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Atmospheric Chemistry and Physics
Discussions

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

Anonymous Referee #2

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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?

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

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?

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

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 proton-transfer 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 MOVI-CIMS 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).

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.

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.

Technical Comments:

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

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 24713, 2013.