*Response to reviewer #2 for "Role of ozone in SOA formation from alkane photooxidation" by X. Zhang et al.*

We thank reviewer # 2 for the constructive comments. Our specific responses can be found below, with reviewer comments in black and our responses in blue.

## Response to Referee # 2

General Comments:

In this study the authors investigated the role of the heterogeneous conversion of hydroxycarbonyls to dihydrofurans and subsequent reactions with OH and O3 on the formation of secondary organic aerosol (SOA) from the reactions of alkanes with OH radicals. The experiments were conducted in large Teflon chambers and gas phase products were monitored with chemical ionization mass spectrometry (CIMS) and aerosol composition with an aerosol mass spectrometer (AMS). The experiments were conducted under high and low NOx conditions, with conditions manipulated so that the effects of O3 on SOA formation in both these regimes could be evaluated. A detailed chemical model was also developed and used to interpret the results. The results indicate that O3 reactions with dihydrofurans should be important under atmospheric conditions and lead to the formation of more highly oxidized products, including esters, ethers, and acids, than would otherwise be the case. These are difficult experiments and were very well done. The results are interesting and have important implications for understanding SOA formation and its composition from reactions of alkanes, which are a significant component of atmospheric VOC emissions. I think the paper should be published in ACP once the following comments have been addressed.

Specific Comments:

1. Page 24719, lines 10-20 and Page 24722 line 25: What were estimated NO3 radical concentrations? It should be remembered that NO3 radicals do not photolyze significantly in blacklights. Can the reaction of NO3 radicals with dihydrofurans be ignored even though the reaction is extremely fast?

The predicted $NO_3$ radical concentration is very low, on the order of ~ $10^4$ molec $cm^{-3}$.

The estimated lifetime of substituted dihydrofuran due to the reaction with $NO_3$ in our chamber is ~ 67 h. Therefore, the reaction of $NO_3$ radicals with substituted dihydrofuran can be ignored in this study. Reactions for the formation and removal of $NO_3$ radicals, together with corresponding reaction rate constants and photolysis rate, are given in Table S1-3 in the Supplementary Materials.

2. Page 24720, lines 5-10: How can a protonated cyclic hemiacetal be distinguished from a protonated dihydrofuran clustered to one water molecule?

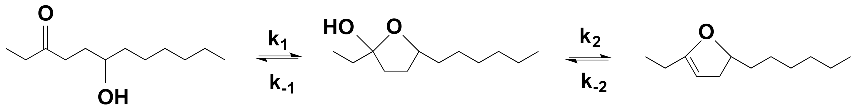
CIMS cannot distinguish a protonated cyclic hemiacetal from a protonated dihydrofuran clustered to one water molecule. In this study, we assigned the CIMS measurement at m/z 183 as alkyl substituted dihydrofuran for the following reasons:

First, the predicted vapor pressures for cyclic hemiacetal ($C_{12}H_{24}O_2$) and substituted dihydrofuran ($C_{12}H_{22}O$) by SIMPOL.1 (Pankow and Asher, 2008) are $7.50 \times 10^{-7}$ and $1.08 \times 10^{-4}$ atm at 298 K, respectively. Under the experimental conditions in this study, e.g., the organic loading is $> 50$ μg/m$^3$ at the point when these two species start to accumulate, one would expect that almost all of the substituted dihydrofuran migrates into the gas phase once formed, whereas a large fraction of cyclic hemiacetal will remain in the particle phase.

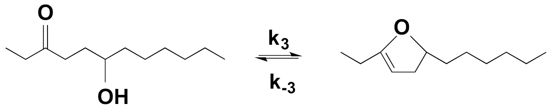
Second, as shown in Figure 5 in the draft, AMS measured ion $C_{12}H_{23}O^+$ peaks ~ 3 h earlier than the CIMS measured ion $C_{12}H_{22}O{\cdot}H^+$ at RH ranging from 3% to 55%. If we assign both ions as cyclic hemiacetal, we will draw the conclusion that the time scale for cyclic hemiacetal achieving gas-particle equilibrium is in the order of several hours. This value is much larger than a typical timescale (in the order of min) for a species to reach gas-particle equilibrium in the presence of $> 10^4$ cm$^{-3}$ particles with a median diameter of ~ 80 nm.

