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***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.***

**Anonymous Referee #1**

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General Comments:

This manuscript describes analyses of the SOA products of the reaction of cyclohexene with ozone in an environmental chamber. The methods employed include GCxGC-TOFMS analysis and LCMS with electrospray ionization and ion trap MS and MS/MS analysis. The major conclusions of the study are that a significant fraction of the SOA is oligomers (mostly dimers), and that the oligomers are formed by combining a fairly limited number of carboxylic acid monomers through ester and anhydride linkages. It appears that adipic acid plays an especially important role in these reactions.

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The analyses appear to be carefully performed, and the interpretation of the LCMS analyses of the oligomers is convincing. My view is that the results of the GCxGC analyses have not been correctly interpreted, as discussed below in comments 7 and 8. Nonetheless, the LCMS analyses present valuable new insights into the products of oligomerization reactions, which are badly needed. The study will be important for understanding these reactions in the atmosphere and for developing appropriate mechanisms. The paper is well written, although I suggest a few changes to figures and references. I also have some additional comments and questions below, which should be addressed. Once this is done I think the paper will be worthy of publication in Atmospheric Chemistry and Physics.

#### Specific Comments:

1. Page 6373: What is the relative humidity in these experiments, and were seed particles used?
2. Page 6373, lines 5-12: If one assumes that all the cyclohexene (120 ppb) reacted, then this corresponds to  $410 \mu\text{g m}^{-3}$ . The SOA mass concentration based on the filter sample is  $794 \mu\text{g}/4.21 \text{ m}^3 = 188 \mu\text{g m}^{-3}$ . This corresponds to an SOA yield of 46%, which is 4-5 times larger than that measured by Kalberer et al. [Environ. Sci. Technol. 34, 4894-4901 (2000)] for a similar amount of reacted cyclohexene. Do the authors have an explanation why their value might be so high?
3. Page 6374, lines 18-26: During electrospray ionization, the source temperatures are 200-300 C. How long are the samples exposed to these temperatures, and might this induce any reactions, as can occur during GC analysis?
4. Page 6374, line 16-17. The solvent used for HPLC contains 0.1% formic acid. Might the presence of this acid promote catalytic reactions that could form some of the proposed products?
5. Page 6375, line 7-9: I expected that the retention time would increase with deac-

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ing volatility and increasing polarity.

6. Page 6377, lines 20-22: Although it is true that standards do not exist for many of these products, there is a fairly good selection of commercially available diacids, oxo-diacids, and hydroxy-diacids. Were any of these analyzed?

7. Page 6377, lines 15-18 (and elsewhere): From the discussion presented here it appears that the authors believe that the compounds observed with GCxGC analysis (Table 1) are those actually present in the aerosol, and that the analysis method is free of artifacts that might lead to chemical modifications of the compounds. The possible artifacts that are mentioned are those that might alter relative amounts of compounds, but not their identity. I believe there are a number of lines of evidence that suggest that this is not the case: (1) essentially all the compounds listed are much too volatile to be present in the aerosol, as would be shown by partitioning calculations, (2) there is no known gas-phase ozonolysis chemistry that will form these cyclic compounds, since for endocyclic alkenes the ozone-alkene reaction always leads to ring-opening products due to the instability of the primary ozonide formed when ozone adds to the double bond (an exception is a secondary ozonide formed when the Criegee intermediate cyclizes), (3) the cyclic products listed in Table 1 can essentially all be explained by cyclization-dehydration reactions of acyclic compounds that have been identified by derivatization-GCMS and LCMS techniques that are less prone to artifacts than GCxGC. Note that many of these acyclic compounds are not observed by GCxGC. Furthermore, the cyclics are not observed by derivatization-GCMS. The latter observation is explained by the fact that the acyclic compounds have been derivatized prior to GC analysis, and so cannot cyclize and dehydrate. It is a straightforward exercise to start with diols, oxoacids, hydroxyacids, diacids, and oxo- and hydroxy-substituted forms of these and create the cyclic species observed by GCxGC. For example, succinic anhydride is formed from succinic acid, 1,2-cyclohexanedione is formed from 6-oxohexanoic acid, cyclopentenone is formed from 1,2-dihydroxy-pentanal, etc. Organic chemistry textbooks discuss these reactions, which only require temperatures that are

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easily reached in the GC.

8. In light of comment 7, it is worth pointing out that one could use these cyclization-dehydration reactions to advantage, since one can make a reasonable guess at the identity of the original parent compounds based on the known cyclization-dehydration reactions. It seems to me that it would not be unreasonable to suggest identities for monomers based on such an analysis.

9. What do the authors think happens to the oligomers in the GCxGC?

10. It should be mentioned in the text that Gao et al. [Environ. Sci. Technol. 38, 6582-6589 (2004)] has studied this same system using ESI-MS/MS and also proposed that acid dehydration reactions form oligomers such as anhydrides. Also, in a recent paper, Surratt et al. [J. Phys. Chem. A 9665-9690 (2006)] have clearly shown that ester formation is important in the formation of oligomers in the photooxidation of isoprene.

11. It is odd to me that all the oligomers that are formed are diacids. Since there appear to be a large concentration of oxo-acids, why do they not also appear in the oligomers, with the two terminal functionalities then being an oxo group and an acid group? Could this be the result of the analytical method or the MS interpretation?

12. In a paper by Ziemann [J. Phys. Chem. A 106, 4390-4402 (2002)], it was shown using real-time MS analysis that high-molecular weight SOA compounds form within the first minute of the cyclohexene-ozone reaction, and that diacids grow in more slowly. He proposed that the low volatility compounds might be diacyl peroxides formed in gas-phase reactions. Some of the characteristic EI fragments observed in that study could be explained on the basis of esters and anhydrides, but the results would not indicate that adipic acid is a key monomer. Could some of the mass spectra observed here be interpreted on the basis of diacyl peroxides?

13. In a paper by Docherty et al. [Environ. Sci. Technol. 39, 4049-4059 (2005)] it was shown that peroxides contribute a large fraction of the SOA mass from the reaction

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of  $\alpha$ -pinene with ozone. Since cyclohexene is often used as a model for  $\alpha$ -pinene, it is not unreasonable that organic peroxides (possibly peroxyhemiacetals formed from reactions of hydroperoxides with aldehydes) might be present in the SOA. Could any of the mass spectra observed here be interpreted on the basis of peroxyhemiacetals?

14. In a paper by Ziemann [J. Phys. Chem. A 107, 2048-2060 (2003)] on SOA formation from reactions of simple cyclic alkenes such as cyclohexene with ozone, it was shown that an alcohol scavenger will react with stabilized Criegee intermediates to form alkoxyhydroperoxides, which can subsequently isomerize to a cyclic peroxyhemiacetal. Both these compounds are stable and can form SOA. Since an alcohol scavenger was used in the present experiments, these compounds should be present. Do the authors see these compounds? If not, this may be evidence that they have decomposed (peroxides are unstable above about 100 C) during analysis, perhaps at the 200-300 C temperatures of the electrospray source. This could also apply to other peroxide compounds such as those mentioned in comments 12 and 13.

## Technical Comments:

15. Page 6383, lines 17-18: I believe loss of CO is meant to be loss of CO<sub>2</sub>.

16. Table 2: I think the mass of dioxo-hexanoic acid is 144 not 146.

17. Table 3: Should the monomer given for the fourth compound in this list be 4-hydroxy-oxobutyric acid?

18. Most of the labels in the figures are too small to read. I suggest they be made larger.

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

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