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Interactive comment on “Role of ozone in SOA formation from alkane photooxidation” *by* X. Zhang et al.

Anonymous Referee #1

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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 suspectible 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).

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?

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 krevlen 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.

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 plans 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.

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.

Specific Comments:

It is unclear which axis in Fig. 5 correspond to which data sets (AMS vs. CIMS). This needs to be more clearly delineated.

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