Referee # 1 (Dr. Bonn)

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 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.

There is no chance that a significant portion of the SOA mass consists of radicals; however "radical accretion reactions" or "reactive uptake" of gas-phase radicals is proposed as an alternative to gas-phase formation of stable products that subsequently condense. The experiments themselves simply reflect the relative propensity for SOA production from two sequences of molecules, each characterized by a common precursor saturation concentration. Thus, if reactive uptake of radicals were a significant contributor to the SOA formation, and if it differed in importance for the various compounds in each sequence, then indeed it could contribute to the differences in observed SOA mass yields. While the evidence suggests that this is not likely, the point is well taken that it should be explored.

The organic radicals formed in our experiments are: alkyl, alkoxy, peroxyl and acyl-oxy (Atkinson and Arey, 2003; Atkinson, 2000). All of them have extremely short chemical lifetimes (Sander, 2006) compared with the experimental condensational sink. The longest lived organic radicals are peroxyl radicals. However, due to the high NO_x *levels in our experiments (in the order of 1 ppm) the chemical lifetime of the peroxyl radicals is also short when compared to diffusion as a condensational sink (Seinfeld and Pandis, 2006, 2nd. Ed.). Consequently, none of the radicals will contribute to SOA. Under atmospheric conditions of low* NO_x*; however, peroxyl radicals could diffuse to the condensed phase before reacting with NO. That was not the case in any of our experiments.*

In the atmosphere the condensational sink is typically 1-10/hr, making the collisional lifetime for gas-phase species roughly 300-3000 s, if the accommodation coefficient is unity, and correspondingly longer for lower accommodation coefficients. Peroxyl radicals in the atmosphere would need to have nearly unit accommodation coefficients to be substantially affected by reactive uptake, and further to influence

organic aerosol formation, the resulting reaction products would need to be significantly different from the gas-phase products to alter the product volatility distribution. While this pathway cannot be completely ruled out in our experiments, we do not believe there is much evidence to support it either.
A statement to this regard will be added in the manuscript that peroxyl radicals do not have sufficient time to diffuse to the aerosol phase in the experiments since they were run under high NO_x*; however, under low* NO_x *conditions diffusion to the condensed phase is possible.*

- 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.

It is certainly true that the data presented here reflect the combined efficiency of SOA formation from the selected precursors in the presence of both HONO and UV near 360 nm. We have not observed losses of aldehydes under UV illumination in our chambers, and the SOA formation generally follows the intensity of OH production (~10^7 *molecules* cm^{-3} *in the first hour, a factor of 5-10 lower thereafter). After the initial formation period, the median particle diameters in the experiment remain constant, suggesting that chemical evolution has slowed to near zero and also that the SOA particles have reached a thermodynamic phase equilibrium.*

- Please name the SMPS type used. Does it cover the whole aerosol size range (LDMA?) or is the upper edge cutted off?

We did state (S2, p 13699, l 13-14) that the SMPS is a TSI 3936, 15 - 700 nm Dp. The upper section of the size distribution was not cut off. All of the particles in the different experiments fit in the range mentioned. Consequently, we don't think we need to state that all of our particles fit in the mentioned range.

We will be more specific about the SMPS type by stating: SMPS, TSI classifier model 3080, CPC model 3772 or 3010, 15 - 700 nm Dp.

- Atmospheric aerosols consist by around 50

This question and/or comment seem to be incomplete, and consequently we can't expand.

- 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?

To clarify, we worked with n-heptadecanal and n-nonadecane, not with "nonadecanal". However, fragmentation is one of several issues we confront when selecting target ions to follow the precursor concentrations. Selectivity and signal strength are others. n-Nonadecane fragments significantly, giving the best (but not overly selective) signals at m/z 43 and/or 57 (Jobson et al., 2005), which we used for this work. The aldehydes give good signal at MW + 1 with minimal fragmentation (Chacon-Madrid et al., 2010). However, a large aldehyde such as n-heptadecanal might start resembling an alkane, making dissociation a likely path. We could not detect the MW + 1 of n-heptadecanal in multiple trials. This is explained in section 2.3 of the main manuscript.

We don't believe the inlet temperature (80° C), while it can promote fragmentation, to be the main reason we couldn´t see n-heptadecanal.

- 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?

A simple back of the envelope calculation confirms that methanol reactions are not a concern. We work with methanol concentrations lower than the precursors themselves, and the rate constant for methanol + OH radical is significantly lower than any of the precursors we worked with (by more than one order of magnitude). Thus the rate of the methanol + OH reaction is at most a few percent of the overall reaction rate of the SOA formation process.

We will add a statement clarifying that the initial concentrations of methanol were always lower than those of the precursors themselves in all the experiments.

- 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?

As we showed on this work, even a C_{17} *n-aldehyde appears to be affected by fragmentation paths through the aldehydic moiety. However, it is reasonable to think that the chemistry of a sufficiently large carbon number aldehyde (we believe longer than a* C_{17}*) might resemble the chemistry of comparably large carbon number alkane. Our experiments have not reached that limit.*

We do not propose that chemical activation (and thus excess reaction energy) is the principal cause of fragmentation. This does occur in reactions of light alkenes, especially after substituted peroxyl radicals react with NO to form an excited substituted alkoxy radical (for example, propene and perflouropropene oxidation). For all of these molecules with carbon numbers well over 6, chemical activation should be minimal, and fragmentation should result from thermal decomposition of C-C bonds that are weakened by surrounding substituent groups, not chemical activation. Thus, energy distribution is not thought to be an issue.

This topic is discussed in detailed in section 4.4 in the main manuscript. The main point made in the section is that an alkoxy radical formed in the backbone of a long aldehyde (C_{17}*) will prefer reacting with the aldehydic hydrogen. Reacting with the aldehydic hydrogen will promote fragmentation.*

Good ideas and results are presented. Thanks.

Thank you for your remarks and comments!

References to Support Answers:

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