Interactive comment on "Secondary organic aerosol yields of 12-carbon alkanes" *by* C. L. Loza et al.

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The authors thank the referee for the helpful comments. Referee comments and responses are listed below.

Loza et al. report alkane SOA yields under low- and high-NO_x conditions. The authors use four C_{12} 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 '$C_x H_y$' 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:

Comment 1

I suggest incorporation of time-dependent AMS ion signals ($C_x H_y^+$, $C_x H_y O^+$, and $C_x H_y O_2^+$) 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 to 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.

Response 1

Displaying the time-dependent AMS ion signals for ions $C_x H_y^+$, $C_x H_y O^+$, and $C_x H_y O_2^+$ as a function of OH exposure is misleading because wall loss affects the ion signals in addition to condensation and particle-phase reactions. Instead, we looked at the

mass fractions of ions $C_xH_y^+$, $C_xH_yO^+$, and $C_xH_yO_2^+$ to the total AMS organic mass as a function of OH exposure. The trends of the three ion fractions were similar to those observed for average carbon oxidation state ($\overline{OS}_C$), which are displayed for cyclododecane experiments in Figure 7. We also looked at SOA yield as a function of each of ion fractions of $C_xH_y^+$, $C_xH_yO^+$, and $C_xH_yO_2^+$ and of average carbon $\overline{OS}_C$ and did not see any trends relating particle chemical composition to specific variations in the SOA yield. It is likely that these variations are linked to changes in chemical composition, and it may be possible to determine the relationship between aerosol chemical composition and yield through a more in-depth analysis of AMS data (i.e., positive matrix factorization), but such analysis is beyond the scope of the present work.

Comment 2

It would be useful to compare yields of gas-phase fragmentation products (e.g. abundances of CIMS $C_nH_{2n}O_2$ and $C_nH_{2n}O_3$ "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 NOx 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)?

Response 2

We agree that presenting low-NO_x CIMS data would support our conclusion that gas-phase fragmentation is more prevalent under high-NO_x. Of all the low-NO_x experiments

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presented in the present work, the CIMS only sampled during Experiments ML2 (29 ppbv methylundecane), DL2 (34 ppbv dodecane), HL1 (16 ppbv hexylcyclohexane), and CL2 (10 ppbv cyclododecane). For hexylcyclohexane and cyclododecane, the initial alkane concentration was low enough that fragmentation product concentrations could have been too low to be detected by the CIMS. For this reason, we chose not to present fragmentation product yields obtained by the CIMS under low-NO_x conditions.

Comment 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?

Response 3

The correlations between SOA yield and mass fraction of Family CH ions containing 9-12 carbons, described by Pearson's correlation coefficients, have been added to the supplementary material as Table S4. Positive correlations are observed for all carbon numbers under both high- and low-NO_x conditions. When comparing yields observed under high- and low-NO_x conditions for each compound, the mass fraction of Family CH ions with 9-12 carbons is smaller under high-NO_x conditions than under low-NO_x conditions. This can be observed by comparing the data for each compound between Figures 8 and 9. We do not feel that an additional figure is necessary to describe the correlations.

Comment 4

The AMS $C_xH_yO_2^+$ 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).

Response 4

Trends were observed for the $C_xH_yO_2^+$ ion family as a whole, as described in Section 3.5. When the ions in that family were grouped by carbon number, no trends were observed between ion mass fraction and parent alkane identity. For that reason, ions in the $C_xH_yO_2^+$ family are not presented or discussed with family CH and family CHO1 ions in Section 3.6.

Comment 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.

Response 5

The figures are correct. The abstract has been changed to read, "SOA yields differed by a factor of 2 between the two limiting cases."

Comment 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 $j_{NO_2} \sim$ 4×10^{-3} s^{-1}) to determine the effect of varying UV intensity by $\sim$ 50%? This could affect the yields of oxidation products that photodissociate.

