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Atmospheric
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# *Interactive comment on* “Formation of secondary organic aerosol and oligomers from the ozonolysis of enol ethers” *by* A. Sadezky et al.

**Anonymous Referee #2**

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The paper describes the observation and analysis of aerosol formed in the ozonolysis reactions of a number of alkyl vinyl ethers. The reactions have been performed in a 570 l spherical glass reactor and atmospheric pressure and temperature. Using HPLC in combination with mass spectrometric techniques it has been shown that compounds with oligomeric structures containing chain units with mass 46 (CH2O2) or mass 60 (C2H4O2) are formed depending on the Criegee intermediate formed in the ozonolysis system under investigation. The paper is generally well written and the evidence supporting the present of oligomers in the aerosol generated by the ozonolysis is clearly presented and documented in the manuscript figures and diagrams and also the supporting information. I have the following questions and comments on the material presented in the manuscript: Ţ The aerosol profiles have been analysed using the adsorption/partitioning model approach developed by Odum et al. and the results obtained are generally in good agreement with those reported by Klotz et al. for methyl vinyl ether and in the recent EU project MOST of different vinyl ethers. In Table 1 the authors report an aerosol yields for the ozonolysis of IBVE performed in the present and absence of excess cyclohexane to scavenge OH. The presence of the scavenger causes a large drop (factor of 4) in the aerosol yield. It is not clear from the statements on pages 9 and 12 if this decrease with the addition of the scavenger is valid only for IBVE or if it has been observed for all the vinyl ethers. Please clarify - I suspect it must apply to all the vinyl ether results. Ţ The work of Docherty and Ziemann (J. Aerosol Sci. Technol. 37 (2003) 877), Ziemann (J. Phys. Chem. A 107 (2003) 2048) and Keywood et al. (Environ. Sci. Technol. 38 (2004) 3343) has clearly demonstrated that the radicals produced from the reactions of the OH (produced in the ozonolysis) with the scavenger have an effect on the SOA yield. The extent and direction of the effect have also been shown to be dependent on the specific alkene (Keywood et al.). Keywood et al. in their paper present evidence that acylperoxy radicals formed in the system play a central role. This point needs to worked into the manuscript. The decrease of the aerosol yield/oligomer formation in the presence of the OH scavenger (cyclohexane) and also the complete disappearance of the oligomer formation in the presence of the CI scavenger (HCOOH) observed in the present study suggest that radical-radical reactions involving the CI are another previously unknown radical chemistry complication in the aerosol studies involing the ozonolysis of alkenes. Ţ It remains to be tested whether the gas-phase oligomer formation phenomena reported in this paper is a peculiarity of vinyl ethers or if it is a general feature of the ozonolysis of all alkenes. If it is a general feature then it could be one of the processes initiating the nucleation in the aerosol formation observed in the ozonolysis of alkenes in dry laboratory reaction systems. It also implies that the ozonolysis of very simple alkenes such as ethane and propene should form some aerosol. Have the authors tested other alkenes? Ţ The discussion in the paper focuses mainly on listing the liquid phase observations of oligomer formation with chain structures similar to those observed in the present gas phase study and also the other reports of SOA formation in the oxidation of VOC which have been attributed the observed oligomerization to acid-catalysed aldol condensation, gem-diol formation and acylradical cross reactions. The discussion of the mechanism(s) leading to the oligomer formation observed in the present work is very limited. Can the authors completely exclude that the oligomer formation process is not occurring on the aerosol? Ţ Based on the oligomer structures reported in the paper its formation must involve peroxy - CI biradical reactions. It is unlikely that alkoxy reactions are involved since formation of this type of radical is more likely to result in chain termination through carbonyl formation. The scavenging of the CI with 20 ppm HCOOH is an indicator of the rates of the oligomer formation. Are the rate coefficients known for the HCOOH + CI reactions or any other CI scavenger? Monitoring of the aerosol formation as a function of the scavenger concentration could help put a rate coefficient estimate on the peroxy - biradical interactions. I anything known in the literature about peroxy - biradical reactions (liquid or gas phase)? Ţ Was any attempt made to try and simulate the formation of the oligomers using a simple gas phase mechanism? For oligomer formation peroxy-biradical reactions will have to much more competitive than other reactions of peroxy radicals. This may be one of the reasons why the oligomers observed only have an RO entity at one end of the molecule. If peroxy-peroxy radical reactions were occurring to any extent then at least some oligomer formation with RO at both ends should have been observed since one of the R*O2 + R*O2 channels will give a peroxide R*OOR* (where R* contains RO). It also mean, however, that the for these radicals the peroxide channel is negligible or the product is unstable. Ţ Even through formation of the CH2OO and CH3CHOO Criegee radicals dominate in the systems studied and are prevalent in the oligomer chains was no evidence found for inclusion of the Criegee radicals (ROCHOO) which are formed when the alkene splits to form HCHO or acetaldehyde? On this point was any attempt made to try and enhance the chain length by deliberately feeding the system with CH2OO or CH3CHOO by adding ethane or 2-butene to the systems? It would also be interesting to mix, for example, ethyl vinyl ether and ethyl propenyl ether to see if chains with mixed CI composition are formed. Ţ I was not able to allocate meaningful chemical structures to final fragment ions reported in the various figures!

This paper presents intriguing new results on gas phase oligomer formation in the ozonolysis of vinyl ethers. Obviously much more work needs to be done to eludicate the formation mechanism and establish whether this is a general feature of all alkene ozonolysis reactions. Taken together with other recent papers it shows how complex the radical chemistry is in ozone-alkene reactions and that a better understanding of radical-radical processes occurring in such systems and their involvement in the observed SOA formation is required for a meaningful interpretation of the atmospheric significant of laboratory derived SOA yields.

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 5629, 2006.

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