# Influence of reaction conditions on the formation of dimers and peroxides from the ozonolysis of α-pinene and the OH reaction of nopinone

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## Introduction

The formation of secondary organic aerosol (SOA) from the oxidation of biogenic volatile organic compounds (BVOC) has been studied intensively in the last decades (see review paper by Hallquist et al., 2009). Nevertheless, little is known about the products formed and the influence of the reaction conditions on the chemical composition. Among several class of compounds, peroxides and higher molecular weight compounds have been the focus of several studies. It was found that both contribute significantly to chamber generated SOA. Docherty et al., 2005 measured a peroxide content of 85% from α-pinene oxidation whereas for β-pinene oxidation a peroxide content of 47% was observed. Several types of peroxides are known such as hydroperoxides, organic peroxides, and peroxyhemiacetals. The latter two are also suggested as a bridging bond for higher molecular weight compounds that were found with up to 50% of chamber generated SOA. Dimers and peroxides are found in chamber generated SOA and ambient aerosol but the formation processes and their contribution to SOA mass remains still unclear. Therefore, a series of chamber experiments were conducted to measure the SOA bound peroxide content and to investigate the influence of the reaction conditions on the formation of SOA bound peroxides and dimers.

α-Pinene    Nopinone
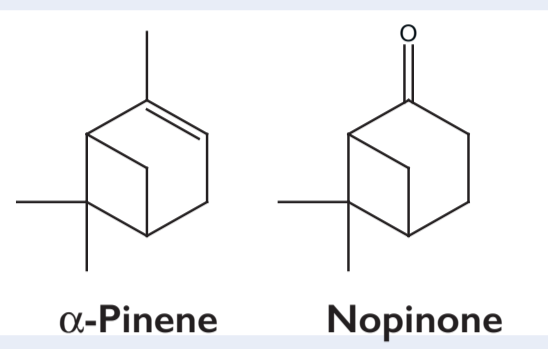
## Measurements

### Aerosol chamber experiments

Several experiments were conducted in the 19 m³ Aerosol chamber LEAK (S/V = 2 m⁻¹). The oxidation of nopinone with OH radicals was conducted using ozonolysis of tetramethylethylene (TME) as OH radical source (A). For the examination of α-pinene, the ozonolysis was conducted in the presence of carbon monoxide (CO) as OH scavenger (B).

Table 1: Experimental conditions.

| | RH % | P_ini E-6 cm³/m³ | T C |
|---|---|---|---|
| Set 1 | 0 | 20 000 | 20 ± 1 |
| Set 2 | 50 | 10 000 | 20 ± 1 |
| Set 3 | 50 | 50 000 | 20 ± 1 |
| Set 4 | 75 | 20 000 | 20 ± 1 |

The experiments were conducted at different relative humidities and initial particle volumes ($P_{ini}$). Table 1 summarises the experimental conditions. The mixing ratios of the initial precursor $HC_{ini}$ and of the formed gaseous products were measured by PTR-MS.

