**Highly oxidized multifunctional organic compounds (HOMs) from the gas-phase reaction of ozone with three sesquiterpenes**

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Sesquiterpenes (C15H24, SQT) are emitted to the atmosphere by plants in quantities of about 15 million metric tons carbon per year (Seinfeld & Pandis 2003). This corresponds to about 1% of the total biogenic volatile organic compound (BVOC) emission of 1150 million metric tons carbon per year (Guenther et al. 1995). Monoterpenes (C10H16) are emitted annually with 130 million metric tons carbon representing one of the dominant emissions beside isoprene (Guenther et al. 1995).

SQTs are oxidized in the gas phase mainly by ozone and OH radicals and resulting oxidation products are an important source of secondary organic aerosol (SOA). The process of atmospheric SOA formation is still subject of intense research.

Organic compounds with very low vapor pressure are thought to dominate early particle growth but could not be detected up to now. Recently, Ehn et al. 2014 observed highly oxidized multifunctional organic compounds (HOMs) from the oxidation of α-pinene, an atmospherically important monoterpene. The oxidation products of α-pinene and other monoterpenes contain up to twelve oxygen atoms and are formed within seconds after initial attack of ozone or OH radicals. Their molar formation yields are in the range of 3-8% (Ehn et al. 2014, Jokinen et al. 2015). The HOM formation mechanism is assumed (Jokinen et al. 2014) to take place similar to the well known autoxidation process in the liquid phase (Jazukowitsch 1875).

This study investigates the HOM formation from the oxidation of three atmospherically relevant sesquiterpenes, β-caryophyllene, α-humulene and α-cedrene. The experiments were carried out at room temperature and atmospheric pressure in a free-jet flow system. Detection was conducted by means of NO3--CI-APi-TOF (chemical ionization – atmospheric pressure interface – time of flight) mass spectrometry which allows to detect HOMs with high resolution and a detection limit of about 104 molecule cm-3.

The molar formation yield of HOMs from SQT ozonolysis lies between 0.2 - 1.2 %, significantly lower than the corresponding values from monoterpene oxidation. That indicates that sesquiterpene HOM formation has a limited contribution to SOA formation which is probably dominated by oxidation products from monoterpene oxidation.

References:

J. H. Seinfeld and J. F. Pankow, *Annu. Rev. Phys. Chem.*, 2003, 54, 121–140.

A. Guenther *et al.*, *J. Geophys. Res.*, 1995, 100, 8873–8892.

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

T. Jokinen *et al.*, *PNAS* 2015, in press.

T. Jokinen *et al.*, *Angew. Chem. Int. Ed.* 2014, 53, 14596-14600.

H. N. Jazukowitsch, Ber. deut. chem. Ges. 1875, 8, 766-769.