Time-resolved chemical composition of chamber generated SOA originated from monoterpene oxidation

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The oxidation of biogenic volatile organic compounds (BVOCs) yields a wide range of oxidation products with multifold functional groups. Depending on the chemical and physical properties of the formed products they are able to undergo gas to particle conversion contributing significantly to the formation of secondary organic aerosol (SOA). Although several studies exist about the formation of SOA originating from the monoterpene oxidation (see review by Hallquist *et al.*, 2009) there is a gap in the knowledge about the involved species. To overcome this issue, the condensation growth and impacting system (C-GIS, Sierau *et al.*, 2003) was connected to the aerosol chamber LEAK (Leipziger Aerosol Kammer) that enables a time-resolved sampling and analysis of chamber generated SOA.

Several experiments were conducted examining the oxidation of monoterpenes (α- and β-pinene) and their first generation oxidation products (pinonaldehyde and nopinone). The oxidation was carried out using OH radicals originated from the photolysis of hydrogenperoxide (H_2O_2) as well as from the ozonolysis of tetramethylethylene (TME). All experiments were conducted in the presence of acidic seed particles (78 mM NH_4HSO_4). The generated SOA was sampled during the course of the experiment for 10 minutes using C-GIS. The suitability of C-GIS was evaluated conducting a comparison between filter measurements and C-GIS using three SOA compounds (Table 1) terpenylic acid, pinic acid, and 3-methyl-1,2,3-tricarboxylic acid (MBTCA).

Table 1. Mean value of the deviation between filter and C-GIS measurements

Compound	Deviation [%] (n=3)
Terpenylic acid	39 ± 2
Pinic acid	21 ± 4
MBTCA	48 ± 3

Despite the underestimation the data obtained by C-GIS show only small deviations from the mean value (below 5%) indicating the suitability of C-GIS for the time-resolved SOA analysis.

From the analysis of the C-GIS samples a time profile of the three SOA compounds can be obtained. It was found that terpenylic acid and pinic acid are early generation oxidation products whereas MBTCA is formed secondary.

These observations are in consistence to the literature (Claeys *et al.*, 2009, Christoffersen *et al.*, 1998). In addition, a correlation was found between the time-profile of the terpenylic acid concentration and the particle growth ΔM (Figure 1) indicating a central role of terpenylic acid for the SOA formation (Claeys *et al.*, 2009). Nevertheless, such a correlation was not found for all of the conducted experiments. Those missing correlations might be explained by additional compounds causing particle growth which are not indentified and quantified jet.

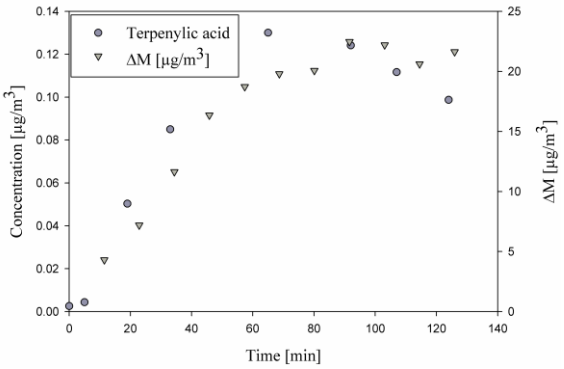

Figure 1: Relationship between the concentration profile of terpenylic acid and the particle growth during the oxidation of nopinone with OH radicals.

The decay of terpenylic acid concentration after 90 minutes of the experiments might be a result of the formation of higher molecular weight compounds (HMWCs). From the analysis it was found that a compound with *m/z* 357 is also formed which corresponds to $C_{17}H_{25}O_8$. Therefore it can be assumed that besides the central role of terpenylic acid for the particle growth it might be also an important precursor compound for the formation of HMWCs.

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