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Atmospheric Chemistry and Physics
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Discussions

Interactive comment on "A model framework to retrieve thermodynamic and kinetic properties of organic aerosol from composition-resolved thermal desorption measurements" *by* Siegfried Schobesberger et al.

Anonymous Referee #3

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The authors present the development of a new model framework with the aim of reproducing thermograms of individual ions, originating from a FIGAERO-CIMS. The model is capable of reproducing the desorption of organic compounds during controlled heating of the filter, by including vapor-surface interactions with the PTFE surfaces, non-idealities from efficient filter heating, together with possible oligomer dissociation and formation processes. Application of this model is performed for calibration experiments and applied to SOA oxidation products originating from the ozonolysis of α-pinene. The optimum model fits, possible implications, model simplifications and challenges

are discussed in detail by the authors. This work provides valuable, new insights into the thermodynamic and kinetic properties of SOA using FIGAERO-CIMS, an evolving and active area of research in the field. This publication is suitable for ACP. My suggestions below are mainly to clarify the context and presentation of the results.

Specific comments

I understand that the focus of this study is on the development of a model framework, nevertheless, it would further improve the manuscript if more information regarding the experimental setup/data/uncertainties can be provided, especially since the model is evaluated based on these experimental results. For example, the authors cite in section 2.3 their previous publications and only briefly discuss the experimental details. More information concerning the consistency of the calibrations performed together with their uncertainty would be essential before comparing to the model. Since calibrations and experiments range from 2014 to 2016 it would be informative to discuss the performance of the instrument in these years and how possible changes in the performance could affect the presented results. For example, was the CIMS operated in the same conditions during the calibrations and the chamber studies? These uncertainties should also be included and/or discussed where experimental results are provided (Fig. 3, Fig. 8 - Fig. 12). Since the chamber was operated at steady-state, thermograms throughout the experiment should be consistent and thus an average thermogram should be provided for comparisons to the theoretical approach together with the standard deviation of this average and not just one random thermogram. Finally, information regarding the loadings on the filters and how often the filters were changed would be of value. Were there, for example, any memory/matrix effects observed?

The authors do a nice job of introducing the different type of thermograms and different ways to improve and define the appropriate model fit. However, there is no discussion regarding the model bulk information, although the authors give the impression that this analysis has been already performed. What is the volatility distribution of the

OA mass measured from the FIGAERO based on the model? How does that compare to other experimental results that focus on the volatility of the a-pinene SOA, e.g. Isaacman-VanWertz et al. (2017), or previous model approaches (Lopez-Hilfiker et al., 2014). I consider that these comparisons will be very informative and will further support the evaluation of this model. At the end of the manuscript, the authors suggest that the application of the model will be described in an upcoming publication in more detail. Nevertheless, for the given manuscript the model evaluation could be extended to further promote its capabilities.

Page 7, line 1-10: The assumption used in the model is nicely discussed but it would be beneficial if a rough range of upper mass loadings for the different FIGAERO sampling geometries was provided. For which collection concentration does this uncertainty overcome the model assumption?

Page 11, line 1-2: The decomposition of a compound observed as an oligomer from FIGAERO to lower m/z's is very likely to happen too. How much uncertainty is added to the model due to this assumption? What is the percent of possible oligomers that FIGAERO is able to directly detect in comparison to its total signal?

Page 12, line 5: Add description and modifications in SI

Section 3.6: It will be very informative if the authors add the 8 differential equations in the SI. Characteristic examples of the changes that are applied to the model when more than a single compound is included or the deactivation of certain simplifications could be provided in addition.

Section 3.7: The model computational costs are low for one or two compounds. Let's assume that 100 ions are the main contributors of the OA mass in an SOA experiment; what would then be the computational time for the analysis of all ions when running the model for ideal and non-ideal heating? What is considered high computational costs?

Page 13, lines 21-22: Both Fig. 5 and Table 1 provide information for the model alone

and no experimental results. Although the authors make a comparison of the model to experimental results in Fig. 3 more clear comparison should be provided. An additional column in table 1 with the experimental Tmax from different studies and/or an additional Figure of C* vs Tmax for experimental and modeled, modeled with surface interactions and modeled including non-idealities from efficient filter heating, would directly show whether the model reproduces the Tmax-C* relationship in general.