The time dependent particle size distribution was measured using a DMPS. After the reaction, samples were collected for 1 h and at a flow rate of 30 L min⁻¹ (total volume 1.8 m³).
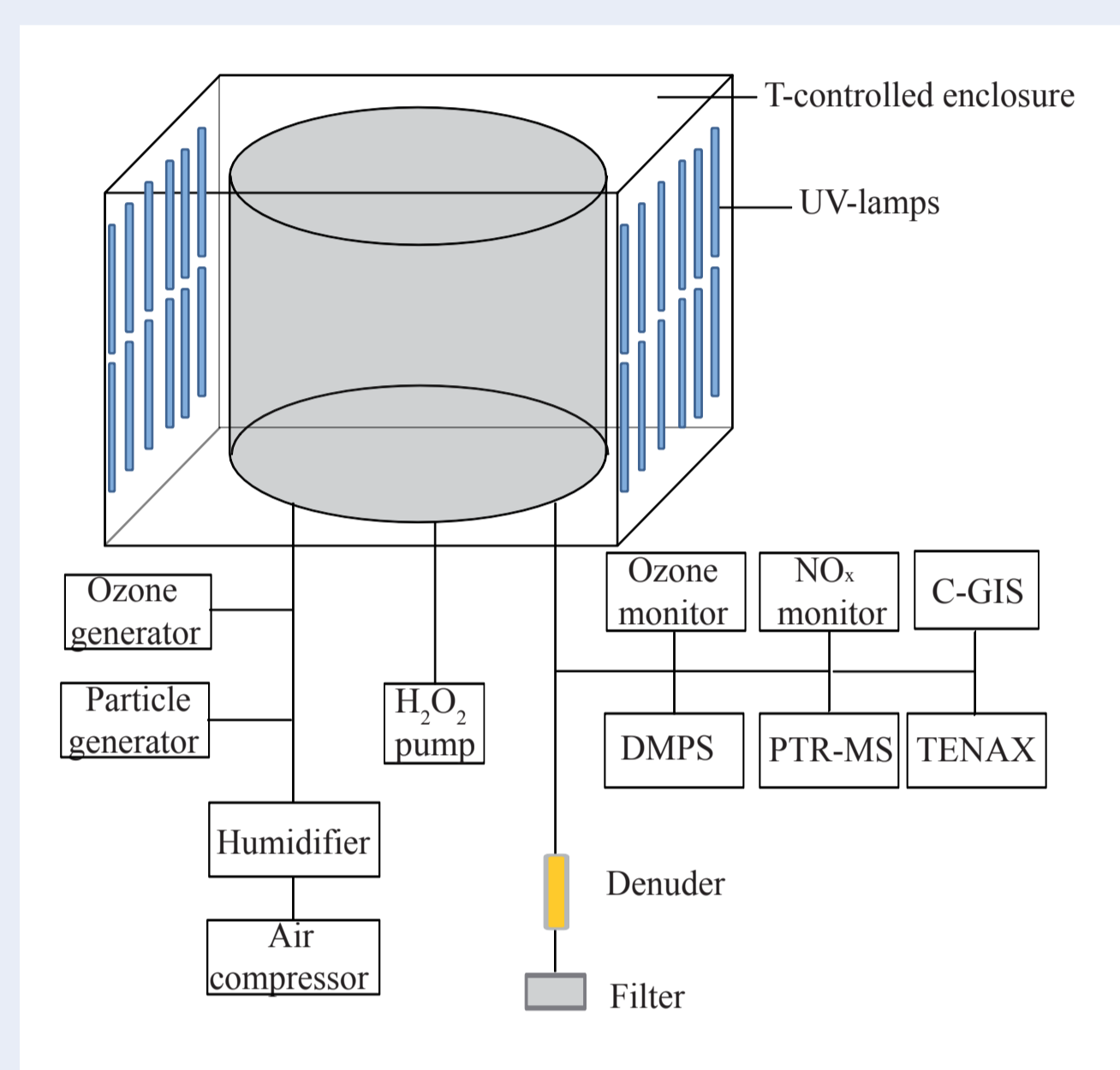
Figure 2: Aerosol chamber LEAK.

### Sampling and analytical procedures

The particle phase products were sampled on a teflon coated borosilicate filter in combination with a XAD-4/DNPH coated denuder to minimise gas absorption artefacts. The filter was analysed regarding carboxylic acids (Figure 2), dimers and the content of SOA bound peroxides. The filter was cut into small pieces and one half was extracted in methanol, dried under a nitrogen stream at 10°C and reconstituted in 200 μL methanol/water (50/50, v/v). The filter was analysed regarding carboxylic acids (Figure 2), dimers and the content of SOA bound peroxides. The extract was analysed using a HPLC/(-)ESI-TOFMS and authentic SOA standard compounds were used for their positive identification (Figure 2).

