Response Letter to Referee #2

The authors thank the reviewer for careful reading and positive feedbacks. We also appreciate the reviewer for the helpful comments and suggestions, which significantly improved the manuscript. All the comments are addressed below point by point in bold text, with our response followed in non-bold text and the corresponding revisions to the manuscript in blue. All updates to the original submission were tracked in the revised version as you can find below.

Anonymous Referee #2:

The authors describe experimental results of the nitrate radical initiated oxidation of isoprene carried out in a batch-reactor for close to atmospheric conditions. Nitrate radical were generated via the O3+NO2 pathway. The reaction was conducted in such a way that multiple nitrate radical attacks were possible leading to product formation of the 2nd and 3rd generation. Product formation was followed by a bromide-CIMS. The results are interesting and worth to be published in ACP. Some points should be considered before acceptance of the manuscript can be recommended.

1. Line 71. "isoprene nitrates"? better: "organic nitrates derived from isoprene oxidation"

Response: Accepted.

2. Line 150, Fig. 1a-c: It is stated that approx. 90% of consumed isoprene reacted with NO3 based on modeling results. The reaction scheme with the used rate coefficients is not given yet. Please provide this information in the SI. The modeling results should be compared with the measurements of the chemical species depicted in Fig. 1 (as done in a couple of other

papers of the Jülich group). That gives the readership an impression how good the processes in the experiment have been understood and how accurate the model is.

Response: Thanks very much for the suggestion, but there was a misunderstanding. The isoprene losses with respect to reaction with different oxidants were calculated from measurements, without using any modelling results. For example, the amount of isoprene consumed by O_3 was calculated from isoprene and O_3 measurements, and the isoprene consumed by NO_3 was calculated from the total isoprene losses using the measured isoprene and subtracting the losses due to O_3 and dilution. The reaction of isoprene with OH was not considered as its concentration was below the detection limit, and thus losses due to reaction with OH could not be quantified from the measurement. However, OH is expected to contribute about 10% of the isoprene losses, with the contribution of the NO_3 reaction accounting for up to 80%, as determined in a recently published modelling work based on the same campaign, which implemented a newly developed NO_3-isoprene mechanism with updated RO_2 and RO chemistry (Vereecken et al., 2021).

To avoid misleading, we revised the original sentence "According to the modeling results, approximately 90% of the isoprene reacted with NO_3, …" to "Calculation from measurements of isoprene, O_3, OH, NO_3 and dilution indicates that NO_3 contributed for more than 90% of the chemical losses of isoprene, as shown in Fig. S1, with reaction with O_3 being a minor pathway in our system. The reaction of isoprene with OH was not considered as OH concentration was below the detection limit of the instrument in this study (Fig. S2). Thus, losses due to reaction with OH could not be quantified from the measurement, but have been determined to contribute about 10% of the isoprene losses according to a recently published modelling work based on the same campaign, with the contribution of NO_3 reaction reducing to about 80% accordingly (Vereecken et al., 2021)."

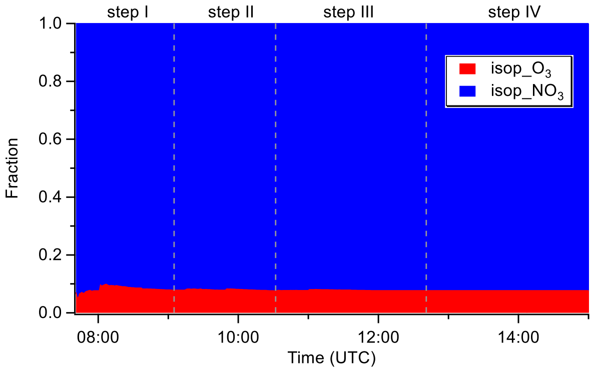

Figure S1: Fraction of isoprene consumed by O_3 and NO_3 calculated from measurements. The amount of isoprene consumed by O_3 was calculated from the measured concentrations of O_3 and isoprene measurements, and that consumed by NO_3 was calculated from total isoprene losses (from isoprene measurements) subtracting losses due to dilution and reaction with O_3. Isoprene losses due to reaction with OH could not be included here, because the OH concentration was below the detection limit. However, according the model calculations OH contributed about 10% to the isoprene consumption (Vereecken et al., 2021).

3. Line 200-212: The authors determined a bulk sensitivity for the organic nitrates. It should be described more in detailed what has been done. It is not clear to me why this calibration was not used to set all the measurements on an absolute scale. The authors argue "that the normalized signals are sufficient". More precise information is better in each case! On the other hand, they did it for C10 products. Why is the calibration only used for higher molecular products? Please comment. It would be fine if the authors could provide the plots of the C5 org. nitrate concentrations (or the yields because the amount of reacted isoprene is known). And please add a discussion regarding the uncertainty of these absolute values.

