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# A HRMS study of oligomer formation through aqueous phase photooxidation of methylvinyl-ketone and methacrolein

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Global estimates of secondary organic aerosol (SOA) formation flux show that the current descriptions miss a large fraction of the sources. Aqueous phase photochemistry in cloud droplets and deliquescent aerosol may provide some of this missing flux. Organic reactions in those media, particularly leading to higher molecular weight products thus need better understanding. Here, we investigated the aqueous phase photooxidation of methacrolein (MACR) and methylvinyl-ketone (MVK), which are the two main oxidation products of isoprene, the volatile organic compound (VOC) that is mostly emitted on the global scale. In our experiments, photolysis of $H_2O_2$ provided OH radicals whose reaction with MACR or MVK produced oligomers.

Firstly, oligomers were analyzed using electrospray ionization coupled with high-resolution linear ion trap Orbitrap$^{TM}$ (Thermo Corp.) mass spectrometer (HRMS). This technique enabled to propose the unambiguous elemental composition of the produced compounds as data were collected for a mass range of m/z 50–2000 amu. The mass of oligomers increased strongly in positive and negative ionization modes when initial concentrations of MACR and MVK were increased from 2 to 20 mM. Typical regular patterns of oligomer formation were observed for both precursors, and extended up to 1400 amu. These patterns were very different from each other for the two precursors although both showed regular mass differences of 70 amu.

In addition, we used a Kendrick analysis and identified more than 20 distinct chemical oligomer series produced by photooxidation of both MACR and MVK, some of which reaching more than 1400 amu. The HRMS investigations allowed us to propose a mechanism of production of oligomers. Upon nebulization, both oligomer systems produce SOA with a mass yield of 2-12%. This mass yield increases with reaction time and precursor concentration.

Moreover, time evolution of the oligomer systems observed with the Orbitrap will be compared to HR-TOF-AMS characterization of the resulting SOA upon nebulization.