

# Pressure dependency of ozonolysis product formation of $\alpha$ -pinene focusing on low volatile compounds such as organic acids and dimeric compounds

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Secondary organic aerosols (SOA) are important for air quality and the global climate. Therefore, a better understanding of formation mechanism, growth, sources and also quantity of SOA is necessary. Today many details concerning these aspects are unknown.

SOA is formed by volatile organic compounds (VOCs) oxidized by ozone, OH- and NO<sub>3</sub>-radicals in the atmosphere. The products of these oxidations have different kinds of functional groups (e.g. acid- and aldehyde-groups). Thus the volatility of the compounds decreases and nucleation or condensation on existing particles occurs. As monoterpenes are an important part of VOCs, the atmospheric oxidation is of high interest in aerosol research.  $\alpha$ -Pinene is a very common monoterpene and therefore an often used model substance for mechanistic studies (Müller *et al.* 2009).

Besides oxidation products with monomeric structure, such as pinic acid for example, dimers were found in SOA. The formation of these is discussed intensively. Various reactions in the gas- and/or particle phase are possible. The dimers of  $\alpha$ -pinene are of high interest due to the quantity of this terpene in the atmosphere. A lot of research hereby is focused on the compounds with the molecular mass 358 and 368. For the former very different formation pathways and chemical structures are suggested in the literature. These two dimers are of special interest because they were also observed in environmental samples. Therefore the possibility of using them as marker substances for various atmospheric conditions is discussed. A much higher number of dimeric compounds can be detected in atmospheric simulation chambers. This is due to the higher concentration of monoterpene and ozone used especially in mechanistic studies (Kundu *et al.* 2012).

Ozonolysis of  $\alpha$ -pinene in the reaction chamber at the University of Göttingen, which can be operated at reduced pressures, is used to get more information about the formation process. This spheric reaction cell has a volume of 64 L with ozone and alkene premixing chambers, which allow well-controlled reactant mixing within two seconds. A FTIR- spectrometer for gas phase species analysis and a SMPS system for measuring particle size distributions and mass are attached to the chamber (Wolf *et al.* 2011). The aerosol particles were sampled on filters after the reaction in the chamber was finished (typically after five minutes) and the chamber was filled to ambient pressure. A methanol-water-solution was used for extraction of the filters. RP-HPLC-ESI-IT/MS<sup>n</sup> was used for analysis.

Experiments were performed at three different reaction pressures (10, 20 and 460 mbar) with almost identically concentrations of ozone (5 ppm at 1 bar) and excess  $\alpha$ -pinene. In general lower pressure yields lower particle number concentrations and smaller aerosol masses.

Therefore, the samples of the high pressure experiments at 460 mbar were used to identify the ozonolysis products. The often reported monomeric products such as terpenylic acid, pinic acid and hydroxypinonic acid were detected. About twenty dimeric compounds with a mass-to-charge ratio (m/z) between 300 and 400 were observed including the above mentioned dimers 358 and 368. For most of these dimers no confirmed or even suggested chemical structures are available in the literature. The MS/MS-experiments showed for the majority of the dimers a fragment with m/z 185 like pinic acid. Therefore, it is assumed that most of these compounds contain a pinic acid analogue or a closely related chemical structure.

The analysis of the filter samples confirmed a decreasing yield with decreasing reaction pressure for most of the compounds. Due to the lack of authentic standards for almost all substances only a semi-quantitative analysis was performed by comparison of the peak area. A roughly classification in six groups was performed (as shown in table 1).

The strong influence of pressure on the relative yields of SOA components seems to be related to the presence and absence of stabilized Criegee intermediates and different degrees of chemical activation of other intermediate species at high and low pressures. After further analysis the results are expected to provide constraints for suggested dimer formation mechanisms.

Table 1. Classification of pressure dependency. 100% represents the product yield at 460 mbar.

Group	1	2a	2	2b	3	4
10 mbar	< 1%	< 1%	1-3%	3-10%	3-25%	>50%
20 mbar	< 5%	5-20%	5-20%	5-20%	20-50%	>50%

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