Response to reviewers for "Role of ozone in SOA formation from alkane photooxidation" by X. Zhang et al.

We thank reviewer # 3 for the constructive comments. Our specific responses can be found below, with reviewer comments in black and our responses in blue.

Response to Referee # 3

Review of "Role of ozone in SOA formation from alkane photooxidation" by X. Zhang, R. Schwantes, M. Coggon, C. Loza, K. Schilling, R. Flagan, and J. Seinfeld [acp-2013- 660].

This paper presents an investigation of the SOA formation from large n-alkanes, focusing on the competition between OH and O3 on the oxidation of dehydrofurans. The paper uses dodecane as the model system. The paper presents experimental data measured in a smog chamber under high and low NOx conditions at different relative humidity (RH). The paper extends existing SOA mechanisms to account for ozonolysis of dihydrofurans. Their analysis suggests that ozonylsis will be the dominant fate of dihydrofurans in most environments. This reduces SOA yields but creates more oxygenated organic aerosol. This is an important effect that should be accounted for in models (and experiments). The paper is interesting and well written. The experiments were well done and the model development appears to be well grounded in the existing literature. Large alkanes are likely an important source SOA in urban environments, but there are gaps in our understanding of the underlying chemistry (especially with respect to SOA formation). This paper attacks an interesting gap – the potential role of ozonolysis on SOA formation from alkanes. I recommend that the paper be published after addressing the following comments.

Model evaluation – A strength of the paper is the combination of the measurements and model development. However, these pieces are not well integrated. It is almost as if there are two separate papers. There is only one figure (Figure 10) in which the model is compared with the data. Two parameters are compared – the decay of dodecane and the production of SOA. The fact that the model reproduces the measured decay of dodecane is no surprise – the data were fit to determine the OH concentration. The good agreement with the SOA formation is potentially more interesting. The agreement is excellent; presumably this is because the model has been fit to reproduce the measured SOA. What free parameters that were fit to match the data? How unique is the solution?

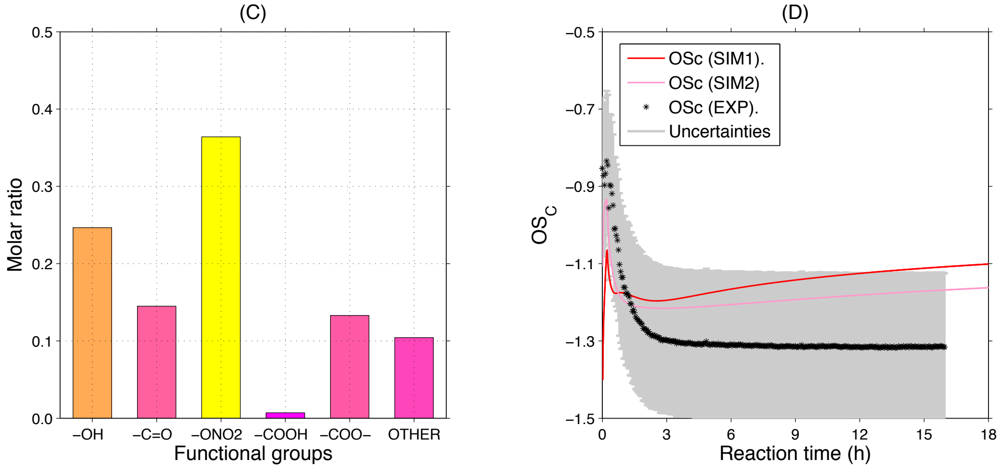
There are no free parameters in this model: 1) The gas-phase reaction rate constants listed in the Supplemental Materials are obtained from Sander et al., 2011; 2) The gas-phase dodecane photooxidation mechanism is developed based on MCM v3.2; 3) The dihydrofuran+O_3/OH reaction mechanism is developed based on Martin et al., 2002; Lim and Ziemann 2005; 2009 a, b, c; and Jordan et al., 2008; and 4) The vapor pressures of all species are estimated by SIMPOL.1 (Pankow and Asher, 2008) at 300 K.

