

Loza et al. report alkane SOA yields under low- and high-NO_x conditions. The authors use four C₁₂ alkanes spanning a range of molecular structures to investigate the role of alkane structure on SOA yield. The authors report the following results:

1. SOA yields increase with extent of cyclization in the alkane precursor, and decrease with extent of branching (similar to previous studies)
2. Yields are higher under high-NO_x than low-NO_x conditions for dodecane and cyclododecane SOA, whereas there are no systematic NO_x-dependent trends for 2-methylundecane and hexylcyclohexane SOA.
3. SOA yield was better correlated with the number of SVOC-particle collisions than the mass of SOA formed (ΔM_o), but the OA loading had a strong influence on the average carbon oxidation state. SOA yield was also correlated with the fraction of AMS organic 'C_xH_y' ion signals containing 9 or more carbon atoms.

In my opinion, this manuscript addresses an important issue regarding the relative influences of precursor structure and NO_x levels on SOA yields. I recommend the manuscript for publication in ACP after my comments are considered in the context of a revised manuscript:

1. I suggest incorporation of time-dependent AMS ion signals (C_xH_y⁺, C_xH_yO⁺, and C_xH_yO₂⁺) as a function of OH exposure into the manuscript. This would supplement the time series of SOA yields shown in Figures 4-5. Depending on the precursor and experiment conditions, the yields either increase continuously, increase and then level off, or increase and then decrease, and the specific patterns seem vary by experiment, even for the same precursor and NO_x regime (e.g. 'ML1' vs 'ML3' in Figures 4-5). The reason(s) for this variability aren't clear at present, but presumably they are somehow related to variations in the detailed SOA chemical composition between experiments.

2. It would be useful to compare yields of gas-phase fragmentation products (e.g. abundances of CIMS C_nH_{2n}O₂ and C_nH_{2n}O₃ "families") under low- and high-NO_x conditions. In the abstract, the authors claim that gas-phase fragmentation is more prevalent under high-NO_x conditions. Wouldn't CIMS data obtained under both NO_x regimes be the ideal way to show this? As far as I can tell the only conclusion drawn from CIMS data is that fragmentation is less significant for cyclodecane SOA than for the other systems under high-NO_x conditions (Figure 10) -- there are no clear trends with respect to structure or yield for the other three precursors. While this is an interesting result, the relevance and scope of the CIMS measurements would be improved if they can be related to the apparent NO_x-dependent fragmentation trends. Presumably relative yields of these ions can be obtained from the low-NO_x alkane oxidation experiments referenced in Yee et al. (2012, 2013)?

3. The authors state: "In the present study, an increase in yield is characterized by larger mass fractions of ions containing 9 or more carbon atoms." (p. 20697, lines 11-12) This could be demonstrated graphically, for example by plotting SOA yields as a function of the relative "familyCH" ion abundance obtained from AMS measurements. How good is the correlation, and is it internally consistent across the low- and high-NO_x regimes? For

example, do systems with higher SOA yields under high-NO_x conditions also have higher mass fractions of >C₉ ions under high-NO_x conditions relative to low-NO_x conditions for the same precursor?

4. The AMS C_xH_yO₂⁺ ion family is mentioned briefly, but as far as I can tell the data are never presented or discussed. Presumably the abundance of this ion family is also related to the extent of fragmentation. I think this should be incorporated into discussion of the AMS family(CH) and family(CHO1) trends (Figures 8-9, Sections 3.5 and 3.6).

5. page 20678, line 7 (Abstract): The text implies that wall-loss-corrected SOA yields have two orders of magnitude uncertainty, but Figure 2 suggests that the uncertainty is about a factor of two. Please clarify this apparent discrepancy.

6. page 20680, lines 27-28: “Different light intensities were used for low- and high-NO_x experiments.” What was the reason for using different light intensities? Did the authors perform any sort of control experiment (e.g. running high-NO_x experiments at jNO₂ ~ 4×10⁻³ s⁻¹) to determine the effect of varying UV intensity by ~50%? This could affect the yields of oxidation products that photodissociate.

7. page 20682, lines 20-29: I think the organic CO⁺, H₂O⁺, OH⁺, and O⁺ ions should be included in the AMS C_xH_yO₂⁺ ion family for the analysis presented in Section 3.5 because they are constrained by the organic CO₂⁺ ion signal. In the current manuscript it is not clear whether this is the case. If these ions were included, this should be stated; if not, I suggest redoing the analysis with this classification to more accurately reflect their association with CO₂⁺ (and C_xH_yO₂⁺) signals.

