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Formation of secondary organic aerosol and oligomers from the ozonolysis of unsaturated ethers

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The gas phase ozonolysis of a series of enol ethers, among them several alkyl vinyl ethers ($ROCH{=}CH_2$) and ethyl propenyl ether ($C_2H_5CH{=}CHCH_3$), has been studied in a 570 l spherical glass reactor at atmospheric pressure (730 Torr) and temperature (296 K). Gas-phase reaction products and mechanisms are investigated by in-situ FTIR, and secondary organic aerosol (SOA) formation is followed by SMPS (TSI 3936). The chemical composition of the formed SOA is analysed by ESI(+)/MS-TOF.

The main stable gas-phase reaction product is the respective alkyl formate ROC(O)H formed with yields of 60 to 80 %, implying similar yields of the corresponding Criegee Intermediates CH_2O_2 (alkyl vinyl ethers $ROCH{=}CH_2$) and CH_3CHO_2 (ethyl propenyl ether $C_2H_5CH{=}CHCH_3$). Measured SOA yields are between 2 to 4 % for all enol ethers. For alkyl vinyl ethers, detectable SOA formation is observed after conversion of a theshold value between 51 and 138 ppb of vinyl ether. Furthermore, SOA formation is strongly reduced or suppressed by the presence of an excess of formic acid or water vapour, which act as scavengers of Criegee Intermediates.

Chemical analysis of the formed SOA by ESI(+)/MS-TOF allows to identify oligomeric compounds in the mass range between 200 and 800 as its major constituents. Chain units are identified as CH_2O_2 (mass 46) for alkyl vinyl ethers ($ROCH{=}CH_2$) and $C_2H_4O_2$ (mass 60) for ethyl propenyl ether ($C_2H_5CH{=}CHCH_3$) and thus have the same chemical compositions as the respective major Criegee Intermediates formed during ozonolysis of these ethers. The oligomeric structure and chain unit identity are confirmed by HPLC/ESI(+)/MS-TOF and ESI(+)/MS/MS-TOF

experiments.