As shown in Figure 5, the decay rate of CIMS measured ion $C_{12}H_{22}O{\cdot}H^+$ is $1.44 \times 10^{-5}$ s$^{-1}$ at 3% RH, which is two orders of magnitude slower than the decay rate ($4.02 \times 10^{-3}$ s$^{-1}$) of AMS measured ion $C_{12}H_{23}O^+$. We suggest that the decay of CIMS measured ion $C_{12}H_{22}O{\cdot}H^+$ is mostly due to reaction of substituted dihydrofuran with both $O_3$ and OH, whereas the decay of AMS measured ion $C_{12}H_{23}O^+$ is due to the dehydration of cyclic hemiacetal.

3. Page 24722, lines 10-20: If the dehydration of cyclic hemiacetals is the rate limiting step in the formation of dihydrofurans, then is it valid to assume that the rate of formation of dihydrofurans is equal to the rate of loss of hydroxycarbonyls?



R(1)



R(2)

We drew the conclusion that the dehydration of cyclic hemiacetals is the rate-limiting step based on the observation that the decay rate of cyclic hemiacetal at 3% RH, which is obtained by optimal fitting to the AMS measured m/z 183 assuming first-order kinetics, is of the same order of magnitude as the decay rate of 5-hydroxy-2-pentanone measured by CIMS. If this is the case, the formation rate of dihydrofuran should be slower than the loss rate of hydroxycarbonyl.

Determining $k_1$, $k_{-1}$, $k_2$, and $k_{-2}$ shown in R(1) is infeasible in this study. Since the cyclization and dehydration are both reversible reactions, we describe these individual steps as an overall process in the model, as shown in R(2). $k_3$ is estimated by monitoring the decay of 5-hydroxy-2-pentanone, which is commercially available, using CIMS in the presence of 20 $\mu m^3$ $cm^{-3}$ acidic $NH_4HSO_4$ seeds at 3% RH. The concentration of 5-hydroxy-2-pentanone eventually reaches a plateau, indicating that equilibrium between 5-hydroxy-2-pentanone and 4, 5-dihydro-2-methylfuran is attained. The equilibrium constant K can therefore be obtained, based on the assumption that the decrease in the 5-hydroxy-2-pentanone concentration is accompanied by stoichiometric formation of the corresponding 4, 5-dihydro-2-methylfuran. Then, we can calculate $k_{-3}$ via the equation $k_{-3} = k_3/K$. Note that the concentration of water vapor is accounted for in the determination of the K value.

4. What might be the effects of wall loss of gaseous products on the results of these experiments?

One would expect the measured SOA yield corrected by vapor phase wall loss is higher, although the extent of this increase is uncertain. The measured vapor loss rate of 2-dodecanone in our chamber is $2.2 \times 10^{-6}$ $s^{-1}$. If this value is uniformly applied to all the products from dodecane photooxidation to account for vapor wall loss, we would not expect a significant change in the SOA yield based on instantaneous equilibrium gas-particle partitioning. Vapor wall loss will significantly affect the measured aerosol yield when the time scale for achieving gas-wall equilibrium is close to the time scale for achieving gas-particle equilibrium. These two timescales, however, depend on a number of unknown parameters, such as the vapor-particle accommodation coefficient.

5. Page 24725, line 25 through Page 24726, line 10: It seems that an alternative explanation for these observations might be that the CIMS m/z 183 ion is formed by dehydration of the cyclic hemiacetal following protonation in the CIMS, so that these curves are representative of the cyclic hemiacetal not the dihydrofuran. We have seen that this is the case when cyclic hemiacetals are analyzed by electrospray ionization-MS: no protonated cyclic hemiacetals are observed, only the dehydrated ions. Thus the same stable ions formed in electron ionization by loss of OH are formed by protontransfer ionization. Dehydration is well known to occur in proton transfer reactions of alcohols, and cyclic hemiacetals dehydrate much more easily than normal alcohols. I believe the same observations were made by Yatavelli and Thornton in their MOVICIMS studies of SOA formed from alkane oxidation. The increase and decrease in m/z 183 under high NOx conditions could then represent the formation and dehydration of the cyclic hemiacetal, respectively, whereas under low NOx conditions the absence of any decay and the occurrence of a plateau could be indicative of an absence of dehydration due to the lack of an acid catalyst (no HNO3 formed from NO2 + OH as in the high NOx cases).

