

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

We thank reviewer # 1 for the constructive comments. Our specific responses can be found below, with reviewer comments in black and our responses in blue.

Response to Referee # 1

The manuscript entitled, “Role of ozone in SOA formation from alkane photooxidation,” by X. Zhang et al., describes experiments looking specifically at the formation and destruction chemistry of substituted dihydrofurans produced by the OH initiated oxidation of dodecane. Dihydrofuran is formed via heterogeneous cyclization of specific hydroxycarbonyls, which are in turn formed by alkoxy radical isomerization. The unsaturated sites in the dihydrofuran are susceptible to attack by not only by OH but also ozone. The study examines this chemistry under “OH” and “Ozone” dominated conditions. The experiments are well described and the instrumental detection methods (e.g. CIMS and AMS) have been validated in previous publications. Overall the paper is well written and addresses an important aspect of SOA formation chemistry. Yet there seems to be no direct quantitative comparison between the detailed chemical mechanism and its predictions presented early on in the manuscript and the experimental data measured for this reaction. In general, the connection between experimental and model throughout the manuscript is ambiguous at best. As presented, one is left with the impression that the manuscript presents a number of experimental observations without a clear way of connecting these observations to a mechanistic model. Before publication the authors should endeavor to make more clear how the detailed predictions obtained from the MCM (and their model) are either quantitatively consistent or inconsistent with their measurements or explain more clearly how the MCM is being used to support their data. If this is not possible the authors should more clearly state up front what the role of the mechanism and MCM is interpreting their experimental results (see General comments).

There are two concerns in terms of comparing the model output with the experimental data. First, products from substituted dihydrofuran oxidation by either OH or O₃

identified by CIMS (as shown in Table 2 and Figure 2 in the draft) cannot be quantified because of the lack the authentic standards. Second, simulating the effect of aerosol water content on the uptake of organics, and as a result the total organic mass yield, is not possible in current models. Thus, we chose to compare the total observed SOA yield under dry conditions with model predictions. We will add the comparison of oxidation state under dry conditions, as the reviewer suggested. We will also compare the CIMS observed trends for ions listed in Table 2 with the model output under dry conditions, subject to the uncertainty noted above.

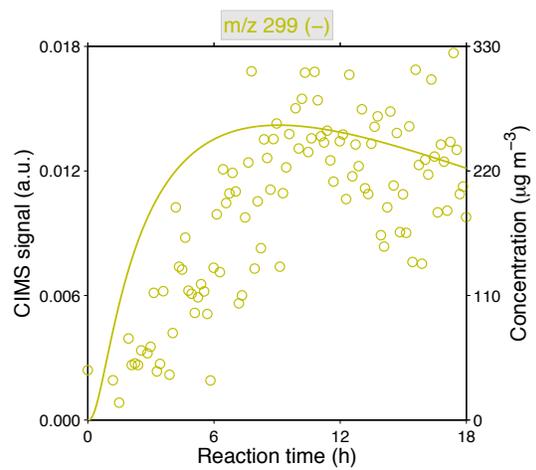
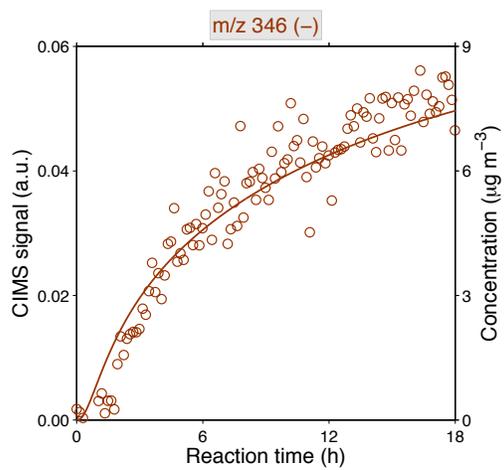
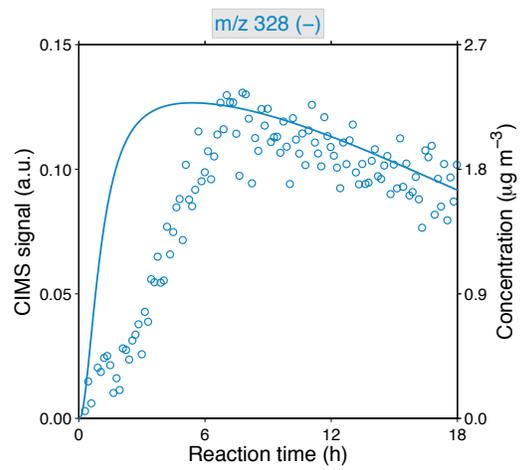
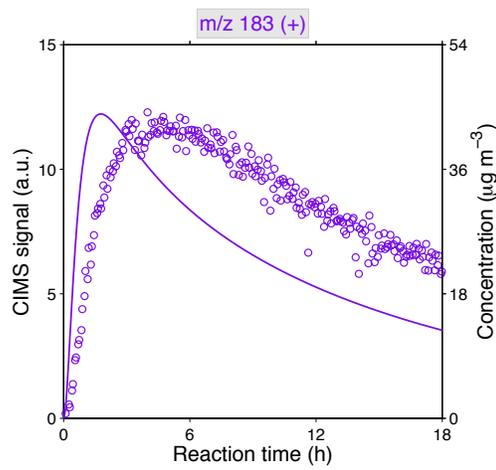
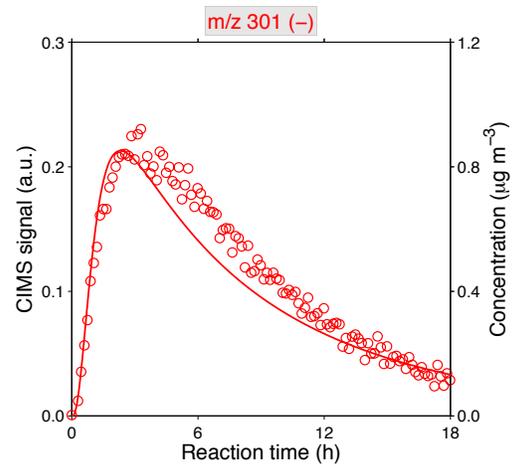
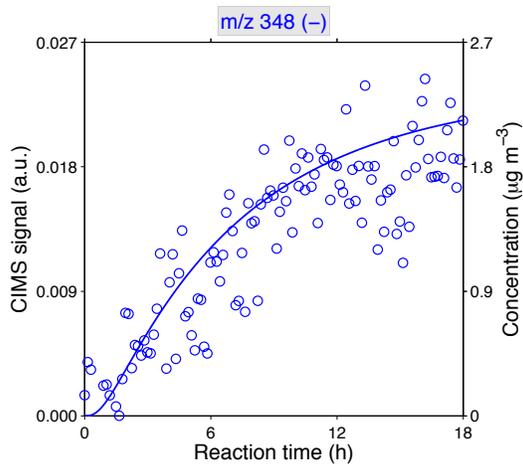
General Comments:

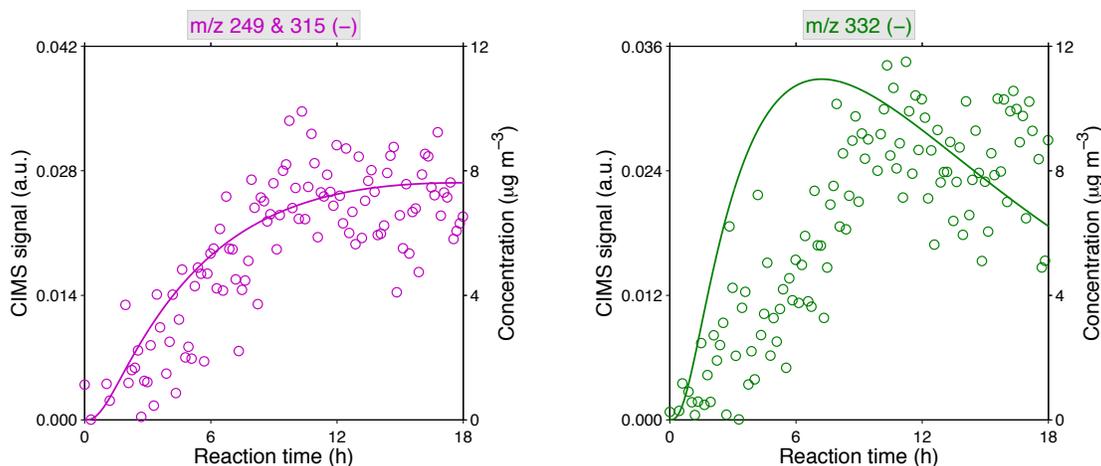
1. On page 24721 (line 5) the authors say that a kinetic scheme (including MCM) is used to estimate particle phase products generated in the chamber. These estimates as a function of reaction time are shown in Figure 3. I don't see a clear explanation as to why these kinetic traces are not directly compared to experimental measurements (shown in Fig. 4 and 5) of the same species detected in the experiments? For example, in Fig. 4 the author show experimental traces for $m/z = 183$. The authors should endeavor to make clear how the chemical mechanism introduced in section 3 is ultimately used to evaluate or interpret their data. For example, on page 24726 (lines 9 and 27) the authors state (for different experimental conditions) that the kinetic profile of the product detected at $m/z = 183$ is consistent with mechanistic predictions. What does consistent mean in this context (absolute concentration vs. time?) Can the authors be more quantitative in this comparison of experiment and model prediction?

