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Atmospheric Chemistry and Physics Discussions

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 #2

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General Comments

This paper describes chemical analysis of secondary organic aerosol (SOA) produced from the ozonolysis of cyclohexene in an experiment performed in the large volume European Photoreactor in Valencia, Spain. SOA was collected on a filter and analysed using 3 different mass spectrometric techniques. The chemical analyses appear to have been performed carefully and the results are of high quality. A wide range of products were detected including a range of C4-C6 carbonyls, acids, diacids and cyclic species. Evidence is also presented for the identification of dimers resulting from the

combination of acids and hydroxy acids via an ester linkage. Although there are several previously reported studies of the composition of SOA produced from the cyclohexene-ozone reaction, this work does provide new information on the species present in the SOA which may also be relevant to other reactions.

The article is well written and most of the discussion is appropriate. However, it seems that a lot of effort has been put into interpretation of the data with little attempt to link the detection of certain species, especially those identified by the GCŒGC-TOF MS technique, to reaction mechanisms (gas-phase or aerosol phase). Nevertheless, I believe that this paper provides some new and interesting information on the chemical composition of SOA that is of interest to many readers of Atmospheric Chemistry and Physics. I recommend publication following revision of the manuscript in line with the following comments and suggestions.

Specific Comments

1. Page 6370, line 26: Not all OH radicals are “formed from sunlight”. Ozonolysis can also produce OH radicals, as pointed out by the authors themselves on page 6372, line 6. This phrase should be omitted or the sentence changed.

2. Page 6373, first paragraph: There is a lot of detail missing here. How much cyclohexene was reacted? Was the aerosol measured using a scanning mobility particle sizer? If so, what was the concentration of particles during the sampling period and what was the yield of SOA? How does the yield compare to previous studies?

3. Page 6375, lines 13-19: Many compounds were identified using the GCŒGC-TOF MS technique. However, the statement that many of the ring-retaining compounds detected are “mechanistically linked directly to the starting reactant” is simply incorrect. Compounds such as 1,2-cyclohexandiol, 1,2-cyclohexandione and 2-hydroxycyclohexanone are not produced from the reaction of ozone with cyclohexene. It is possible that some of these cyclic species may be produced through the reaction of OH radicals with the alkene, but an OH radical scavenger was used in the experiments.

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Are the cyclic products formed as a result of chemical reactions with the aerosol? In addition, how can hexanal be formed? - there are no -CH3 groups within the starting compound. I suggest that the authors identify which products in Table 1 can arise from the cyclohexene-ozone reaction and those that might be produced from reaction within the aerosol or elsewhere. This information should be backed up with possible mechanisms or reference to the published literature where appropriate.

4. Pages 6376 and 6377: Were the 7 acids the only species identified by LC-MS/MS? Were any of the 30 or so carbonyls identified by GCŒGC-TOF MS detected using this method?

5. Page 6377: Comparison of the results with those obtained by previous workers (Gao et al., 2004a and Kalberer et al. 2000) is given very little thought. This section should be expanded to highlight the new information that is presented here. In addition the authors completely miss an early study on the cyclohexene-ozone system by Hatakeyama et al. (Environ., Sci. Technol., 1985, 19, 935-942).

6. Pages 6378 - 6380: This section, which describes the results obtained using the high resolution TOF apparatus, whilst also referring back to the LC MS/MS data, becomes a little disjointed and could be improved.

7. Page 6381, lines 15-18: I believe loss of CO2 is responsible for the 101 peak and OH2 + CO2 for the 83 peak.

Technical Comments

1. Page 6371, line 20: The extra “dash” in the chemical names is not needed, i.e., should be 1,3,5-trimethylbenzene and cycloalkenes.

2. Page 6371, line 25: MALDI is Matrix-assisted laser desorption ionisation.

3. Page 6371, line 29: Change sentence to read “Ĕ using a quadrupole time of flight (Q-TOF) mass spectrometerĔ”

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4. Page 6372, line 3: Change phrasing to read “Ĕ on the exact structures of oligomers and hence...”

5. Page 6372, line 14: Photo-reactor is one word, i.e. Photoreactor.

6. Page 6373, line 1: Photo-reactor is one word, i.e. Photoreactor.

7. Page 6379, line 14: Should be “Ĕ[M-H]- = 231 DaĔ”

8. Page 6379, line 21: Monomers should be singular.

9. Page 6379, lines 23-25: Sentence starting “The combination ofĔ” is confusing and should be re-written.

10. Page 6379, line 27: Formulae not formulas.

11. Page 6380, line 3: Formulae not formulas.

12. Page 6381, line 7: Ageing not aging

13. Page 6390, Fig 1: The caption uses the acronym TIC. This is not mentioned in the text. In addition the GCŒGC-TOF MS acronym has been further lengthened by placing a TD in front of it, which is not consistent with the acronym used in the text. There are also other points in the manuscript where the acronyms and abbreviations are changed slightly. The authors should use one term and stick to it.

14. Page 6391, Fig. 2: The positive ion mode chromatogram contains peaks which are 24 Da higher than thos in the negative ion mode. The reason for this should be explained (possibly in the text) for those not fully aware of the intricacies of the method.

15. Page 6396, fig. 7: Caption should contain the word formulae not formula.

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

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Interactive Comment