3-Methyl-1,2,3-butanetricarboxylic acid (MBTCA)    Terpenylic acid    Diaterpenylic acid acetate (DTAA)
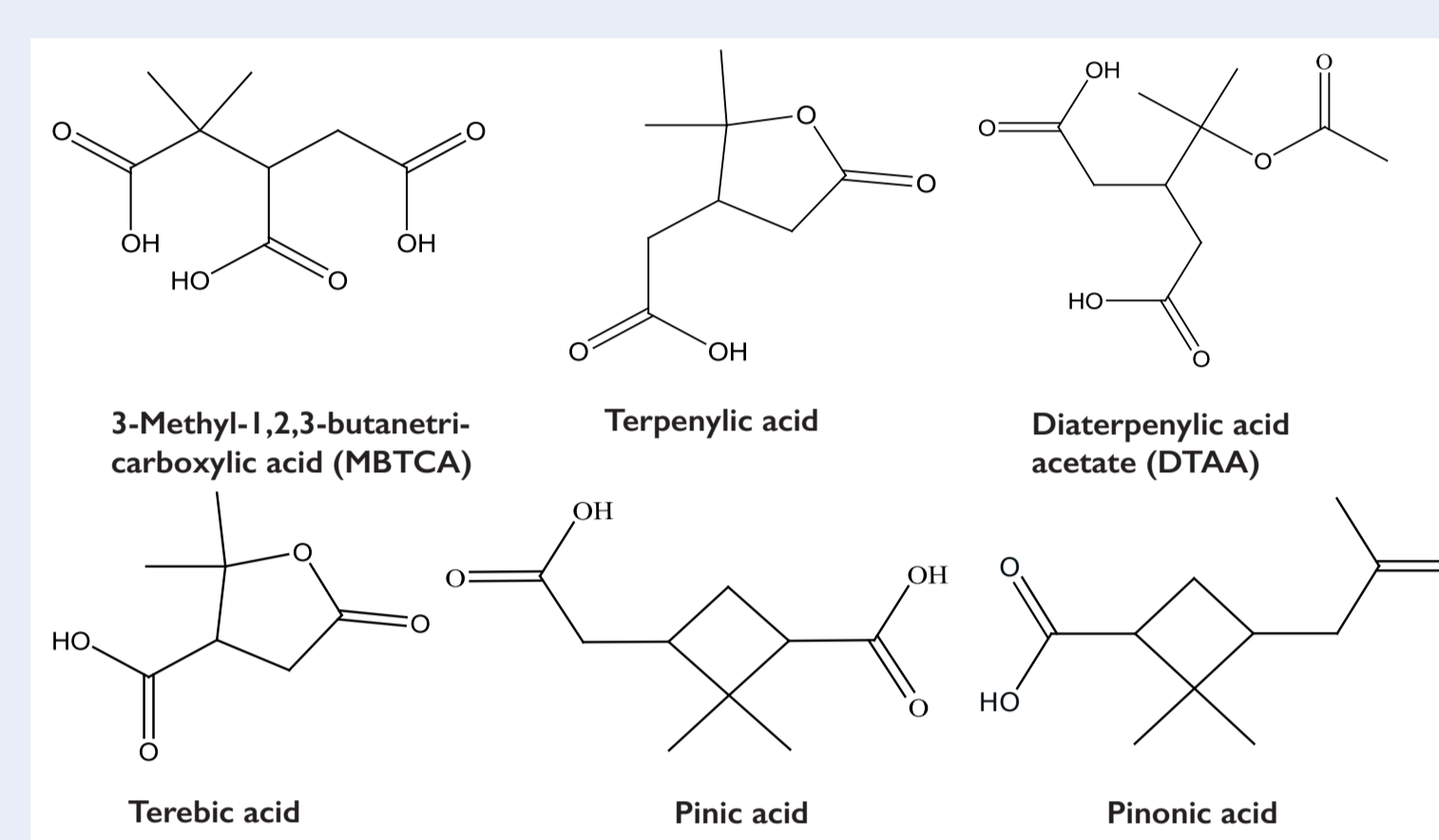
Terebic acid    Pinic acid    Pinonic acid

Figure 3: Constituents of the authentic SOA standard.

