

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

C. L. Loza et al.

clloza@gmail.com

Received and published: 13 December 2013

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

General comments:

Loza et al. present measurements of SOA yield from the photo-oxidation of four aliphatic hydrocarbons, each containing 12 carbon atoms per molecule (dodecane, cyclododecane, hexyl cyclohexane, and methylundecane). The paper is the most recent in a series of papers from CalTech investigating SOA formation, organic aerosol dynamics, and gas-phase chemical mechanisms from the oxidation of C12 aliphatic

C9962

hydrocarbons.

Overall the measurements presented in the paper are appropriate for Atmospheric Chemistry & Physics, and the interpretation of the results is sound. The data are of high quality and contribute to the community's knowledge of both the studied chemical systems and methods for performing smog chamber experiments. However, there is room for improvement in the manuscript. While I suggest publication after minor revision, I hope that the authors will consider the following comments to make the manuscript more readable and hopefully more impactful.

My primary criticism of the manuscript is that some of the key findings are buried in the text, rather than strongly stated and put on display. The primary deliverable of the paper are SOA yields, but along the way the authors raise several interesting observations that can improve future smog chamber experiments. These should be stated more clearly and given focus as outcomes of this work, rather than as links tying this paper to the recent works by Yee et al and Shiraiwa et al on the same chemical system.

For example, the experiments presented in this paper make a strong case for using models such as APE and KM-GAP to interpret chamber data. It should be stated explicitly that future smog chamber studies need to consider such modeling tools, because in many cases, these models are not used. If the authors had relied on “traditional” analysis of the data (i.e., without KM-GAP), the yields obtained with different initial VOC concentrations would be nearly impossible to interpret.

Other comments:

Comment 1

Use consistent jargon for high-NO_x/low-NO_x. The abstract notes that experiments were conducted in conditions where RO₂ react with NO or HO₂ - make it explicit that this is your definition for high-NO_x and low-NO_x, and consider using “NO-dominant” and “HO₂-dominant” in place of high- and low-NO_x.

C9963

Response 1

We prefer to use "high- NO_x " and "low- NO_x " because these terms are common in the literature. To clarify the definitions of high- and low- NO_x conditions in the manuscript, the first sentence of the abstract has been rewritten as "Secondary organic aerosol (SOA) yields were measured for cyclododecane, hexylcyclohexane, *n*-dodecane, and 2-methylundecane under high- NO_x conditions, in which alkyl proxy radicals (RO_2) react primarily with NO , and under low- NO_x conditions, in which RO_2 reacts primarily with HO_2 ." To reiterate the definitions of high- and low- NO_x , the first sentences of the second and third paragraphs in the Introduction have been rewritten as "SOA formation under high- NO_x conditions, in which alkyl proxy radicals (RO_2) react primarily with NO , has received much attention." and "SOA formation under low- NO_x conditions, in which RO_2 reacts primarily with HO_2 , has received less attention."

Comment 2 Page 20680, Line 27-28 - The light intensities for high- and low- NO_x experiments differ by 50%. How might this affect SOA yields? Especially under low- NO_x conditions there may be the formation of peroxides could therefore photolyze.

Response 2

Please see the response to Comment 6 from Reviewer 1.

Comment 3

The discussion of dihydrofuran lifetime versus the different oxidants (O_3 , OH , NO_3) is confusing. Are you arguing that the experiments have an atmospherically relevant mix of losses for the dihydrofurans? Also, you begin this discussion by claiming that O_3 does not affect SOA yields, which immediately prompts questions about the role of dihydrofurans, and then move into the discussion of relative lifetimes in an indirect fashion.

C9964

Response 3

We claim that the variance in O_3 concentrations observed in the present experiments is not expected to affect SOA yields, but we do not claim that O_3 concentration is not expected to affect SOA yields. The paragraph on page 20684 has been rewritten as,

