Interactive comment on “Investigating the composition of organic aerosol resulting from cyclohexene ozonolysis: low molecular weight and heterogeneous reaction products” by J. F. Hamilton et al.

J. F. Hamilton et al.

Received and published: 26 September 2006

The authors wish to thank the reviewers for their constructive comments.

Referee 1
1. No seed aerosol was used in this experiment and the RH was around 3%. This has been added to the text.

2. Some of the experiment details were incorrect. The original protocols were not available but we now have access to them. The filter samples were collected at the end of the experiment, after there had been a number of injections of cyclohexene to the
chamber. As such, we cannot be confident about the aerosol yield calculations. The concentration of SOA in the chamber from the filter was 177 ug/m³, from the TEOM was 127 ug/m³ and from the SMPS 120 ug/m³. This extra information and corrections have been added to the text. If we assume complete consumption of the total of 600 ppb added to the chamber, then we calculate a yield of 9 % based on the filter mass. This is in agreement with previous studies.

3. The samples are exposed to these high temperatures for only a few milliseconds and mixtures of standards show no degradation or reaction during electrospray. Some of the diacids form dimers in water with Na⁺ ions but these can easily be identified and in some cases are beneficial giving further structural information.

4. The same products were identified with a water only mobile phase. The formic acid was used purely to increase sensitivity only.

5. The referee is correct and this oversight has been corrected.

6. A comprehensive set of standards were ran including the di-acids (succinic, glutaric and adipic) as well as hydroxy-acids and oxo-acids. Where possible the mass spectra and retention characteristics of the standards have been compared to proposed structures with similar functionalities. Sample limitations restricted our ability to quantify using these standards. This information has been added to the manuscript.

7. A series of experiments have been carried out where a standard solution of an acyclic compound (succinic acid, glutaric acid, adipic acid, 4-oxo-2-pentenal, Levulinic acid, Maleic acid, 4-acetyl butyric acid and DL-Hydroxy-capric acid) has been spiked onto clean pieces of filter paper and analysed using the same method as the SOA samples. In all cases only the non-cyclic analogues were found. We see no evidence of the cyclization-dehydration reactions suggested. Although this list does not cover all the possible compounds which would form the species identified by GCXGC, the authors are confident that the filter desorption method does not cause artefacts through cyclization reactions of individual acyclic compounds. It is possible that any oligomer
compounds which break down during the analysis could undergo these reactions. It is also true that there are no obvious gas phase reaction mechanisms leading to these compounds. It could be possible that these cyclic compounds are formed via reactions within the aerosol phase itself. A section has been added in the text to describe the artefact testing using standards and the possibilities of where these cyclics come from.

8. Since we have determined that the cyclics do not form from individual acyclic compounds we feel it would be misleading to suggest identities based on unknown formation mechanisms. The text added for the section above will cover this.

9. The authors believe the oligomers may be either fragmented during thermal desorption or during EI. Indeed there are a number of peaks eluting late in the GCXGC chromatogram which cannot be identified, fragmenting in the EI mass spectra to give very limited data i.e. one or two low molecular weight fragments and no molecular ion. Work is ongoing to improve the analysis of these peaks within our laboratory. It is also possible that in-volatile oligomers remain within the inlet as a residue at these temperatures.

10. The isoprene paper had not been published when this paper was submitted. However, the results presented by Surratt et al. are very interesting with respect to the current manuscript. This evidence for the formation of esters in isoprene photo-oxidation is in agreement with our work and the manuscript has been updated to reflect this. Gao proposed acid ahydrides and gave a single MS/MS spectra and proposed structure. This has been included in the text, along with a extended discussion of previous studies.

11. The most abundant oligomers found were di-acids. However, there were a total of 18 dimers identified and mass spectra indicate that they are not all di-acids. Mass spectra of low concentration peaks indicate that acid-aldehyde and aldehyde-aldehyde combination were also present. The manuscript does not mention these and so this information has been added to the text.
12-14. Using the 4 compounds which have known molecular formulae in this paper, there is no evidence to suggest these could be either diacyl-peroxides, peroxyhemiacetals, a-acyloxy-alkylhydroperoxides or diperoxides. The mass spectra and the molecular formulae together indicate that these compounds are not present. For example, for M=246 and C11H18O6, the diacylperoxide would have either A) aldehyde at one end and a hydroxyl at the other end, or B) acid at one end and methyl at the other end. Neither of these can easily be rationalised from the reaction mechanism. In addition, the most likely site for cleavage during fragmentation would be at the peroxide bond. This would not match the mass spectrum obtained. For analytes with unknown molecular formulae, the mass spectra also do not indicate the occurrence of any of these classes of compounds. The lower concentrations used in this study (600 ppb cf Ziemann ppm levels) seems to reduce the amount of oligomers formed through reactions of the stabilised criegee intermediate. A section describing the lack of evidence in this system of previously identified compounds has been added.

14. Ziemann (2003) found that alkoxyhydroperoxides were not found in the cyclohexene ozonolysis SOA in the presence of alcohols. We also see no evidence of these compounds using the high T electrospray ionisation. Although we cannot disprove losses of alkoxyhydroperoxides during electrospray, the Ziemann work carried out at lower temperatures found no evidence of these compounds. Either they are unstable or too volatile to form significant SOA.

Technical comments have been corrected and some of the figure labels increased in size.

Referee 2
1. The referee is correct that a small amount of OH radicals are not formed via sunlight. This phrase has been emitted.

2. The experimental section has been updated to include more experimental detail, including the yield and the aerosol concentration from the TEOM and SMPS. Some
of the experiment details were incorrect. The original protocols were not available but we now have access to them. The filter samples were collected at the end of the experiment, after there had been a number of injections of cyclohexene to the chamber. As such, we cannot be confident about the aerosol yield calculations. The concentration of SOA in the chamber from the filter was 177 ug/m³, from the TEOM was 127ug/m³ and from the SMPS 120 ug/m³. This extra information and corrections have been added to the text. If we assume complete consumption of the total of 600 ppb added to the chamber, then we calculate a yield of 9 % based on the filter mass. This is in agreement with previous studies.

3. The reviewer is correct that the compounds identified using GCXGC can not easily be reconciled using gas phase reaction mechanisms. We propose that these compounds are formed either through the fragmentation of larger molecules followed by cyclization of the monomer units or via some unknown aerosol chemistry. We feel that it is not possible at present to include possible formation mechanisms as these are simply not well understood. An investigation of the formation mechanisms of these cyclic compounds is underway in our laboratory to provide better understanding.

4. The 7 acids were the only compounds identified using LC analysis. We suggest that the carbonyl compounds do not ionise efficiently with electrospray ionisation. Many of the compounds found in the GCXGC analysis were at very low concentrations which would be below the detection limits of the LC analysis.

5. The section comparing previous studies of cyclohexene SOA has been expanded and now contains a more comprehensive description. The types of compounds found in previous studies have been compared to the work presented here. In particular, we find no evidence of the diacyl-peroxides, peroxyhemiacetals, a-acyloxy-alkylhydroperoxides or diperoxide compounds found in previous studies.

6. The authors feel that this section is systematic and clear and has not been changed.

7. The referee is correct and this oversight has been corrected.
Technical comments have been corrected. The occurrence of ions 24 Da apart in the negative and positive spectra has been explained within the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 6369, 2006.