The SOA bound peroxide content was determined using an iodometric spectrophotometric method. A quarter of the filter was cut into small pieces and extracted with 3 mL water, and sparged with nitrogen for 5 minutes. While sparging 30 mg KI were added and the reaction vial was locked directly afterwards (Docherty et al., 2005). After 1 h of reaction time the sample was measured by a UV-VIS photospectrometer at λ = 351 nm and ε = 26,400 L mol⁻¹ cm⁻¹ (Awtrey and Connick, 1951).

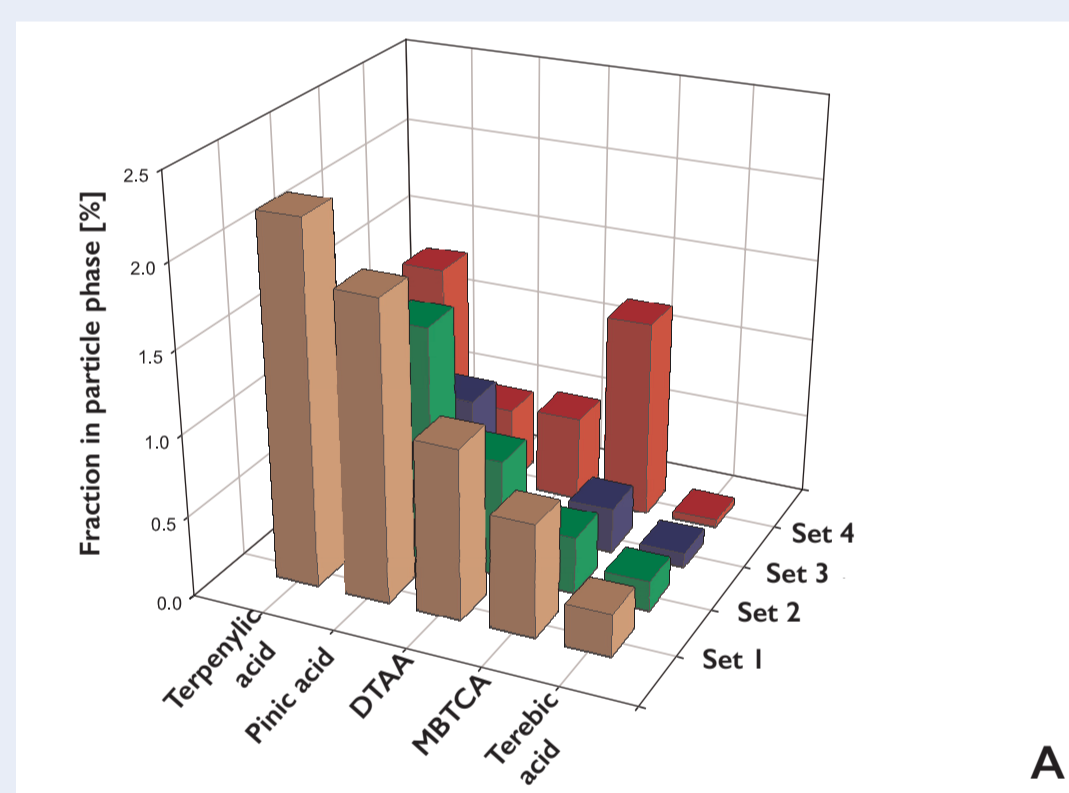## Results and Discussion

### I - Carboxylic acids

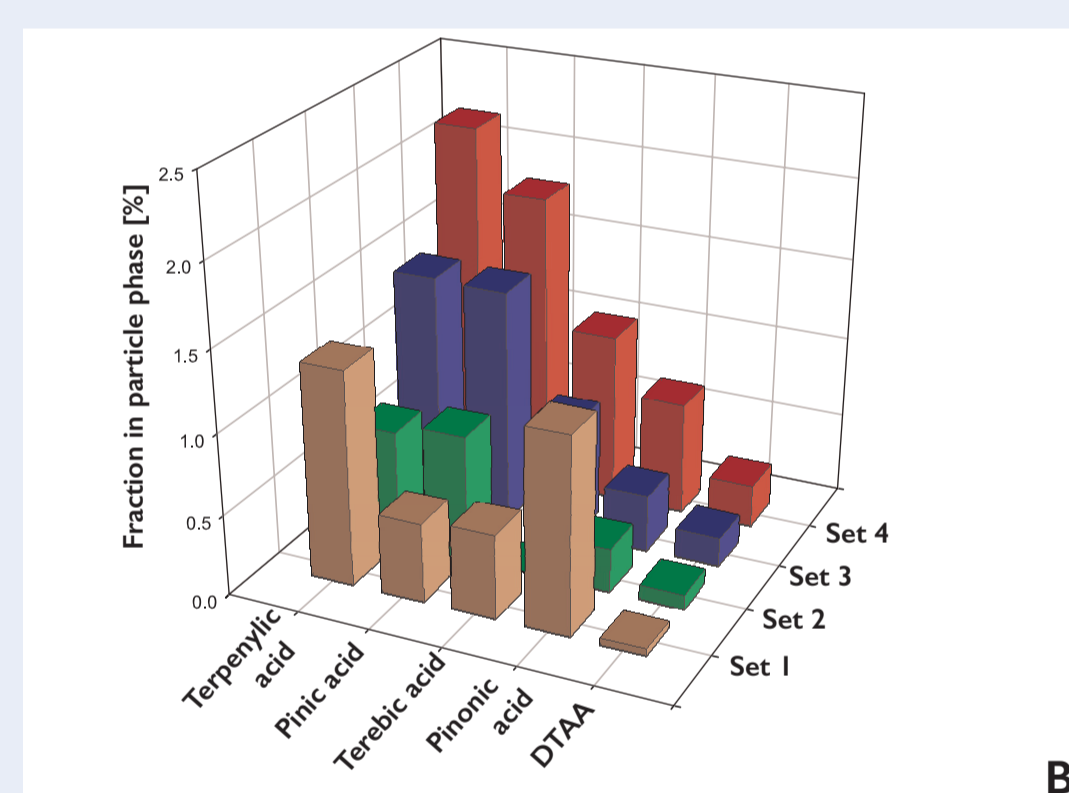Figure 4A: Identified particulate compounds from the OH radical reaction of nopinone.

Figure 4B: Identified particulate compounds from the ozonolysis of α-pinene.

➤ Terebic acid, terpenylic acid, pinic acid, and DTAA were detected from both the OH radical reaction of nopinone (A) and the ozonolysis of α-pinene (B). From the OH radical reaction of nopinone, MBTCA was found whereas pinonic acid was only detected from the ozonolysis of α-pinene.

➤ RH and $P_{ini}$ influence both reaction systems. Significantly higher amounts of the oxidation products were detected under dry conditions for the OH radical reaction of nopinone though $P_{ini}$ had little influence on the products. For the ozonolysis of β-pinene, the amounts of detected oxidation products increased with humidity and $P_{ini}$.

