

Highly oxygenated multifunctional organic compounds from anthropogenic precursors

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Volatile organic compounds (VOCs) from biogenic and anthropogenic sources are the precursors for atmospheric oxidation products in the gas and particle phase. While globally the concentration of biogenic VOCs (BVOCs) is a factor of 10 higher than anthropogenic VOCs (AVOCs), the latter may dominate in the urban atmosphere. Recently, it was shown that highly oxygenated multifunctional organic compounds (HOMs) are produced via an auto-oxidation process from α -pinene and other terpenes and may play an important role in new particle formation (Ehn et al., 2014).

AVOCs contain a high fraction of aromatic hydrocarbons (ArHC), such as benzene, toluene, xylene and mesitylene, e.g. from handling and combustion of fuels (Atkinson and Arey, 2003), and are important precursors for the formation of secondary organic aerosol (Metzger et al., 2010). Despite their recognized importance as atmospheric reactants, their auto-oxidation mechanism and the subsequent formation of HOMs in the gas phase has not been studied yet.

Here we present HOM formation from OH-triggered auto-oxidation for six single-ring ArHC (benzene, toluene, xylene, mesitylene, ethylbenzene), one oxygenated single-ring ArHC (phenol), as well as two conjugated polycyclic ArHC (naphthalene and biphenyl). Experiments were performed in a flow tube.

A Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-TOF-MS) (Jordan et al., 2009) measured the concentrations of the ArHC. The OH radicals were generated separately by photolysis of water vapor and quickly mixed with the VOC under study in the flow tube. A nitrate ion based Chemical Ionization with the Atmospheric Pressure interface Time-Of-Flight mass spectrometer (CI-API-TOF) (Jokinen et al., 2012) measured the chemical composition of the HOMs, which are formed after addition of an OH to the aromatic ring followed by an auto-oxidation process. The HOMs are detected either through acid-base reaction or adduct formation with a nitrate ion.

We observed HOMs from the oxidation of all eight aromatic compounds. Figure 1 shows that the HOM formation occurs by addition of two oxygen atoms, i.e. a peroxy functional group. We also observed the recombination of two peroxy radicals forming a dimer, which contains two carbon skeletons of the precursor compound. For polycyclic ArHC, naphthalene and biphenyl, we detected even larger clusters (trimer and tetramer).

Accordingly, these HOMs and thus AVOCs are expected to substantially contribute to new particle

formation events detected in urban areas. We will present the chemical mechanism involved in the formation of HOMs from different ArHC and assess their contribution to the total condensable gases.

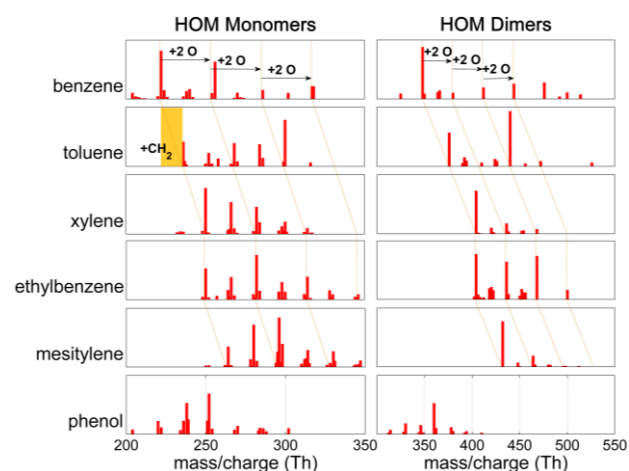


Figure 1: HOMs from 5 single-ring ArHC (benzene, toluene, xylene, ethylbenzene, mesitylene) and 1 oxygenated single-ring ArHC (phenol). HOMs are divided in two main categories: HOM monomers and HOM dimers.

Atkinson and Arey (2003) *Chem. Rev.*, 103(12), 4605-4638.

Ehn et al. (2014) *Nature*, 506, 476-479.

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