Response: Sorry again for obviously unclear formulations.

To calculate the bulk sensitivity for organonitrates, the sum of organic nitrate signals from Br^- CIMS (in units of norm. count s^{-1}) was used and divided by measurements of the total alkyl nitrates (in units of ppb) from a thermal dissociation-cavity ring-down spectrometer during the experiment. This gave us an idea about how large the concentrations may be at all.

In the revised manuscript, the original sentence in line 200-204 is revised to "Due to a lack of authentic standards for the products, it is difficult to quantitatively determine their individual absolute concentrations, but we calculated the bulk sensitivity for organonitrates using the sum of organic nitrate signals from Br^- CIMS divided by measurements of the total alkyl nitrates from a thermal dissociation-cavity ring-down spectrometer during the experiment."

The bulk sensitivity of Br^- CIMS for organic nitrates estimated in this study is a single-average value, so applying this value to convert the normalized signal to absolute concentration will not change any of the conclusions which are mostly based on the time behaviors of products (generations) and the relative changes of their normalized signals with time. Instead it may pretend a level of accuracy we cannot provide. By taking these two points into consideration, we prefer to keep using normalized signals rather than absolute concentrations for the analysis in this work.

However, as mentioned in the text, the bulk sensitivity was applied to estimate the potential SOA yield by condensation of the observed species. Here, several species contribute to SOA formation and application of an average sensitivity seems to be justified. The uncertainty of the estimated instrument sensitivity for organonitrates (~ 22%) is included in the calculations of the relative uncertainty of the SOA yield (32%) by error propagation, which includes also the uncertainty of the isoprene consumption concentration (~ 10%), the uncertainty of the alkyl nitrate concentration (~ 10%), and the uncertainty of the dimer content (~ 20%)., This is described in the caption of Fig. S8. In the revised manuscript, we add the uncertainty of the estimated SOA yield.

4. Line 417, Fig. 2: In Fig.2 an average spectrum from the complete experiment is given. It would be fine having also a spectrum from the first injection showing mainly 1st generation products. A couple of possible reaction pathways were mentioned/ discussed in the paragraph before, incl. possible RO2 isomerization step leading possible to HOMs. Nothing is said here regarding the relevance of RO2 isomerization in this reaction system based on the measurements. It would be also very helpful for the readership to have a reaction scheme in the main body that explains the formation of the observed main products, i.e., C5H9NO5, C4H7NO5, C5H9NO4, C5H9NO6, … What about the formation of the carbonyls HCHO, MVK, MACR? The Vocus PTR-MS is very sensitive at least for the C4-carbonyls.

Response: Thanks for the comment. Actually, mass spectra from different injections (denoted as step I, step II, and step IV) are shown in Fig. 3 in the manuscript (also shown below for illustration). We can determine from the plot that the major products in step I were 1N-monomers (in the mass range of *m/z* 220-280) and 2N-dimers (in the mass range of *m/z* 370-440), which are mostly expected to be first-generation products as discussed in the manuscript.

The general reaction schemes of NO_3-initiated oxidation of isoprene and the possible reaction pathways of the major products (including C5H9NOx, C4 carbonyls, C5 dinitrates and trinitrates, 2N- and 3N- dimers) are discussed in sect. 2.5.2, sect. 2.5.3 and sect. 2.5.4, with the corresponding schematic plots provided as supplementary materials. We moved on purpose the schemes to the supplement as they are not in the center of the manuscript but serve as a tool to get information about potential functionalization of the products for the vapor pressure calculations. We summarized all the underlying mechanistic information in Sect. 2.5, so that we did not need distribute them or repeat them throughout the text. Therefore, we did not repeat the discussion of the possible formation mechanisms of the major products in sect. 3. We would prefer to keep the manuscript as it is.

In the same sense, since this study focuses on the organic nitrate products of several generations which can be well detected by bromide CIMS, and we are more interested in multi-functional low-volatility molecules which can contribute to SOA formation, small compounds like HCHO, MVK/ MACR are of interest for the analysis in this study. Indeed, the referee is correct, Vocus identified C4 species with different chemical formulas than those measured by Br^- CIMS. We only utilized the measurements of the isoprene precursor from Vocus. Analysis of the VOCUS data will surely provide many insights, but it is not needed for our purposes. A deeper analysis of VOCUS data is out of the scope of our manuscript.