➤ These results indicate that water influences the formation of the detected compounds rather than their uptake behaviour.
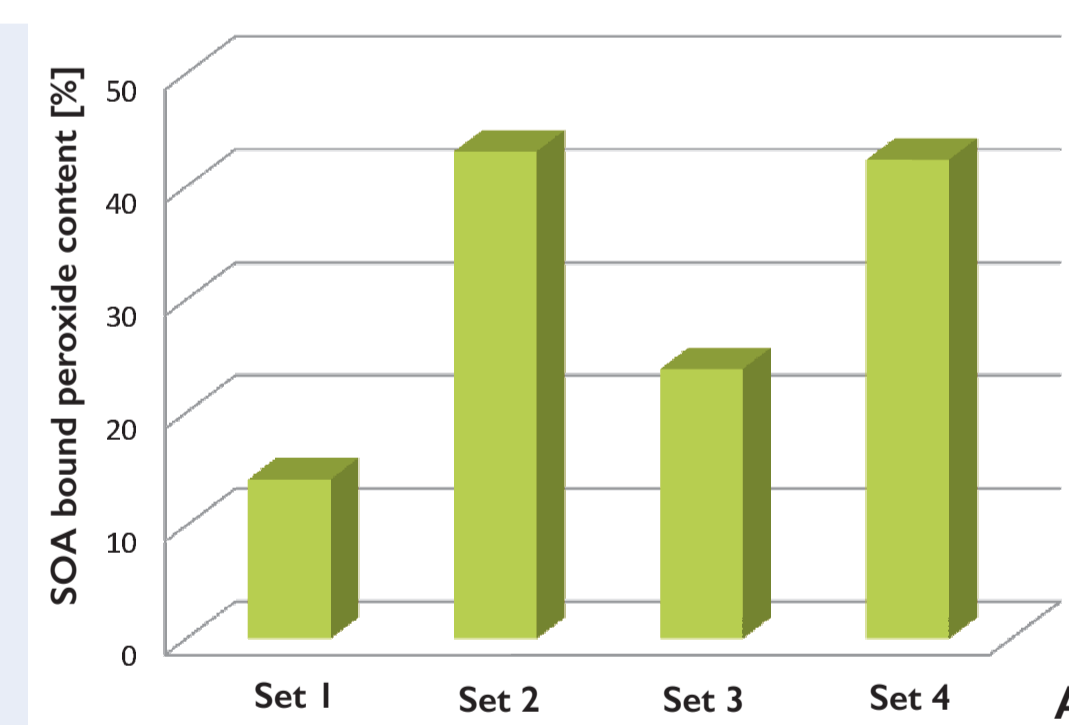
### II - Peroxides

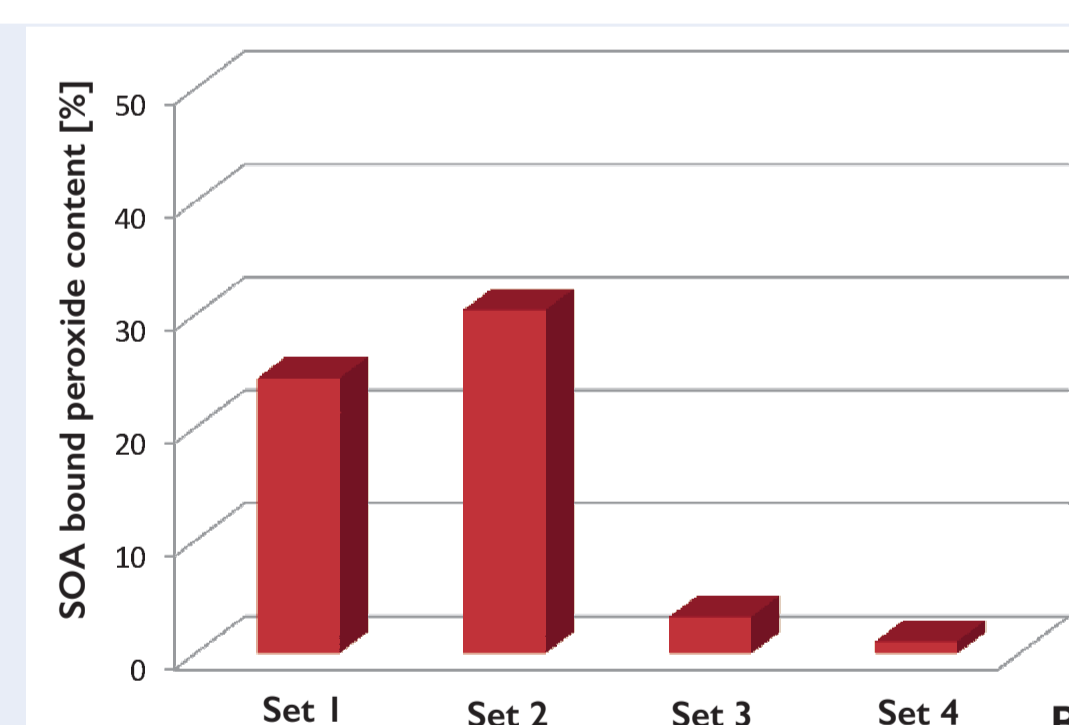Figure 5A: Content of SOA bound peroxides from the OH radical reaction of nopinone.

