Atmospheric Chemistry and Physics
An Interactive Open Access Journal of the European Geosciences Union

Atmos. Chem. Phys., 8, 2667-2699, 2008
www.atmos-chem-phys.net/8/2667/2008/

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

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Abstract. An important fraction of secondary organic aerosol (SOA) formed by atmospheric oxidation of diverse volatile organic compounds (VOC) has recently been shown to consist of high-molecular weight oligomeric species. In our previous study (Sadezky et al., 2006), we reported the identification and characterization of oligomers as main constituents of SOA from gas-phase ozonolysis of small enol ethers. These oligomers contained repeated chain units of the same chemical composition as the main Criegee Intermediates (CI) formed during the ozonolysis reaction, which were CH_2O_2 (mass 46) for alkyl vinyl ethers (AVE) and $C_2H_4O_2$ (mass 60) for ethyl propenyl ether (EPE). In the present work, we extend our previous study to another enol ether (ethyl butenyl ether EBE) and a variety of structurally related small alkenes (*trans*-3-hexene, *trans*-4-octene and 2,3-dimethyl-2-butene).

Experiments have been carried out in a 570 l spherical glass reactor at atmospheric conditions in the absence of seed aerosol. SOA formation was measured by a scanning mobility particle sizer (SMPS). SOA filter samples were collected and chemically characterized off-line by ESI(+)/TOF MS and ESI(+)/TOF MS/MS, and elemental compositions were determined by ESI (+)/FTICR MS and ESI(+)/FTICR MS/MS. The results for all investigated unsaturated compounds are in excellent agreement with the observations of our previous study. Analysis of the collected SOA filter samples reveal the presence of oligomeric compounds in the mass range 200 to 800 u as major constituents. The repeated chain units of these oligomers are shown to systematically have the same chemical composition as the respective main Criegee Intermediate (CI) formed during ozonolysis of the unsaturated compounds, which is $C_3H_6O_2$ (mass 74) for ethyl butenyl ether (EBE), *trans*-3-hexene, and 2,3-dimethyl-2-butene, and $C_4H_8O_2$ (mass 88) for \textit{trans}-4-octene. Analogous fragmentation pathways among the oligomers formed by gas-phase ozonolysis of the different alkenes and enol ethers in our present and previous study, characterized

by successive losses of the respective CI-like chain unit as a neutral fragment, indicate a similar principal structure. In this work, we confirm the basic structure of a linear oligoperoxide – $[CH(R)\text{-}O\text{-}O]_n$ – for all detected oligomers, with the repeated chain unit CH(R)OO corresponding to the respective major CI. The elemental compositions of parent ions, fragment ions and fragmented neutrals determined by accurate mass measurements with the FTICR technique allow us to assign a complete structure to the oligomer molecules. We suggest that the formation of the oligoperoxidic chain units occurs through a new gas-phase reaction mechanism observed for the first time in our present work, which involves the addition of stabilized CI to organic peroxy radicals. Furthermore, copolymerization of CI simultaneously formed in the gas phase from two different unsaturated compounds is shown to occur during the ozonolysis of a mixture of \textit {trans}-3-hexene and ethyl vinyl ether (EVE), leading to formation of oligomers with mixed chain units $C_3H_6O_2$ (mass 74) and CH_2O_2 (mass 46). We therefore suggest oligoperoxide formation by repeated peroxy radical-stabilized CI addition to be a general reaction pathway of small stabilized CI in the gas phase, which represents an alternative way to high-molecular products and thus contributes to SOA formation.

Final Revised Paper (PDF, 1856 KB) Discussion Paper (ACPD)

Citation: Sadezky, A., Winterhalter, R., Kanawati, B., Römpp, A., Spengler, B., Mellouki, A., Le Bras, G., Chaimbault, P., and Moortgat, G. K.: 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, Atmos. Chem. Phys., 8, 2667-2699, 2008. Bibtex EndNote Reference Manager