Response 6

The light intensities were dictated by the chamber characteristics and experiment time constraints. A higher UV intensity was selected for the high-NO_x experiments to decrease the experiment duration. A high-NO_x experiment was not conducted at lower UV intensity to act as a control. During alkane photooxidation under high-NO_x conditions, the most likely species to undergo photolysis are orgonitrates. Organonitrates will also react with OH. Competition between the two organonitrate sinks can be addressed by a photochemical model. Using recommended rate data from the Master Chemical Mechanism (http://mcm.leeds.ac.uk/MCM), organonitrate photolysis would be competitive with OH reaction at an OH concentration of 8×10^4 molec. cm^{-3} for the high-NO_x experiments described in the present work ($j_{NO_2} = 6 \times 10^{-3}$ s^{-1}). The observed OH concentration in any of the reported high-NO_x experiments was at least 1×10^6 molec. cm^{-3}, and OH is the dominant organonitrate sink. If the same simulation is run with a UV intensity corresponding to $j_{NO_2} = 4 \times 10^{-3}$ s^{-1}, photolysis and OH reaction would be competitive at an OH concentration of 5×10^4 molec. cm^{-3}. The lowest OH concentration observed in the simulation was 2×10^6 molec. cm^{-3}. Based on the simulation results, photolysis is not expected to be a dominant process at either UV intensity. We do not think it is necessary to make changes to the manuscript in response to Comment 6.

Comment 7

page 20682, lines 20-29: I think the organic CO^+, H_2O^+, OH^+, and O^+ ions should be included in the AMS $C_xH_yO_2^+$ ion family for the analysis presented in Section 3.5 because they are constrained by the organic CO_2^+ 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 CO_2^+ (and $C_xH_yO_2^+$) signals.

Response 7

Organic ions CO^+, H_2O^+, HO^+, and O^+ were not included in the AMS $C_xH_yO_2^+$ family. The data were analyzed again with H_2O^+, OH^+, and O^+ included in the $C_xH_yO_2^+$ family; however, these changes did not affect any of the results presented in the manuscript. The following sentence was added to section 3.4 regarding ions H_2O^+, HO^+, and O^+, "Note that for both NO_x conditions, the ions O^+, HO^+ and H_2O^+ are included in the mass fraction of $C_xH_yO_2^+$ ions because concentrations of these ions are calculated from that of CO_2^+."

Although V-mode CO^+ ion intensities were estimated from the V-mode CO_2^+, they were not included in the $C_xH_yO_2^+$ because the relationship between CO^+ and CO_2^+ was confirmed for most experiments from W-mode data for both ions.

Comment 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.

Response 8

The data presented in Section 3.4 are results and are not appropriate for presentation under the Materials and methods section. Instead, Section 3.4 has been moved to Appendix B so that the content remains in the manuscript but does not interrupt the flow of the SOA yield discussion.

Comment 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 $\Delta HC < 100$ g/m^3. However, the spread in dodecane SOA yield values seems to be even larger than hexycyclohexane (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."

Response 9

This paragraph is discussing the difference in spread between yields at high and low ΔHC for each hydrocarbon, not amongst the hydrocarbons. The following sentence has been added before the last sentence of the paragraph to clarify the comparison, "The difference between upper and lower limit yields for dodecane and 2-methylundecane is similar for all ΔHC."

Comment 10

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

Response 10

The calculations described in this paragraph (estimating maximum potential SOA mass from AMS elemental ratios) are not directly related to those described in Appendix A (calculating upper and lower limit yields from DMA particle number size distributions). We think that it is best to leave the calculations in their present location.

Comment 11

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page 20688, line 7: The authors assume unit density here, yet they measured an effective SOA density $\rho \sim 1.3$ g cm^{-3} (Table 1). Shouldn't $\rho \sim 1.3$ g cm^{-3} also be used for this comparison?

