

Studies on the Effect of Sub-zero Temperatures on the Formation of Extremely Low Volatility Dimer Esters in Secondary Organic Aerosol from Alpha-Pinene

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The oxidation of volatile organic compounds (VOC) is considered a major source of secondary organic aerosols (SOA) in the atmosphere. Recently, extremely low volatility organic compounds, or ELVOC, formed from the oxidation of VOCs have been shown to play a crucial role in new particle formation (Ehn et al., 2014). In addition, higher molecular weight dimer esters originating from the oxidation of the biogenic VOC alpha-pinene have been observed in both laboratory-generated and ambient SOA (Kristensen et al., 2013). The low volatility of the dimer esters along with an observed rapid formation makes these high molecular weight compounds likely candidates involved in new particle formation from the oxidation of alpha-pinene. Furthermore, laboratory experiments show that the dimer esters only form in the presence of ozone, thus may be used as tracers for the ozone-initiated oxidation of alpha-pinene, and are therefore indicative of enhanced anthropogenic activities.

In this work, we present the results of a series of oxidation experiments performed in the newly constructed cold-room smog chamber at Aarhus University. This unique and state-of-the-art Teflon chamber allows for atmospheric simulations of the oxidation VOCs and subsequent SOA formation at temperatures down to -16 $^{\circ}$ C. In this study, ozonolysis and photochemical oxidations of alpha-pinene are performed at temperatures ranging from +20 to -16 $^{\circ}$ C.

Chemical characterization of the formed SOA is performed using liquid chromatography coupled to quadrupole time-of-flight mass spectrometry. The results show significant differences in the chemical composition related to the experiment temperature. In particularly, the concentration of the high molecular weight dimer esters showed to be highly affected by temperature. Interestingly, preliminary results show higher formation of dimer esters related to increased SOA formation rate, thus indicating that these particle-phase ELVOCs may be linked with new particle formation.

Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., Canagaratna, M., Dal Maso, M., Berndt, T., Petaja, T., Wahner, A., Kerminen, V. M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, Nature, 506, 476-+, 10.1038/nature13032, 2014.

Kristensen, K., Enggrob, K. L., King, S. M., Worton, D. R., Platt, S. M., Mortensen, R., Rosenoern, T., Surratt, J. D., Bilde, M., Goldstein, A. H., and Glasius, M.: Formation and occurrence of dimer esters of pinene oxidation products in atmospheric aerosols, Atmospheric Chemistry and Physics, 13, 3763-3776, 2013.