The good agreement in SOA data shown Figure 10 could be interpreted by the reader as "validation" of the proposed mechanism. Is this the correct interpretation? Presumably other models / mechanisms could also reproduce the data. The paper presents lots of Figures with just data (Figure 4, 5, 6, 7, 8, 9) or just model results (Figure 3) but few Figures that compare both (only Figure 10). The paper should compare the model predictions against other measured parameters to test whether or not the proposed mechanism is correct.

We have added the comparison of oxidation state between observations and predictions under dry conditions, see Figure 11. We also tentatively compare the CIMS observed trends for ions listed in Table 2 with the model output under dry conditions, see Figure 10. The discussion given below has been added:

Oxidation state:

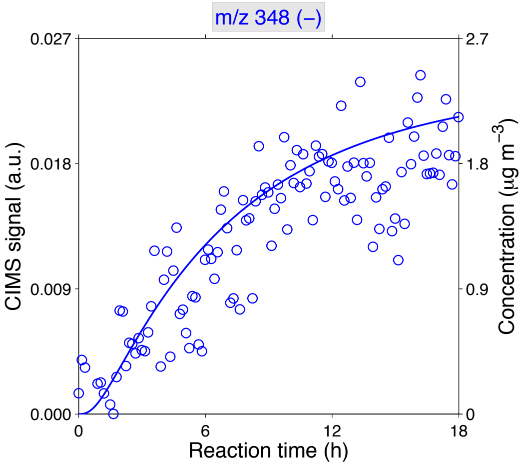
"*The predicted the average carbon oxidation state is ~ 7 – 15% higher than observations. The overprediction is within the uncertainties in the O:C (31%) and H:C (10%) measurement by AMS (Aiken et al., 2008). Incorporation of the substituted dihydrofuran formation and removal pathways in the model leads to an increase in the simulated* OS_C*. Compared with compounds produced from dodecane photooxidation under high-*NO_x *conditions, products from dihydrofuran chemistry tend to have a higher O:C but lower H:C due to the formation of ether, ester, and carboxylic acid functional* *groups. As a result, the calculated average carbon oxidation state is higher in the presence of chemical reactions that accelerate the aerosol aging process.* ”

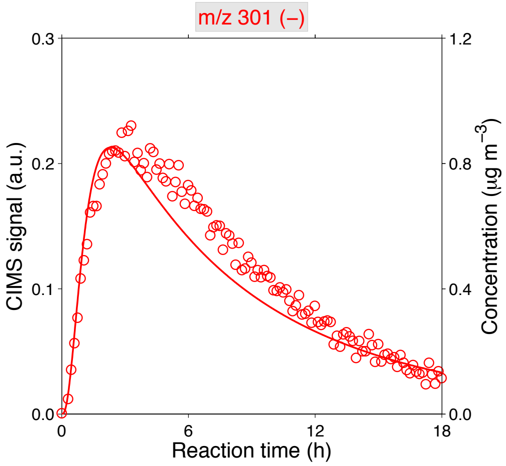


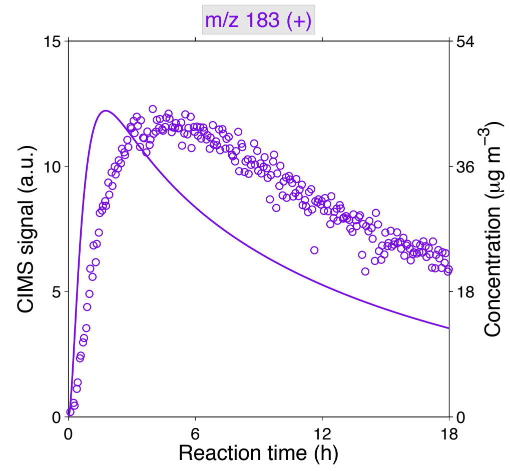
CIMS ions:

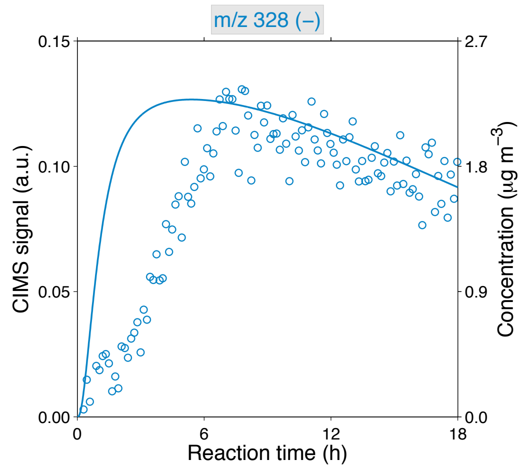
“ *Figure 10 shows the temporal profiles of CIMS measured ions in (+/–) mode, with structures proposed in Table 2, together with the corresponding model predictions under conditions of Exp. #2. In general, four time-dependent growth patterns are observed in experiments, which are also captured by model predictions. “Pattern #1” denotes species with rapid removal pathways, e.g., m/z 301 (–), with a proposed structure of δ-hydroxycarbonyl. In the current mechanism, the overall heterogeneous conversion rate of δ-hydroxycarbonyl to substituted dihydrofuran is taken as* 3×10^{-3} s^{-1}*. The model output is consistent with the observed time-dependent trend when this rate is used. Up to ~ 90% of m/z 301 (–) is consumed due to this rapid heterogeneous reaction pathway at 3% RH after 18 h of photooxidation. “Pattern #2” is indicative of a species that also reacts rapidly, but with a much slower consumption rate than species of “Pattern #1”. Typical example here is m/z 183 (+), which represents the alkyl-substituted dihydrofuran. The reaction rate constants of alkyl-substituted dihydrofuran with either OH or* O_3 *are at least an order of magnitude higher than the generic reaction rate constant for the OH abstraction reaction, which is the dominant gas-phase pathway in the dodecane photooxidation mechanism. The simulated peak occurs ~ 2 h earlier than observations, indicating that the formation rate of alkyl-substitued dihydrofuran might be slower than the decay rate of its precursor δ-hydroxycarbonyl, considering that fact that the acid-*

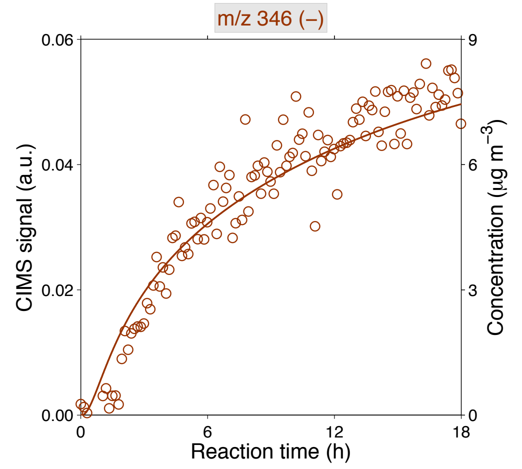
catalyzed dehydration process in the particle phase is the rate-limiting step. The extent to which the formation rate is slower than the decay rate, however, is unknown since the measurement of rate constants for individual steps is infeasible in this study. "Pattern #3" reflects the temporal profiles for a majority of ions here, e.g., m/z 328 (–), 299 (–), 249 (–), 315 (–), and 332 (–). Compounds proposed for the above m/z can be categorized as semi-volatile products. In the gas phase, they undergo functionalization or fragmentation, or partition into the particle phase as the precursors of SOA. Overall, the temporal profiles of species in "Pattern #3" are governed by the progressive photochemistry in the gas phase and gas-particle equilibrium partitioning. "Pattern #4", including m/z 346 (–) and 328 (–) here, represent "nonvolatile" species. Owing to their low volatilities, they will immediately partition to the particle phase once formed and the gas-phase photooxidation becomes negligible, although it might still occur via the OH attack on C-atoms."