"Three oxidants, OH , O_3 , and NO_3 , were produced under high- NO_x conditions. All oxidant concentrations varied over the course of the experiment due to the continuous addition of NO . While O_3 is not expected to react with most alkane photooxidation products, it can react with dihydrofurans, which also react with OH and NO_3 . Jordan et al. (2008) estimated C_{12} dihydrofuran + OH rate constants as approximately $2.4 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. The rate constants for C_{12} dihydrofuran + O_3 and C_{12} dihydrofuran + NO_3 were taken as 3.49×10^{-15} and $1.68 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, respectively, as measured for 4,5-dihydro-2-methylfuran by Martin et al. (2002). Using measured O_3 concentrations and OH concentrations calculated from the alkane concentration decay, the lifetime of dihydrofuran against reaction with O_3 was calculated to be an order of magnitude less than the lifetime against reaction with OH for OH exposures $> 5 \times 10^6 \text{ molec cm}^{-3} \text{ h}$ (elapsed time $> 2 \text{ h}$). At lower OH exposures, reaction of dihydrofurans with OH were expected to dominate over that with O_3 . NO_3 concentration was not measured during the experiments; instead, it was estimated from a photochemical model. The modeled NO_3 concentration varied by 3 orders of magnitude as O_3 , NO_x , and OH concentrations changed during the modeled experiment as a result of continuous NO addition. For the highest estimated NO_3 concentrations ($1 \times 10^7 \text{ molec cm}^{-3}$), the lifetime of dihydrofuran against reaction with NO_3 was comparable to that of reaction with O_3 , and at the lowest estimated concentrations, the lifetime was an order of magnitude larger than that of reaction with OH . In an urban area such as Mexico City with peak OH , O_3 , and NO_3 (daytime) concentrations of 4.6×10^6 , $(0.74\text{--}2.0) \times 10^{12}$, and $2.4 \times 10^7 \text{ molec cm}^{-3}$, respectively (Molina et al., 2010; Stephens et al., 2008; Volkamer et al., 2010), the estimated lifetimes of dihydrofuran against reaction with these compounds are 15 min, 2.4–6.4 min, and 4.1 min, respectively. The

C9965

conditions in the present experiments produce atmospherically relevant ratios of dihydrofuran sinks. Additionally, NO_3 is not a significant sink of either the parent alkane or RO_2 radicals even at the largest estimated NO_3 concentration."

Comment 4

The data averaging in Fig 1 is odd – the points seem to show averages of every hour. Continuous lines might be a better way to present the data.

Response 4

Most of the data presented in Figure 1 come from instruments with a time resolution of 1-2 min. Over an 18 h experiment, hundreds of data points are recorded. The data are presented as hourly averages because trends progressed slowly, and displaying average data represents the trends well without requiring an excessive number of data points. Presenting the data as continuous lines implies that the data follow a known functional relationship. We do not know the functions that govern the data presented; therefore, we do not wish to display the data as lines.

Comment 5

Fig 3 is a little inaccessible, primarily because of the experiment labels (e.g., DH1) require referring back to the tables. This is repeated in subsequent figures. Readability would improve if the name of the VOC was printed instead of the experiment code.

Response 5

For Figure 3, "Dod:" and "Mud:" have been added to the figure legend before the experiment numbers to help the reader determine the hydrocarbon for each experiment. In Figures 4-6, the hydrocarbon is identified in the figure in addition to the experiment

C9966

number. In Figure 7, the hydrocarbon is identified in the figure caption. In Figures 8-10, the hydrocarbon is now used in the legend and the specific experiment number is given in the figure caption.

Comment 6

I am not completely clear on what I am supposed to learn from Figures 4 and 5. Figure 2 shows the spread in SOA yield differences between the high and low case, so replotting them here could be viewed as redundant. Is the ordering – e.g., compound A > compound B – dependent on the wall loss correction method?

Response 6

We agree with the reviewer that Figures 4 and 5 are not necessary in addition to Figure 2. Figures 4 and 5 and references to these figures have been removed from the manuscript. The first paragraph of Section 3.3 has been placed before the first paragraph of Section 3.5. Section 3.3 has been renamed SOA growth parameterization.

Comment 7

Section 3.4 - it seems that uncertainty in vapor wall losses are already considered as part of the upper limit SOA yield, so this section seems superfluous.

Response 7

For vapor wall losses, losses to deposited particles must be considered separately from losses to the walls themselves. The deposited particle surface area represents only a fraction of the total wall surface area, and vapors could be taken up by walls and deposited particles differently.

C9967

Comment 8

How much can we learn from the C# fragments in the AMS for Figures 8 and 9? The AMS heater and EI impart much of the fragmentation in that instrument, so it's not clear that slight changes in C2 versus C3 fragments are terribly meaningful. There is a fundamental difference between the C# analysis with AMS and with the CIMS, though this is not noted. The CIMS (more-or-less) preserves carbon number, and therefore provides somewhat different information in these plots than the AMS.

Response 8

Figures 8 and 9 show that while the AMS heater and EI fragment most of the species that enter the instrument, a larger carbon backbone is retained in some fragments. The discussion of Figures 8 and 9 focuses on ions with 9 or more carbon atoms and not those with 2 or 3 carbon atoms. To clarify differences between C# analysis with the CIMS and AMS, the following sentence has been added on page 20698 at line 11, "For the CIMS ions presented here, the carbon chain is preserved as ionization occurs, whereas heating and ionization in the AMS tends to break the carbon chain, and the ions presented in Figs. 6 and 7 could come from longer-chain parent molecules."

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

C9968