

Highly Oxidized RO₂ Radicals and Consecutive Products from the Ozonolysis of Three Sesquiterpenes

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Sesquiterpenes (C₁₅H₂₄, SQT) are emitted to the atmosphere by plants in quantities of about 18 - 24 million metric tons of carbon per year (Messina et al., 2015; Sindelarova et al., 2014). This corresponds to up to 3% of the annual global biogenic volatile organic compound (BVOC) emission of 750 - 1150 million metric tons of carbon (Guenther et al., 1995; Sindelarova et al., 2014). Monoterpenes (C₁₀H₁₆) are emitted annually with 130 million metric tons of 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, α -cedrene, β -caryophyllene, and α -humulene. 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 molecules cm⁻³.

The molar formation yield of HOMs from SQT ozonolysis lies between 0.5 - 1.8% (see Figure 1), 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.

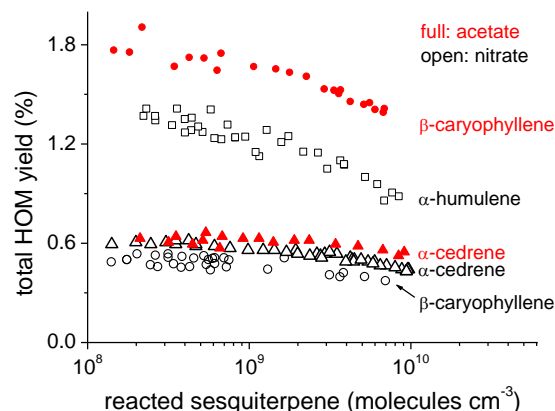


Figure 1. Total HOM yield from the ozonolysis of the three SQTs α -cedrene, β -caryophyllene and α -humulene as a function of the reacted SQT.

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