and the resulting lower-limit calibration factor was applied to both modes. This approach is justified by the use of the same Eisele inlet and the assumption of near-collision-limit reagent-analyte reactions for all products. This factor was applied universally to the wide range of species detected, because in the absence of oxygenated organic molecule standards, it remains challenging to directly determine calibration factors for the different organic products.

We estimated the uncertainty of quantification to be at least ± 50%, as stated in the manuscript, thus quantification remains a major challenge, as also noted in Section 3.4: "Moreover, the lack of more specific standard calibration compounds than sulfuric acid (Section S2) limits our CIMS quantification for the larger organic compounds." To remain still a bit more conservative, we added "**at least**" before "± 50%" in both the manuscript and supplementary.

Comment #2:

Line 360, did the Vocus see one O-atom products? If so, do they fill the gap in the product closure and explain the mechanism?

We refer back to our response to the specific Comment #5 from Referee #1. In short, the VOCUS PTR was not measuring from the flow-tube system during the actual experiments, and we have modified both main text and supplementary to clarify this.

Comment #3:

Figure 2B, at around 11am, is there a reason for the increase and then decrease in C10H14O7 and several other species?

Yes, the reason is that AP was accidentally injected at a rate of 120 ppb, and after we noticed it, we corrected it back to 20 ppb. This was indicated by the initial [AP] displayed above the subplot: "120 → 20". However, from this accident, we could see clearly $C_{10}H_{15}O_8$, $C_{10}H_{15}O_{10}$, and $C_{10}H_{14}O_7$ were from O_3/OH oxidation. To clarify this, we added the following sentence at the end of the fig. 2 caption: "**Note that the sharp spike in $C_{10}H_{15}O_{8,10}$ and $C_{10}H_{14}O_7$ at approximately 11:00 (panel B) resulted from an initial AP injection of 120 ppb, which was subsequently corrected to 20 ppb. While a mistake initially, this confirms that these three species originate from O_3/OH oxidation.**"

Comment #4:

What were the NO mixing ratios in these experiments? Likely low but a sentence mentioning NO would be helpful.

The NO mixing ratios are negligible compared to NO_2 levels, as we only injected NO_2 (from 0.1% NO_2 cylinder) in the absence of UV lamps that can photolyze NO_2 to NO. From our NO_x analyzer, NO increased slightly from the background level, which may simply be instrument interference but it is in any case estimated to be less than 1% of the NO_2 levels. Also, we did not notice any products from reactions involving NO. To clarify this, we added the following sentence in the second paragraph of Section 2.2: "**NO levels were negligible due to the lack of NO_2 photolysis, consistent with the very low signals from our NO_x analyzer and the lack of detectable products from NO termination.**"

Comment #5:

Line 274-277, can the box model estimate HO2 concentration and understand whether HO2 is an important RO2 sink?

The discussion regarding potential involvement of HO_2 (Line 274–277) was based primarily on the observed product distribution. Currently, the box model used in this study is designed to estimate the amount of

monoterpenes consumed by each oxidant (O_3, OH, and NO_3) to determine specific product yields. While modeling HO_2 levels would be interesting, it would require a much more detailed model, and it would still have inherent uncertainties due to uncertainties in several relevant reaction rates. In this work, we cannot definitely conclude whether HO_2 was a relevant RO_2 sink or not, but earlier studies with similar reactants have tended to find that the role of HO_2 is minor.

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