1) We have compared the time-dependent trends of CIMS measured ions, with structures proposed in Table 2, with the model output. As noted, due to the absence of authentic standards, the sensitivity of CIMS to the different ions is not available. This comparison can reflect only the similarity of formation and removal kinetics of each species.

We have added a paragraph discussing how we use the mechanism to support the CIMS speciation in Section 4.5 'Experiment and model comparison', also as shown below, together with figures:

“ 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 $3 \times 10^{-3} \text{ s}^{-1}$. 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”. A 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-substituted 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. ”





2. The authors present AMS data in Figure 8 for marker ions F44 vs. F43. There is a great deal of complexity observed for oxidation as a function of experimental number in these plots. The authors spend little time in the manuscript giving the reader and idea what these plots actually mean. For example, as a function of increasing OH the fraction of $m/z = 44$ actually goes down at first. They say that curvature has been observed in previous studies, but give no chemical explanation why this counter intuitive result should occur. I would expect F44 to always increase upon increasing OH. While there may be some utility in reporting SOA in this space for some kind of data base of AMS results, I don't really see what robust quantitative conclusions about SOA formation chemistry can be obtained by this representation, minimal discussion and figure. A more chemically useful and general representation of this kind of mass spectrometry data is the Van krevelen diagram. I would suggest that this approach be adopted. Otherwise, the authors should provide a more detailed explanation of Fig. 8 or move it to the supporting information.

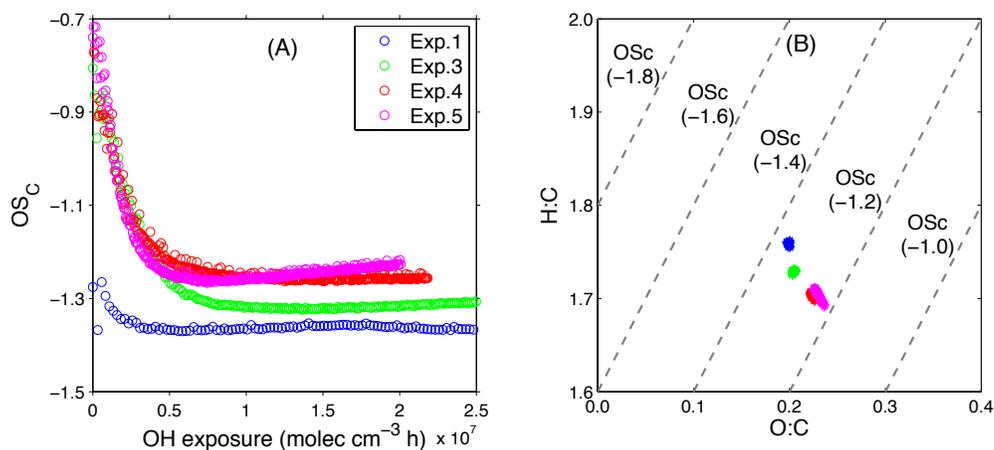
1) The curvatures in f_{44}/f_{43} plots have been observed in many studies and suggest a progression from earlier generation products containing carbonyl functional groups to later generation products containing acidic functional groups. As the reviewer suggests, we have added explanations for the curvature in the f_{44}/f_{43} plot:

“When the organic loading is small, only the highly oxygenated and least volatile species partition to the particle phase. As particles grow, more volatile and less oxidized species

are able to participate in equilibrium partitioning, leading to a decrease in $f_{CO_2^+}$. Progressive oxidation of semi-volatile products in the gas phase eventually leads to multi-functionalized species contributing to the increase of $f_{CO_2^+}$.”