Response 11

The data to which we are comparing were calculated using unit density, an assumption that is made by the authors of those studies and not confirmed with experimental data. All studies used a SMPS to measure aerosol volume, which was then converted to mass by multiplying the volume by a density. For this specific comparison, to remove any bias in using non-unit density to convert SOA volume to mass, we applied the same assumptions to our data that were applied to the data of Presto et al. (2010) and Tkacik et al. (2012).

Comment 12

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

Response 12

Calculation details have been moved to Appendix C.

Comment 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 be-

tween 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.

Response 13

The last sentence of the paragraph has been changed to read, "This result indicates that analysis of chamber experiments for any SOA system with kinetic-flux modeling is instructive and provides an alternative to parameterizing SOA yields as a function of ΔM_o." With this wording, we suggest that authors of future studies should consider that SOA growth can be quasi-equilibrium or kinetically limited and show how a model can be used to the evaluate the latter assumption.

The KM-GAP model can be used to evaluate any SOA system. We have now made this point clear in Section 3.3 and do not think that we need to reiterate this point in the Conclusions section.

Comment 14

page 20693, line 16: typo – should "sorbed" be "adsorbed"?

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Response 14

We prefer to use the more general term "sorbed" so as not to suggest a specific sorption mechanism.

Comment 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.

Response 15

While the same trends are observed for C4-C12 ions in the CH family, the trend does not begin until C9 ions for the CHO1 family. C9 is chosen as a benchmark because it is the lowest carbon number for which the trends begin for both ion families for the SOA in the present study. The sentence has been changed to read, "In the present study, an increase in yield is characterized by larger mass fractions of ions containing 9 or more carbon atoms for both families CH and CHO1."

Comment 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.

Response 16

This statement would be self-evident if there were only 2 families to which ions belong.

There are more than 2 families in which to group ions. We prefer to leave this statement in the manuscript.

Comment 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.

Response 17

This trend pertains to the yield after which 95-100 % of the initial alkane had reacted, which occurs at the point of greatest OH exposure in each experiment. This trend is also apparent in the data presented in Figure 2. The manuscript has been changed to read, "Under high-NO_x conditions, SOA yields at 95-100 % of the initial hydrocarbon reacted, i.e., the yield at the largest OH exposure for each experiment, for dodecane and cyclododecane are larger for lower initial alkane concentration."

Comment 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.

Response 18

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Figure 3 has been updated accordingly.

Comment 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 methyl-cyclohexane 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.

Response 19

The low-NO_x KM-GAP model output data for dodecane are as appropriate as data for high-NO_x dodecane and 2-methylundecane to evaluate the assumptions of kinetically limited or quasi-equilibrium SOA growth. Although the discussion was motivated by findings from high-NO_x SOA growth, the discussion is intended to be general enough to apply to any hydrocarbon system.

Comment 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.

Response 20

We re-plotted the data coloring the marker by SOA mass concentration and found that the coloring made the markers for different experiments more difficult to distinguish

from one another. The original plot has been kept in the manuscript.

Comment 21

Figures 8-9: The AMS $C_xH_yO_2^+$ 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?

Response 21

Please see the response to Comment 4 regarding discussion of the AMS $C_xH_yO_2^+$ ion family. In the figure, the mass fractions for C9-C12 ions were multiplied by a factor of 20 to make the mass fractions more visible on the same scale used for the rest of the ions. Figures 8 and 9 have been modified to show mass fractions for C8-12 multiplied by a factor of 20. Now in Figure 8, it is clear that for ions in family CHO1, there is a difference in trend for ions with 9 or more carbon atoms.

The duration of high-NO_x experiments was half that of low-NO_x, and changes to gas and aerosol concentrations changed more quickly in high-NO_x experiments.. The same 2:1 time period relationship was applied to the averaging periods for the experiments; therefore, the data in Figure 8 from high-NO_x experiments were averaged over 30 min, whereas the data in Figure 9 from low-NO_x experiments were averaged over 60 min.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 20677, 2013.

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