Figure 5B: Content of SOA bound peroxides from the ozonolysis of α-pinene.

➤ Similar dependencies on RH and $P_{ini}$ to carboxylic acids was observed for the SOA bound peroxide contents.

➤ In the OH radical reaction of nopinone the peroxide content decreased with increasing humidity and $P_{ini}$. A positive effect of both RH and $P_{ini}$ on the peroxide content was observed for the ozonolysis of α-pinene.

➤ Interestingly, a maximum at RH = 50% and low $P_{ini}$ can be found in both reaction systems indicating that the peroxide formation is enhanced under this conditions.
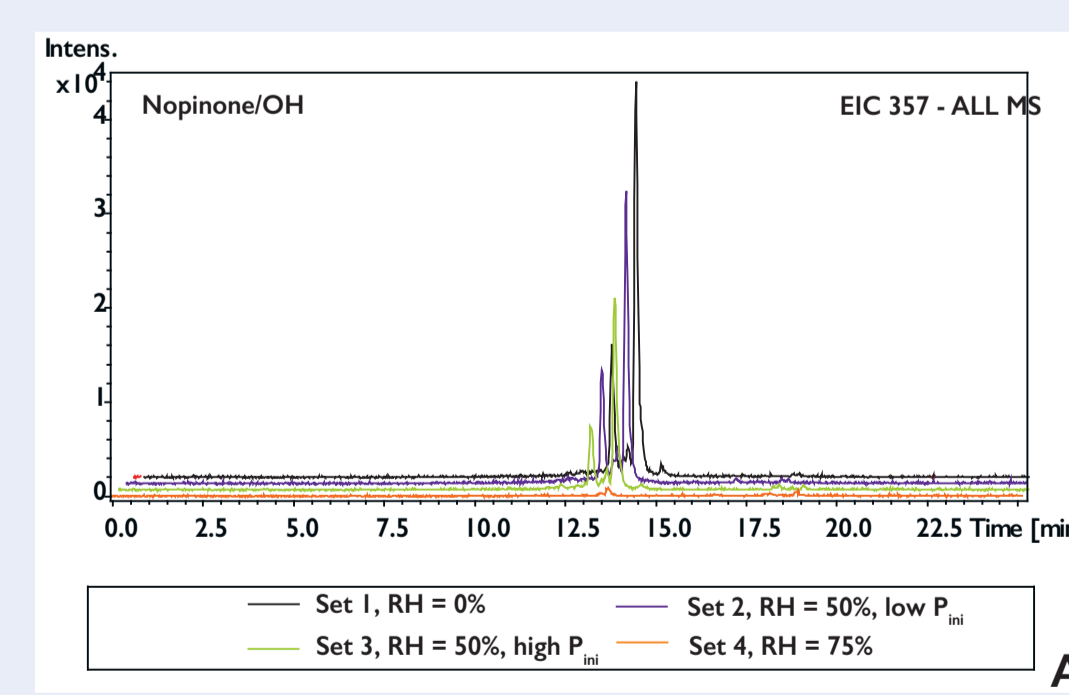
### III - Dimers