Page 14, line 1: Delete "less than". For 150 nm particles, the difference between Tmax when excluding and including vapor-surface interactions is very similar to the Tmax difference when changing one volatility bin. This would mean that the underestimation should be around one order of magnitude and not less.

Page 16, line 14: No bulk behavior information is provided in this work.

Page 16, line 15-20: Experimental uncertainties should be added and discussed. See comment above.

Page 16, line 25-26: Provide more details in the SI of how the equations were modified in order to include ammonium sulfate particles.

Page 25, line 12: Define "many". Distribution of the thermograms to the different categories could be provided in more detail.

Technical comments

Page 6, equation (1): For better guidance for the reader it would be nice if the parameters of equation (1) are explained from left to right. This means rearranging the parameters in the equation or/and their explanation on page 6, line 10 to page 7, line 10.

Page 3, line 12: Since the PTR-MS is included as a separate ionization technique, compared to CIMS, a proper citation should be added. An overview of PTR techniques to measure organic aerosol is given by Gkatzelis et al. (2018).

Page 3, line 23: Citations are repeated.

Page 3, line 27: Starting a sentence with “But” sounds odd. Maybe rephrase.

Page 5, line 4: “. . .for a vast majority. . .”

Page 9, line 11: For clarity the authors should add a sentence of how the model runs were performed, e.g. running equations (1) parallel to (5), and relate this to Fig. 1.

Page 10, line 8: Section 3.4 has the same name as section 3.3.

Section 3.4: There is no consistency between equation numbers (equation (10a) and (10b)), and text (referred as equation (10)).

Page 12, line 29: correct to “Eq. (10a)”

Page 14, line 31: Delete “:”

Page 16, line 4: Delete “a”

Page 21, line 6: Further explanations regarding the different conditions should be provided. What is the RH during these experiments? What is the expected phase-state of the particles?

Page 23, line 1: Missing “are”

Figure 3: These figures are informative but hard to follow. I would recommend that the authors add an additional figure on the right of each panel that represents: x-axis: (temperature of peak desorption)modeled - (temperature of peak desorption)experiment, y-axis: (Full width at half maximum)modeled - (Full width at half maximum)experiment, color: Indicator of the compound as already given from the annotation. This way the difference between modeled and experimental results will show up clearly while the left panels will still be informative regarding the tailing observed.

Figure 4: Panel B and C should be the other way around.

Figure 6: I recommend that the default parameters normalized model thermogram

(C*0=0.1 ug/m3, a=1 etc.) is indicated in all graphs as a dash, bold line and explained in the caption. This way the reader will have a common reference for all cases studied.

Figure 8, 9 and 10: Change the color for high and low volatility for Panel D.

Figure 11 and Figure 12: The colors are not consistent.

References

Gkatzelis, G. I., Tillmann, R., Hohaus, T., Müller, M., Eichler, P., Xu, K.-M., Schlag, P., Schmitt, S. H., Wegener, R., Kaminski, M., Holzinger, R., Wisthaler, A., and Kiendler-Scharr, A.: Comparison of three aerosol chemical characterization techniques utilizing PTR-ToF-MS: a study on freshly formed and aged biogenic SOA, Atmospheric Measurement Techniques, 11, 1481-1500, 10.5194/amt-11-1481-2018, 2018.

Isaacman-VanWertz, G., Massoli, P., O’Brien, R. E., Nowak, J. B., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., Su, L., Knopf, D. A., Misztal, P. K., Arata, C., Goldstein, A. H., and Kroll, J. H.: Using advanced mass spectrometry techniques to fully characterize atmospheric organic carbon: current capabilities and remaining gaps, Faraday Discussions, 200, 579-598, 10.1039/C7FD00021A, 2017.

Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Lutz, A., Hallquist, M., Worsnop, D., and Thornton, J. A.: A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROsols (FIGAERO), Atmos. Meas. Tech., 7, 983-1001, 10.5194/amt-7-983-2014, 2014.

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