8. page 20686, end of Section 2.2: I think it would be better to just summarize Section 3.4 here, since Section 3.4 seems out of place in the current manuscript: it describes control experiments that are important but not directly referenced in any of the results.

9. page 20687, lines 8-26: This paragraph is a confusing. There is a detailed explanation of the large spread in hexylcyclohexane and cyclododecane SOA yield values at Δ(HC) < 100 μg/m³. However, the spread in dodecane SOA yield values seems to be even larger than hexylcyclohexane (e.g. Figure 2a) despite the claim that “Less overall SOA growth is observed for dodecane [...]; as a result, less difference is observed between the lower and upper limit yields.”

10. page 20687-20688, lines 27-20: Details of these calculations could be moved to the Appendix.

11. page 20688, line 7: The authors assume unit density here, yet they measured an effective SOA density ρ ~1.3 g cm⁻³ (Table 1). Shouldn't ρ~1.3 g cm⁻³ also be used for this comparison?

12. page 20691-20692, lines 26-12: Details of the KM-GAP model could be moved to the Appendix.

13. page 20692, lines 15-17: “The SOA yields from both experiments trend similarly with C_{sum} . This result indicates that analysis of chamber experiments with kinetic-flux modeling is instructive and that parameterizing SOA yields simply as a function of ΔM_{O} may not always be suitable.”

This statement could use clarification because there are still significant differences between the DL1 and DL2 parameterizations shown in Figure 6. For example, at 10^{14} SVOC-particle collisions, the yield corresponding to DL1 is ~ 0.04 and the yield corresponding to DL2 is ~ 0.08 . What level of quantitative agreement makes the analysis “instructive” versus “not suitable”?

How general is this statement? Are the authors suggesting that kinetic-flux modeling is appropriate for SOA systems, or specifically for alkane SOA, and why? This could be discussed in Conclusions.

Also, see comment #19 about Figure 6 below: the current analysis compares the assumption of quasi-equilibrium growth for high- NO_x dodecane SOA to the assumption of kinetically-limited growth for low- NO_x dodecane SOA. This should be fixed - the same system should be modeled in both cases.

14. page 20693, line 16: typo – should “sorbed” be “adsorbed”?

15. page 20697, lines 11-12: The authors state: “In the present study, an increase in yield is characterized by larger mass fractions of ions containing 9 or more carbon atoms.” It is not clear to me why C9 is chosen as the benchmark carbon number, because Figures 8-9 suggest that the trends observed for AMS “familyCH” C9-C12 ions are basically the same for C4-C8 ions as well.

16. page 20697, lines 16-17: The authors state: “...compounds with a larger mass fraction of family CH ions have smaller mass fractions of family CHO1 ions.” This statement seems self-evident, it could probably be deleted.

17. page 20699, lines 11-13: The authors state: “Under high- NO_x conditions, SOA yields for dodecane and cyclododecane are larger for lower initial alkane concentration.”

In the case of cyclododecane SOA, this appears to be true from Figure 5d, but in Figure 4d, at a specific OH exposure, the yield for ‘CH2’ (initial cyclododecane concentration of 61 ppb) is similar to, or higher than, the corresponding yield for ‘CH1’ (initial cyclododecane concentration of 8.5 ppb). It seems to me that this trend is inconclusive based on the uncertainty in the wall loss correction. I suggest revising this statement and the accompanying discussion.

18. Figure 3: It would be easier to see the data at low loadings if the Presto et al. (2010) and Tkacik et al. (2012) trendlines are placed behind the data from the present work.

19. Figure 6, and related discussion: The authors motivate the KM-GAP analysis from

the range of SOA yields at a specific ΔM_o for SOA produced from dodecane and methylcyclohexane under high- NO_x conditions (Figure 3, DH1-DH3 and MH1-MH2). Why, then, does Figure 6 show the modeling of a different system (low- NO_x dodecane SOA, DL1-DL2)? It would be more appropriate to evaluate the assumptions regarding treating SOA growth as “quasi-equilibrium” versus “kinetically limited” by instead modeling the DH1-DH3 and/or MH1-MH2 experiments.

20. Figure 7: Since the authors state that carbon oxidation state is correlated with the SOA loading, it could be useful to underscore this point by coloring the markers in this figure by OA concentration.

21. Figures 8-9: The AMS $\text{C}_x\text{H}_y\text{O}_2^+$ ion family should be presented and discussed. What is the reason for segregating ion signals above and below C9? Also, why did the authors use a 30-min average of the AMS data presented in Figure 8, compared to a 60-min average of the data presented in Figure 9?