

Interactive comment on “Fragmentation vs. functionalization: chemical aging and organic aerosol formation” by H. J. Chacon-Madrid and N. M. Donahue

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General:

This kinetic study on the formation of secondary organic aerosol addresses one of the hot topics highly discussed nowadays: The transformation of initial aerosol constituents into compounds of higher stability and increased functionality. This affects notably the properties of secondary organic aerosol matter in the atmosphere such as its consequences on CCN formation and climate in general as well as on health effects. Because of that this study fits well in the scope of the journal. Since investigation in

C4031

the field is too challenging and since there is a need to carefully control the conditions of the reactions the experiments have been conducted under laboratory conditions. In order to elucidate the role of fragmentation and functionalization the authors selected a series of semi-volatile organic aerosol precursors with rather similar saturation vapour pressures to be reacted with OH. This leads to the formation of organic peroxy radicals and carbonyl compounds, subsequently participating in the mass formation process. High NO was present to simplify the chemistry taking place after the initial OH attack, allowing alternative products to be neglected and yield calculations for individual compounds. Since all experiments are started with compounds of nearly identical concentrations and vapour pressures one would expect a rather similar yield for each of them in case no other effects such as fragmentation and functionalization play a role. In testing this hypothesis the authors demonstrate clearly that the increase in oxidation grade of a molecule causes a tendency of the OH-products to easier fragment and to lead to smaller aerosol yields. To cite the authors of this study: *“We show that while more oxidized molecules are more likely to fragment, they will also contribute significantly to organic aerosol formation.”*, which can be seen as the one line summary. This finding is evident in a couple of figures displaying the individual saturation vapour pressure groups and different functionalities. The findings are important and merit publication in *Atmos. Chem. Phys.*. Before that I would like to raise a couple of detailed comments, which should be answered previously.

Detailed comments:

The approach and the results are convincing and I'd really appreciate the efforts and the progress being made.

- There is one point I would like to make with respect to Figure 1 and the atmospheric conclusions: The authors name three different processes influencing the

C4032

amount of SOA, i) the accretion reaction, ii) the functionalization of gaseous molecules due to reaction e.g. with OH and the resulting drop in saturation vapour pressure and iii) the fragmentation, i.e. the split into smaller products, thus leading to more volatile compounds. I am not convinced that only the partitioning process of semi- and non-volatile organic compounds is responsible for the aerosol mass gained. The authors oxidize the precursor compounds by OH forming radicals in a first stage. Those will be transformed into carbonyl compounds or organic nitrates later on. It is assumed that the aerosol phase consists only of the compounds investigated. What would result if those first stage radicals cause a notable mass yield? This would have additional consequences on the interpretation. OK, the high alkene, ozone and NO concentrations narrow down not only the product spectra but limit the concentration of radicals too. However they are expected to be notable in number concentration. This could have implications on the mass yields gained when extrapolating to different initial concentrations. Under ambient conditions the "radical accretion reaction" would increase in importance and the effect would be highly aerosol size dependent, i.e. dominating at smaller sizes where Kelvin effect prevents effective partitioning. Because of that the approach is nice but might lead to an underestimation of SOA formation, functionality and fragmentation at ambient conditions. Please comment on that, because the importance for the atmosphere was addressed in different sections of this study and is certainly of high relevance.

- HONO-photolysis is being performed for OH production. Is there any overlapping spectral region of the lamp with the absorption bands of the carbonyl compounds used (e.g. pinonaldehyde) or is that effect negligible? If this would play a notable role other products might be expected too.
- Please name the SMPS type used. Does it cover the whole aerosol size range (LDMA?) or is the upper edge cutted off?

C4033

- Atmospheric aerosols consist by around 50
- PTR-MS masses measured: I am aware of the easy fragmentation of larger organic substances during the proton-transfer process, which is a challenging issue. Maybe heptadecanal and nonadecanal should be stable than yielding primarily 43 and 57 in m/z. What about the inlet temperature of the PTR-MS?
- The use of methanol as OH-marker is a nice idea, but will lead to HCHO, HO₂ and CO formation that will affect somewhat the radical reactions. Has this effect been checked by a box model?
- Highly interesting results on the series and mass yields. The authors clearly show the negative effect on SOA yield, if the precursor was already oxidized especially in the case of aldehydes. This has been explained by the contribution of the fragmentation process to the aerosol mass budget. Is there any change by carbon number, i.e. is there a carbon number above which the process declines and becomes negligible because of a distribution of reaction energy over a large molecule?

Good ideas and results are presented. Thanks.

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C4034

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C4035