Figure 6A: Detected dimer m/z 357 ($C_{17}H_{25}O_8$) from the OH radical reaction of nopinone.
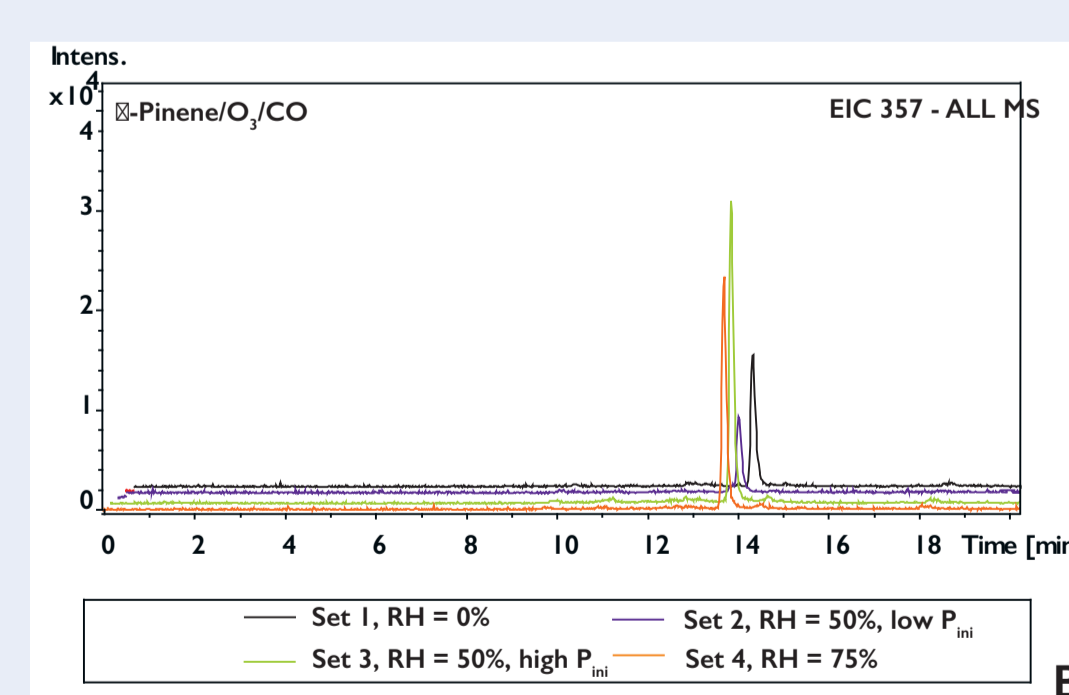
Figure 6B: Detected dimer m/z 357 ($C_{17}H_{25}O_8$) from the ozonolysis of α-pinene.

➤ Among several higher molecular weight compounds the dimer with the mass to charge ratio (m/z) of 357 with the elemental formula $C_{17}H_{25}O_8$ was detected from both investigated reaction systems.

➤ Its formation by the ozonolysis of α-pinene is affected by the experimental conditions (high RH and high $P_{ini}$) in the same manner as the carboxylic acids (Figure 4B) whereas the OH radical reaction of nopinone showed an opposite trend (low RH and low $P_{ini}$).

➤ For the α-pinene ozonolysis, no relationship can be seen between the relative abundance of the dimer (Figure 6B) and the peroxide content (Figure 5B) but a relationship was observed between the peroxides and carboxylic acids in case of the OH radical reaction of nopinone (Figure 4A, 5A and 6A).

## Acknowledgement

## References

Awtrey, A.D. and Connick, R.E., The Absorption Spectra of $I_2$, $I_3^-$, $I^-$, $IO_3^-$, $S_4O_6^{2-}$ and $S_2O_3^-$. Heat of the Reaction $I_3^- = I_2 + I^-$. Journal of the American Chemical Society 1951, 73 (4), 1842-1843.
Docherty, K. et al., Contributions of Organic Peroxides to Secondary Aerosol Formed from Reactions of Monoterpenes with $O_3$. Environmental Science and Technology 2009, 39, 4049 - 4059.
Hallquist, M. et al., The formation, properties and impact of secondary organic aerosol: current and emerging issues. Atmospheric Chemistry and Physics 2009, 9, 5155-5236.

## Conclusion

➤ Similar products were observed from both investigated systems though the dependencies on the reaction conditions (RH and $P_{ini}$) showed different behaviour. Carboxylic acids and SOA bound peroxides were found as major particle phase constituents with a peroxide fraction of 42% for the α-pinene ozonolysis and 24% for the nopinone OH radical reaction, respectively.

➤ The observed influence of RH and $P_{ini}$ indicates that water plays a significant role in the formation of the detected carboxylic acids, peroxides and dimers rather than for their uptake behaviour.

➤ For the α-pinene ozonolysis, no relationship between the dimer m/z 357 and the peroxide content was found. On the other hand, a relationship was observed for the nopinone/OH system. This could result from different formation processes or a different structure of the detected dimer.