

Oxidation of nopinone - Influence of relative humidity and particle acidity on particulate products

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The oxidation of biogenic volatile organic compounds (BVOCs) leads to the formation of low volatile compounds. Especially, the formation of secondary organic aerosol (SOA) from the oxidation of monoterpenes has been investigated extensively in the past years (see a review paper by Hallquist et al., 2009). The first generation oxidation products of monoterpenes are still volatile and are further oxidized in the gas phase to form a wide range of products that contribute to SOA formation. Although, a spate of studies report SOA products from monoterpene oxidation, little is known about the influence of relative humidity and seed particle acidity on the formation of monomeric and oligomeric compounds from the first generation oxidation products.

In the present study, we conducted a series of chamber experiments to study the influence of the reaction conditions on the formation and composition of SOA in the OH radical reaction of nopinone (Table 1). Nopinone is one of the first generation products that originates from β -pinene oxidation. Three different reaction parameters were examined: seed particle acidity, relative humidity and NO_x mixing ratio. Each set of experiment was performed using two different OH sources: the ozonolysis of tetramethylethylene and the photolysis of methylnitrite in the presence of nitrogen oxide.

Table 1. Conditions for the oxidation of nopinone.
(Initial mixing ratio 50 ppb, temperature $20 \pm 1^\circ\text{C}$)

Relative humidity [%]	Set 1 (0.07M)	Set 2 (0.076M/0.003M)	Set 3 (0.04M)
0	Na_2SO_4	$(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$	NH_4HSO_4
50	Na_2SO_4	$(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$	NH_4HSO_4
80	Na_2SO_4	$(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$	NH_4HSO_4

The formed particulate products were collected using a denuder/PTFE filter sampling device. The filter were extracted and analyzed using HPLC/(-)ESI-TOFMS. The analysis of the particle-phase revealed a number of monomeric and oligomeric compounds.

The major monomeric products were detected at the mass to charge ratios (m/z) 157, 171, 185, 203 and 231 corresponding to terebic acid, terpenylic acid (Claeys, 2009), pinic acid, 3-methyl-1,2,3-butanetricarboxylic acid (Szmigielski, 2007) and diaterpenylic acid acetate (Iinuma, 2009). These compounds are not influenced by relative humidity or particle acidity but their yields decreased in the presence of NO_x .

A decrease in the yield of monomeric compounds and the associated decrease in SOA mass in the presence of NO_x can be explained by the favoured production of more volatile compounds such as aldehyds over low volatile acidic compounds due to the reaction of the alkylperoxyradical (RO_2) with NO (Kroll and Seinfeld, 2008).

The analysis of the higher molecular weight compounds indicates two major oligomeric products with m/z 357 and 371, corresponding to $\text{C}_{17}\text{H}_{25}\text{O}_8$ and $\text{C}_{18}\text{H}_{27}\text{O}_8$, respectively. Both compounds showed an influence of NO_x levels and particle phase acidity though only m/z 371 compound was influenced by relative humidity. In the presence of NO_x the formation of both compounds was reduced. The highest amount of the m/z 371 compound was observed under higher relative humidity and in the presence of strongly acidic particles, indicating that this compound likely formed through acid catalysed accretion reaction. Surprisingly, an opposite behaviour was observed for the m/z 357 compound, which decreased in the presence of acidic particles. This observation gives a hint that the formation of this compound is either not related to acid catalysed accretion reaction or decomposed in the presence strong acidity.

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Claeys, M. *et al.*, (2009), *Environ. Sci. Technol.* **53**, 6976-6982

Hallquist, M. *et al.*, (2009) *Atmos. Chem. Phys.* **9**, 5155-5236

Iinuma, Y. *et al.*, (2009), *Environ. Sci. Technol.* **43**, 280-285

Kroll, J.H. and Seinfeld, J.H. (2008) *Atmos. Environ.* **42**, 3593-3624

Szmigielski *et al.*, (2007) *Geophys. Res. Lett.* **34**, L24811, DOI: 10.1029/2007GL031338