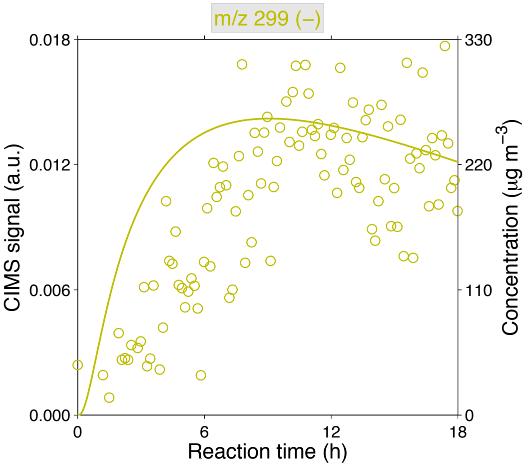


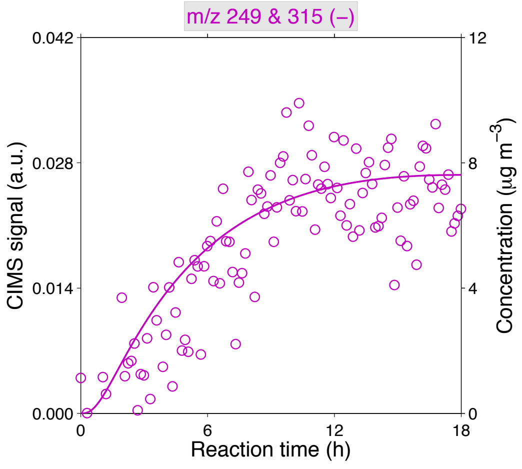


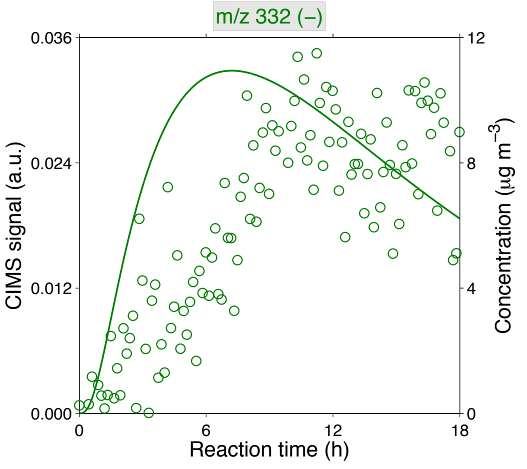

m/z 183 (+)
CIMS signal (a.u.)
0
5
10
15
Concentration (μg m^{-3})
0
18
36
54
Reaction time (h)
0
6
12
18


m/z 328 (–)
CIMS signal (a.u.)
0.00
0.05
0.10
0.15
Concentration (μg m^{-3})
0.0
0.9
1.8
2.7
Reaction time (h)
0
6
12
18


m/z 346 (–)
CIMS signal (a.u.)
0.00
0.02
0.04
0.06
Concentration (μg m^{-3})
0
3
6
9
Reaction time (h)
0
6
12
18


m/z 299 (–)
CIMS signal (a.u.)
0.000
0.006
0.012
0.018
Concentration (μg m^{-3})
0
110
220
330
Reaction time (h)
0
6
12
18


m/z 249 & 315 (–)
CIMS signal (a.u.)
0.000
0.014
0.028
0.042
Concentration (μg m^{-3})
0
4
8
12
Reaction time (h)
0
6
12
18


m/z 332 (–)
CIMS signal (a.u.)
0.000
0.012
0.024
0.036
Concentration (μg m^{-3})
0
4
8
12
Reaction time (h)
0
6
12
18

Role of water / RH – The experiments varied the RH inside the chamber from _3% to _55%. There was relatively little discussion of these results. For example, it appear to slow the decay of C12H23O+ in the AMS. Why was that? I would encourage the authors to add a bit more discussion on the effects of RH to the manuscript. Smog chamber experiments are often done at very low RH. How much affect does RH appear to have on the SOA formation? The effect is directly on the chemistry? Or is it indirect on the partitioning? The experiment did not consider RH greater than 50%, which are very common in the atmosphere. What are the implications of the results if one extrapolates to higher RH?