We agree with the reviewer. We also have reasons to assign the CIMS measurement at m/z 183 as alkyl substituted dihydrofuran, as discussed in our response to comment #2. We have added discussion in terms of the chemical structure assignment of m/z 183 in Section 4.2, as given below:

"*An alternative explanation for the temporal profiles of (+) m/z 183 under low-*$NO_x$ *conditions is that this ion is formed by dehydration of the cyclic hemiacetal following* *protonation in CIMS. The occurrence of a plateau could be indicative of an absence of dehydration in the particle phase due to the lack of an acid catalyst (no $HNO_3$ formation from $NO_2$+OH reaction as in the high $NO_x$ cases). However, based on the model prediction, cyclic hemiacetal is not likely to accumulate since the formation of its precursor, δ-hydroxycarbonyl, is a minor pathway when the $RO_2$+$HO_2$ reaction is dominant and the photolysis of the resulting peroxide is not important.*"

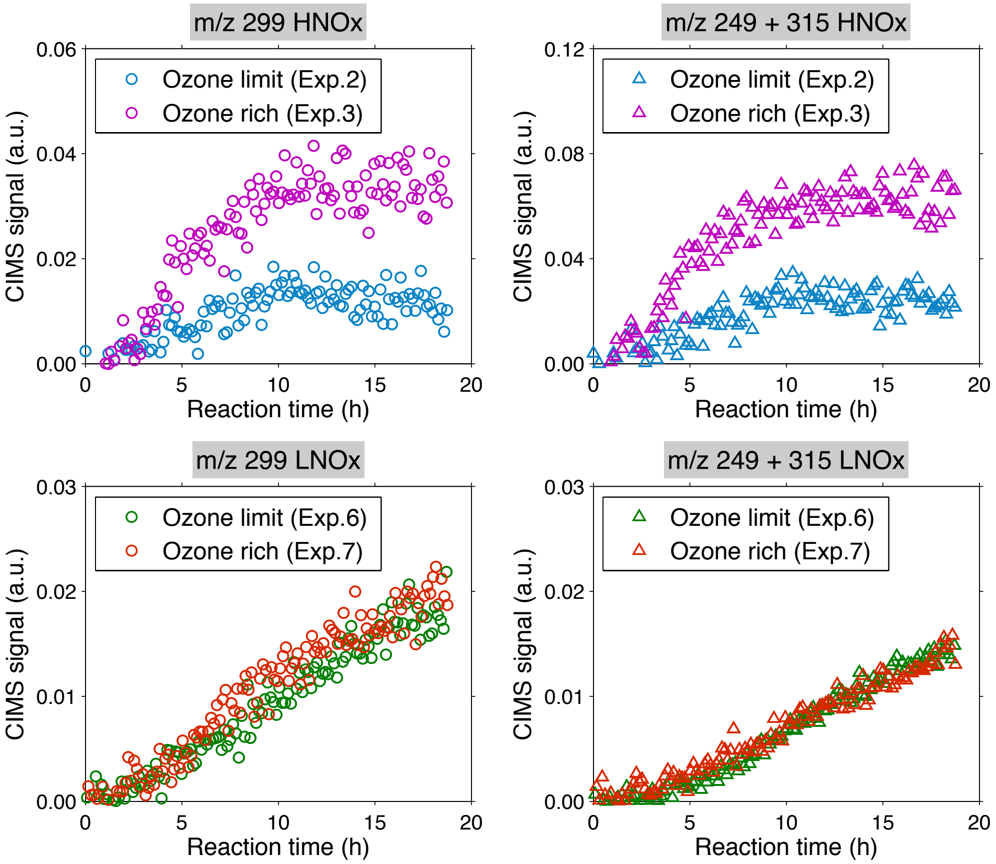
6. As a follow-up to comment 5, the paper has no discussion of the role of strong acid in the conversion of hydroxycarbonyls to dihydrofurans. Both Atkinson et al. 2008 and Lim and Ziemann 2009c have shown that when acid is neutralized by pyridine or ammonia the conversion (especially dehydration) is slowed dramatically and possibly even terminated. If the m/z 183 curves are monitoring cyclic hemiacetals and not dihydrofurans, then what evidence do the authors have that dehydration occurs in the low NOx experiments? It seems that Exp. 7, which is low NOx and high O3, should provide evidence for the formation of dihydrofurans in the absence of strong acid if ester, ether, and acid products were observed. But I found no discussion of the results of that experiment.

