

Interactive comment on “Characterization of organic nitrate constituents of secondary organic aerosol (SOA) from nitrate-radical-initiated oxidation of limonene using High-Resolution Chemical Ionization Mass Spectrometry” by Cameron Faxon et al.

Anonymous Referee #1

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This manuscript describes data collected from a FIGAERO-CIMS during laboratory studies using the flow reactor GFROST. Focus is given on the major organic nitrate constituents of secondary organic aerosol from the NO₃ oxidation of limonene. A cluster-analysis method is used in order to distinguish the groups of ions based on their thermodynamic properties and molecular formula information. Mechanisms of dimer formation are suggested based on the grouping performed. The paper is suitable for publication in ACP. My suggestions below are mainly to clarify the presentation

and context of the results.

Specific comments

1. Recent studies have shown that fragmentation due to thermal dissociation in the FIGAERO-CIMS could strongly affect the chemical formula attribution (Stark et al., 2017). It would be beneficial if a comparison of the different methods of assigning a chemical formula to the major ions could be performed. If not, then the possible uncertainties introduced should be further discussed.

2. In line 98 it is mentioned that one of the main focuses of this paper is to determine the molecular formula of species that could contribute significantly to SOA formation. Although the uncertainty of calculating the mass concentration using FIGAERO-CIMS would be high it could still indicate whether the compounds measured are indeed a large fraction of the overall mass as has been done from Isaacman-VanWertz et al. (2017).

3. FIGAERO-CIMS collects both the gas and particle phase compounds on the filter. More information on the gas phase compounds detected would bring light concerning the extent of possible gas phase “interference” during desorption. When the signal of the compounds in the gas phase is high then their contribution to the aerosol during desorption could increase more. Have there been any checks on the contribution of gas phase signal during desorption? How much is it expected to be in the monomer and how much in the dimer range? A figure to illustrate this effect in the supplementary would be very informative. For example, in lines 346-348 this could also be due to gas phase compounds collected on the filter that undergo evaporation and thus contribute to the aerosol. What is the gas phase concentration of these compounds compared to the aerosol?

4. In Figure 3 for many of the compounds there is a residual signal above zero. How would that affect the signal of the next desorption? When FIGAERO reaches stable conditions what does that exactly mean? It would be fruitful for the reader if background

measurements could be provided during these experiments on the Supplementary material. An additional figure to support the stability of the thermograms would be very instructive. For example the average cumulative signal (with error bars indicating the standard deviation of the average) vs temperature, for each compound, with each compound indicated with a different color would be a suggested way.

5. What is the atmospheric relevance with the mixing ratio of N₂O₅ used? What is the NO₃ expected mixing ratio in the system? A discussion would better inform the reader.

6. In Figure 4 what is the fit function used? What is the information we gain from this fit choice? Further discussion in the manuscript would clarify these questions. This figure doesn't provide all the data points seen in Table 1. The high N₂O₅/limonene ratio of 113.3 is missing. Could that be included or provided in the supplementary? Is this point included in the fit function applied now? Finally, error bars for the y-axis are missing and the fit function should be applied by taking into account this error.

7. In section 2.3 was it both gas and particle phase data used as identified species to compare to the MCM? A sentence to make clear that this work is focused on the particulate phase and not the gas phase would better direct the reader at this point.

8. It would be beneficial for the reader if the discussion in section 3.4 was extended on how the suggested mechanisms can be directly inferred from the grouping technique and the volatility of the compounds.

Technical comments

Line 47. A broader view of organic nitrates is given by Kiendler-Scharr (2016).

Line 154. Units are missing.

Line 167. Delete one dot.

Line 234. Recent findings suggest that fragmentation due to thermal dissociation occurs in systems like the FIGAERO-CIMS (Stark et al., 2017). See comment 1.

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Line 324-337. The authors provide four characteristic desorption patterns and the numbering stops at two.

Line 361-362. It would be more informative to add the positive correlation in the supplement as a figure.

Line 387. Please define what extremely low signal would be as a value.

Line 428. Should be 0-2?

Table 1. Sorting of the lists would make the table more readable. Sorting the N₂O₅ from low to high and within each N₂O₅ group sorting the limonene from low to high would be one way of performing the sorting. Adding the expected NO₃ concentration would be fruitful. Errors for the average SOA mass measured from an SMPS are missing. An additional column of the mass FIGAERO-CIMS could detect (with its much higher uncertainty), as discussed above, would be an indicator of how much of the overall SOA mass is measured in this system.

Table 2. What is the information we gain from the (N/C)x10? Based on all uncertainties the temperature precision could be rounded. Error of the average contribution is missing.

Figure 3. Certain double peak compounds are not highlighted like C₁₀H₁₅NO₇, C₂₀H₂₉NO₅, C₂₀H₂₄N₂O₈ etc. The C₂₀H₂₄N₂O₈ is not written correctly in the annotation. Since there are more compounds that have double peaks plotted it would be clearer to include the double peak compounds with dash lines and avoid highlighting.

Figure 5. It improves the figure if (a) and (b) have the same annotation introduced on the right side outside both figures once. This way you avoid the change in font size that is seen for annotation from Figure (a). For Figure (b) the oxidation state is not mentioned in the axis and the range is not going to minus when it is below zero. It would be beneficial if Figure (c) was separated in two graphs. On the left side a figure of the MW (left-axis) and Tmax (right-axis) and on the right side a figure of the oxidation

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state (left-axis) and the O/C (right-axis). Box-and-whiskers instead of bars and markers would provide more information on the dataset. This would also show more clearly the temperature increase that is suggested to correlate to the O/C increase. Finally the colors of Figure (c) are similar to the colors of the clusters thus confusing the reader.

References

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Kiendler-Scharr, A.: Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol, *Geophys. Res. Lett.*, 43, 7735–7744, doi:10.1002/, 2016.

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