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The central role of the Criegee Intermediate in the formation of oligomers in SOA from the gas-phase ozonolysis of small unsaturated VOC

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Small unsaturated compounds with three to six carbon atoms and simple aliphatic structures have been observed to form significant amounts (up to 5 %) of secondary organic aerosol (SOA) during gas-phase ozonolysis. In our previous study (Sadezky et al., 2006), we identified the oligomeric compounds (m/z 200-800) in SOA from small enol ethers (mainly alkyl vinyl ethers), and suggested that the Criegee Intermediate (CI) plays a central role as repetitive chain unit in their formation. In the present work, we extended our previous study to another enol ether (ethyl butenyl ether) 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 filter samples were analyzed by ESI(+)/MS-MS-TOF. The results for all investigated unsaturated compounds confirm the observations of our previous study. Analysis of the collected SOA revealed the presence of oligomeric compounds (range m/z 200-800). The repetitive chain units of these oligomers are shown to systematically have the same chemical compositions as the respective major CI formed during ozonolysis of the unsaturated compounds. A “peroxidic unit” -[CH(R)-O-O]- as basic oligomer repetitive chain link is proposed, corresponding to the CI. This new reaction pathway of the CI in the gas phase has not been reported before, and represents an alternative way of SOA formation.

Sadezky et al., Atmos. Chem. Phys., 6, 5009-5024, 2006.