Based on our model prediction, the formation of δ-hydroxycarbonyl, which is the precursor of cyclic hemiacetal and alkyl-substitued dihydrofuran, is negligible in the absence of $NO_x$. Under current low-$NO_x$ experimental conditions, most $RO_2$ radicals are predicted to react with $HO_2$, producing peroxide. The only source of the RO radical is the photolysis of peroxide, which is very slow as compared with the OH oxidation of peroxide. As a result, the formation of cyclic hemiacetal and alkyl-substitued dihydrofuran is not important under low-$NO_x$ conditions. However, we did still observe signals at m/z 183 and we assigned this ion as a characteristic fragment of carbonyl-hydroperoxide-derived peroxyhemiacetal based on a parallel study (Yee et al., 2012).

According to the reviewer's suggestion, if the m/z 183 curves are monitoring cyclic hemiacetals not alkyl-substituted dihydrofurans, we need to know if cyclic hemiacetals still dehydrates, producing alkyl-substituted dihydrofurans, under low-$NO_x$ conditions. We compared the temporal profiles of m/z 249 and 315, and m/z 299, which represent carboxylic acid and carbonyl products from the dihydrofuran+$O_3$ reaction, under "$O_3$ limiting" (Exp. #6) and "$O_3$ rich" (Exp. #7) conditions. We did not find any substantial increase in these two ion signals due to the increase in $O_3$, as shown in the figure below. This can be attributed to, as the reviewer suggests, the slowdown or even termination of the dehydration of cyclic hemiacetal in the absence of strong acid catalysis. Also note that the temporal trends of these three ions are different from those measured under high-$NO_x$ conditions, indicating that they might represent different chemical structures other than those assigned in Table 2.

We have added a paragraph discussing the role of strong acid in the conversion of hydroxycarbonyls to dihydrofurans in Section 4.3:

"*Figure 6 shows the temporal profiles of (−) m/z 299, as well as (−) m/z 249 and 315, under "$O_3$-limiting" (Exp. #2) and "$O_3$-rich" (Exp. #3) conditions. The decay rates of their precursor (+) m/z 183, as calculated by assuming first-order kinetics, are $1.19 \times 10^{-5}$ $s^{-1}$ and $1.44 \times 10^{-5}$ $s^{-1}$, respectively. Under "$O_3$-rich" conditions, both species increase and eventually level off. When $O_3$ reaction is less competitive, the CIMS signals start to decrease after 10 h photooxidation. Note that these three ions were also detected under low-$NO_x$ conditions. No significant increase in their signals was observed in the "$O_3$-rich" environment (Exp. #7), compared with the "$O_3$-limiting" case (Exp. #6). If they were assigned the same chemical structures as those proposed under high-$NO_x$ conditions, their growth pattern would suggest a minor formation of their precursor alkyl-substituted dihydrofuran. This can be attributed to the slowdown or even termination of the dehydration of cyclic hemiacetal in the absence of strong acid catalysis (Atkinson et al., 2008; Lim and Ziemann, 2009 c).*"



7. Atmospheric Implications: The effect of particle acidity on the extrapolation of these results to the atmosphere should be discussed, since this has a major effect on the second of the two listed factors.

We have added the following discussions:

" *It has been suggested that the heterogeneous formation of substituted dihydrofuran is acid-catalyzed (Atkinson et al. 2008; Lim and Ziemann, 2009 a, b, c). Aerosols generated in the chamber environment in the presence of* $NO_x$ *are expected to be highly acidic due to the formation of* $HNO_3$*. In the atmosphere, where ambient particles are less acidic or even neutralized, the heterogeneous conversion of δ-hydroxycarbonyl to substituted dihydrofuran might be a minor process."*

Technical Comments:

1. Abstract, line 7: I suggest changing to "cyclization and dehydration".

Done.