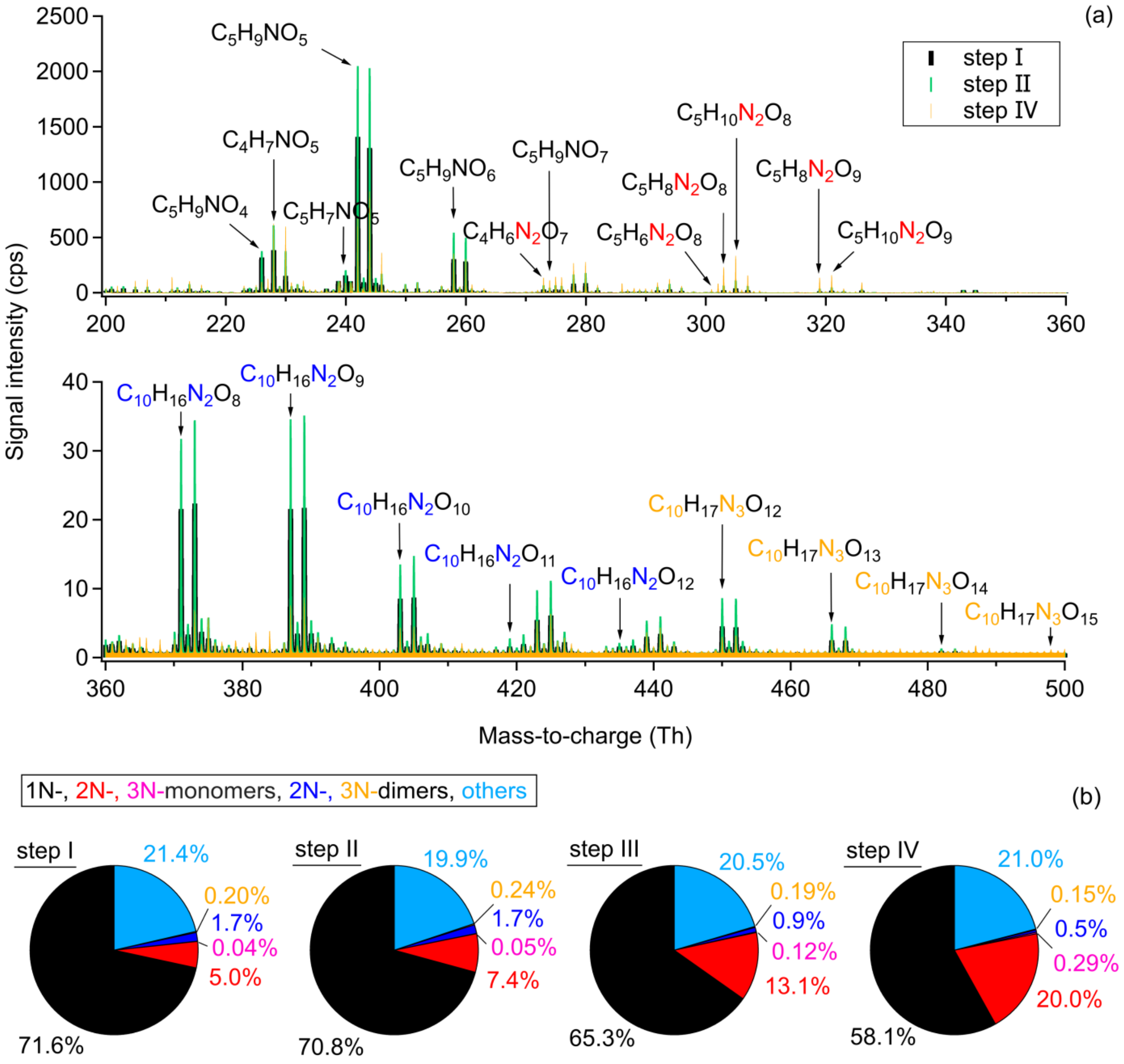

Figure 3: Comparison of the chemical composition of each oxidation step. (A) Averaged mass spectra for step I, II, and IV, with the omitted spectrum of step III being very similar to that of step II. (B) Relative contribution of different chemical groups for each oxidation step. Only organic products were counted for analysis. 'Others' refers to CHO compounds without containing nitrogen atoms (e.g., $C_5H_8O_2$ and $C_5H_8O_3$).

References

Vereecken, L., Carlsson, P., Novelli, A., Bernard, F., Brown, S., Cho, C., Crowley, J., Fuchs, H., Mellouki, W., and Reimer, D.: Theoretical and experimental study of peroxy and alkoxy radicals in the NO3-initiated oxidation of isoprene, Phys. Chem. Chem. Phys., 23, 5496-5515, 2021.