2) We think the f_{44}/f_{43} plot is very important here. CO_2^+ is expected to result mainly from the thermal decarboxylation of an organic acid group (Alfarra, 2004). In addition, the f_{44} (ratio of m/z 44, mostly CO_2^+ , to total signal in the component mass spectrum) axis is also considered to be an indicator of photochemical aging (Alfarra et al., 2004; Aiken et al., 2008; Kleinman et al., 2008). In this study, both OH oxidation and ozonolysis of substituted dihydrofuran contribute to the $f_{CO_2^+}$ intensity. The contribution of each reaction pathway to the intensity of CO_2^+ can be evaluated based on the f_{44}/f_{43} plot since the O_3 and OH concentrations are known. If we compare the intensity of $f_{CO_2^+}$ at the same OH exposure, i.e., 2×10^7 molecules cm^{-3} h, the intensities of $f_{CO_2^+}$ in Exp #1, #3, #4, and #5 are 0.019, 0.020, 0.028, and 0.030, respectively. As mentioned in the original manuscript, the percentages of substituted dihydrofuran reacting with O_3 are 27%, 96%, 97% and 98%, respectively, for these four experiments. The RHs for these four experiments are 3%, 11%, 20%, and 55%, respectively. One concludes that at the same OH exposure, the more substituted dihydrofuran that reacts with O_3 under higher RH, the more CO_2^+ will be produced. Another way to evaluate the contribution of O_3 and OH to $f_{CO_2^+}$ is to compare the $f_{CO_2^+}$ intensity at the highest OH exposure in each experiment. As can be seen from Figure 8, Exp #1 exhibits the highest OH exposure, i.e., 3.8×10^7 molecules cm^{-3} h. But the $f_{CO_2^+}$ in Exp #1 is the least at the end of the experiment, i.e., 0.017, compared with 0.023, 0.027, and 0.031, respectively, in Exp #3, #4, and #5.

3) As the reviewer suggests, the van Krevelen plot is now added to Figure 9, also given below:



3. Figure 9 shows average carbon oxidation state vs. OH exposure. This data is presented with only a scant discussion of it and its meaning in the manuscript. The authors conclude that this plot indicates that ozonolysis of dihydrofuran plays an important role in the formation of highly oxidized aerosol. An oxidation state of -1.25 is still on average a fairly reduced hydrocarbon, so I don't understand the context in which the authors draw this conclusion. A more detailed discussion of oxidation state and this figure is needed perhaps by comparing what other groups have observed in the literature so as to give the reader some context as to what the data shown in Fig. 9 really means.

We have revised this paragraph, as given below:

“ The difference in elemental composition of organic particles produced from “O₃ dominant” vs. “OH dominant” environments is also examined via the AMS measured O:C and H:C ratios in van Krevelen plot and the time-dependent evolution of the average carbon oxidation state ($OS_C = 2 \times O:C - H:C$), see Fig.9. In general, the OS_C values calculated fall into a region characterized by oxidized primary organic aerosol and semivolatile oxidized organic aerosol (Kroll et al., 2011). The measured O:C (~ 0.2) and H:C (~ 1.7) ratios at the OH exposure in the order of $\sim 10^7$ molecules $\text{cm}^{-3} \text{ h}$ agree well with those measured for organic aerosols generated from C₁₀-C₁₇ alkanes (Lambe et al., 2011 and 2012). As mentioned earlier, the four experiments (Exp. #1, #3, #4, and #5) were conducted in such a way that the total OH exposure is decreasing whereas the total O₃ and RH exposure is increasing along with increasing experimental numbers (e.g.,

Exp. 5 has the least OH exposure but the largest O₃ and RH exposure). A clear trend observed from the van Krevelen plot is that O:C increases whereas H:C decreases under elevated O₃ and RH levels. The effect of ozonolysis of substituted dihydrofuran chemistry on the aerosol chemical composition can be evaluated by comparing OS_C (O:C vs. H:C) for these four experiments under the same OH exposure. Consistent with our findings in $f_{\text{CO}_2^+} - f_{\text{C}_2\text{H}_3\text{O}^+}$ space, the highest OS_C is observed under the highest O₃ exposure and RH level, but lowest OH exposure (98% substituted dihydrofuran reacts with O₃ at 55% RH). With the same OH exposure, e.g., 1.5×10^7 molecules cm⁻³ h, the average carbon oxidation state increases from -1.36 in “O₃ limiting” environments (Exp. #1) to -1.25 in “O₃ dominant” environments (Exp. #5). One concludes that ozonolysis of substituted dihydrofuran plays an important role in the formation of highly oxidized aerosol in alkane SOA. ”

4. In the introduction the authors say that recent modeling studies (Cappa and Wilson and Zhang and Seinfeld) indicate that particle phase chemistry (the subject of the current manuscript) might play a potentially important role in C12 alkane SOA formation, since these models fail to reproduce elemental O/C and H/C ratios. Do the model results shown in Fig. 10 (which include substituted dihydrofuran formation channel) correctly predict the observed oxidation state results shown in Fig. 9? Again I don't understand why the authors choose to compare their model predictions with what looks like to me only a small subset of their experimental data? They show functional group distributions in Fig. 10 so elemental composition should be trivial to compute. If there is some fundamental reason why this cannot be done (i.e. lack of authentic experimental standards) this should be clearly stated in the manuscript.

We have added the oxidation state comparison between experiments and models in Figure 10 and corresponding discussion, as given below:

“ 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 can accelerate the aerosol aging process.”

