Aqueous phase oligomerization of α,β-unsaturated carbonyls and acids investigated using ion mobility spectrometry coupled to mass spectrometry (IMS-MS)

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One of the current essential issues to unravel our ability to forecast future climate change and air quality, implies a better understanding of natural processes leading to secondary organic aerosol (SOA) formation, and in particular the formation and fate of oligomers. The difficulty in characterizing macromolecules is to discern between large oxygenated molecules from series of oligomers containing repeated small monomers of diverse structures.

In the present study, taking advantage from previously established radical vinyl oligomerization of methyl vinylketone (MVK) in the aqueous phase, where relatively simple oligomers containing up to 14 monomers were observed, we have investigated the same reactivity on several other unsaturated water soluble organic compounds (UWSOCs) and on a few mixtures of these precursor compounds.

The technique used to characterize the formed oligomers was a traveling wave ion mobility spectrometry coupled to a hybrid quadrupole - time of flight mass spectrometer (IMS-MS) fitted with an electrospray source and ultra-high performance liquid chromatography (UPLC). The technique allows for an additional separation, especially for large ions, containing long carbon chains. We have shown the efficiency of the IMS-mass spectrometry technique to detect oligomers derived from MVK photooxidation in the aqueous phase. The results were then compared to other oligomers, derived from ten other individual biogenic UWSOCs. The technique allowed distinguishing between different oligomers arising from different precursors. It also clearly showed that compounds bearing a non-conjugated unsaturation did not provide oligomerization. Finally, it was shown that the IMS-mass spectrometry technique, applied to mixtures of unsaturated conjugated precursors, exhibited the ability of these precursors to co-oligomerize, i.e. forming only one complex oligomer system bearing monomers of different structures.

The results will be discussed in terms of atmospheric implications for the detection of oligomers in complex chamber and/or field samples.

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