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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Oligomer formation during gas-phase ozonolysis of small alkenes and enol ethers: new evidence for the central role of the Criegee Intermediate as oligomer chain unit” *by* A. Sadezky et al.

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The authors thank the anonymous referee 2 for carefully reading this large manuscript and giving specific comments and suggestions. The assumption that the oligomers are formed in the gas phase is based on the following observations: 1) In the presence of the Criegee Intermediate (CI) scavenger HCOOH the aerosol formation and oligomer formation is completely suppressed, indicating the role of the CI in the process of oligomer formation. 2) Condensed phase oligomerization has been observed only in the presence of seed aerosol and is strongly enhanced especially with acidic seed aerosol (e.g. Iinuma et al., 2004). All experiments in this study were conducted in the absence of seed aerosol. Prior to the start of the reaction the background aerosol concentrations have been measured and were always below 200 particles cm-3. Since the initial aerosol concentration is very low and no other compounds with sufficient low vapor pressure like organic acids or poly-functional compounds have been detected, which could lead to nucleation from the gas phase and provide the particle surface for heterogeneous reactions in the condensed phase, it is assumed that the oligomerization takes place in the gas phase. The particles form then by aggregation of the high molecular weight compounds followed by condensation. The referee mentioned the possible formation of non-covalent complexes, which has been excluded in the first version. In response also to the comments of the anonymous referee 1, the samples have been re-measured with the FTICR MS with improved resolution. The exact masses determined now correspond to the sodium adducts of the oligomers. Adding LiCl solution to the sample, the lithium adducts instead of the sodium adducts have been observed. These new results have been added to the revised manuscript. The analysis of Reinhardt et al. (2007) has not been performed since the exact masses could be determined with the improved mass resolution as presented in the revised manuscript. This enabled the assignment of molecular formulas to each observed ion using the Analyst Software. The exact elemental composition of parent ions, fragment ions and fragmented neutrals determined by accurate mass measurements using the ESI(+)/FTICR technique allowed us to assign a complete structure of the oligomer molecules. The number of entries in Table 3 has been reduced and only the molecular formulas for the M+H and M+Na ions are presented to demonstrate the lower mass error of the sodium adducts compared to the original interpretation in the first version of the manuscript, when the mass resolution was too low.

References: Iinuma, Y., Böge, O., Gnauk, T. and Herrmann, H.: Aerosol-chamber study of the alpha-pinene/O3 reaction: influence of particle acidity on aerosol yields and products, Atmos. Environ., 38, 761-773, 2004.

Reinhardt, A., Emmenegger, C., Gerrits, B., Panse, C., Dommen, J., Baltensperger, U., Zenobi, R. and Kalberer, M.: Ultrahigh mass resolution and accurate mass measurements as a tool to characterize oligomers in secondary organic aerosols, Anal. Chem., 79, 4074-4082, 2007.

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