1) A discussion of the effect of water on the formation and removal of AMS measured ion $C_{12}H_{23}O^{+}$ and CIMS measured ion $C_{12}H_{22}O \cdot H^{+}$ has been added in Section 4.2:

" *Aerosol water content could slow down the formation and removal rate of AMS ion* $C_{12}H_{23}O^{+}$*, mainly because: 1) water could accelerate the hydration rate, thus changing the equilibrium coefficient of the interconversion between cyclic hemiacetal and dihydrofuran; and 2) the addition of water might neutralize the particle-phase acid (e.g.,* HNO_3*) which is thought to catalyze the cyclization of δ-hydroxycarbonyl to cyclic hemiacetal (Lim and Ziemann, 2009 c). Water vapor influences CIMS sensitivity to certain compounds in negative mode by clustering with the reagent ion* CF_3O^{-} *to form* $[H_2O \cdot CF_3O]^{-}$*. The decreasing intensity of the ion* $C_{12}H_{22}O \cdot H^{+}$ *as RH increases is likely indicative of this effect.*"

2) The effect of aerosol water content on organic vapor condensation, and as a result SOA formation, is compound specific: for hydrophilic organic compounds, liquid water could facilitate organic uptake by formation of an aqueous phase; for hydrophobic organic compounds, RH-driven changes in the gas-particle distribution of individual compounds result from changes in the compound-dependent gas-particle partitioning coefficient (Seinfeld et al., 2001). Predicting the interaction of water content and organic compounds in the particle phase is beyond the scope of the current study. This is also one important reason that we only chose to compare the model output with experimental observations at ~ 3% RH.

3) Ambient RH affects the importance of substituted dihydrofuran chemistry in the

overall alkane SOA formation mechanism in the following two ways. First, aerosol water content could inhibit the substituted dihydrofuran formation by shifting the equilibrium of the dehydration pathway and by neutralizing the particle-phase acid, which is the catalyst for the cyclization of δ-hydroxycarbonyl to cyclic hemiacetal. Figure 5 in the main text provides evidence for the less intense formation of alkyl-substituted dihydrofuran under higher RH. Second, increasing water vapor level could accelerate the formation of ester-containing carboxylic acid and carbonyl from the reaction of stabilized Criegee intermediates with H_2O. As shown in Figure 8 in the main text, water vapor at 50% RH compensates for the production of the less substituted dihydrofuran, leading to an eventually higher yield of carboxylic acids.

4) Ambient measurements of organic aerosol composition have shown that the carboxylic acid functional group (–C(O)OH) is closely associated with products from fossil fuel combustion sources (Liu et al., 2011; Russell et al., 2011). The current study provides explanations for the field observations and indicates the potential atmospheric importance of substituted dihydrofuran chemistry. The uptake of water onto inorganic aerosols becomes significant when ambient RH exceeds the corresponding deliquescence points. Organic coatings have been found to retard the mass transport rate of water. In this study, $(NH_4)_2SO_4$ is employed as the seed. When the ambient RH is lower than ~ 85%, the water content in the particle phase is sufficiently low so that the interconversion between δ-hydroxycarbonyls and substituted dihydrofuran could potentially occur. One would expect the formation of carboxylic acid from the dihydrofuran+O_3 chemistry over a large range of RHs.

Experimental matrix – Table 1 provides the experimental matrix. It appears that experiments were done only at each experimental condition once. Is this correct? Given the complexity of smog chamber experiments, the paper should discuss the repeatability of the results.

The eight experiments listed in Table 1 were carried out based on the model predictions: a series of simulations were run ahead of time to design the experimental conditions. The initial concentrations of gas-phase precursors (dodecane, H_2O_2, and NO_x) were chosen to obtain certain reaction regimes: 'RO_2+NO' vs. 'RO_2+HO_2' dominant.

Under high-NO_x conditions, continuous NO injection was also conducted over the course of the experiment to control the fraction of dihydrofuran that reacts with O_3 (dihydrofuran+OH vs. dihydrofuran+O_3 dominant).

Typos

Page 24723 line 21 – mˆ3 missing negative sign

Done.

Page 24729 line 12 – this should be 44 (f44 is presumably mass fraction of 44 not 43)

Done.