Organic nitrate contribution to new particle formation and growth in secondary organic aerosols from α-pinene ozonolysis

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Secondary organic aerosols (SOA) are a major component of atmospheric particulate matter and play a central role in atmospheric chemistry, climate and public health. In recent years it has been found that SOA contain substantial amounts of organic nitrates, affecting atmospheric chemistry by altering the total aerosol mass yield from secondary sources and acting as reservoir of NOx. However, organic nitrates are difficult to quantify with standard analytical techniques; hence, formation kinetics and abundance are still poorly characterized.

In this study we applied the short-lived radioactive tracer ¹³N produced by the PROTRAC facility at the Paul Scherrer Institute to quantify the amount of organic nitrates produced and retained in SOA particles. This online technique gives an accurate estimate of the total nitrogen that entered the particle phase. We found that organic nitrates accounted for ~40 % of SOA mass during initial particle formation, decreasing to ~15 % upon particle growth to the accumulation mode size range (>100 nm). Experiments with OH scavengers and kinetic model results suggest that organic peroxy radicals formed by a-pinene reacting with secondary OH from ozonolysis are key intermediates in the organic nitrate formation process. Direct reaction of a-pinene with NO3 was found to be less important for accumulation of organic nitrates in the particle phase. The organic nitrate content of SOA particles decreased slightly upon increase of relative humidity to 80 %. The experiments show a tight correlation between organic nitrate content and SOA particle number concentrations, implying that the condensing organic nitrates are among the extremely low volatility organic compounds (ELVOC) that may play an important role in the nucleation and growth of atmospheric nanoparticles.