Evidence of organic hydroperoxides derived from the ozonolysis of α- and β-pinene measured by on-line atmospheric pressure chemical ionization mass-spectrometry

M.-C. Reinnig, J. Warnke and T. Hoffmann

Department of inorganic chemistry and analytical chemistry, Johannes Gutenberg University, Duesbergweg 10-14, 55128 Mainz, Germany

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Because of its potential effect on climate and health secondary organic aerosol (SOA) is subject of intensive research. The formation of secondary aerosols in the atmosphere takes place when volatile compounds react to low volatile substances. These substances can condense on existing particles or they may even generate new particles. An important source of SOA is the ozonolysis of monoterpenes emitted by plants.

Latest studies predict that a major fraction of SOA from monoterpane ozonolysis consists of organic peroxydes and hydroperoxides (Docherty, et al. 2005). Due to their reactivity organic peroxydes may have effects on human health. These peroxydes might also be involved in the formation of oligomers in the particle phase. Possible reaction pathways leading to organic peroxydes were presented in the literature (Jenkin, et al. 2000; Jenkin 2004; Docherty, et al. 2005), but distinct identifications of certain peroxyde structures in SOA are rare. However, there is little knowledge and understanding of the contribution, the reaction and degradation pathways of peroxydes in SOA.

For this reason chamber experiments were carried out to investigate the formation of organic peroxydes during the reaction of α- and β-pinene with ozone. Particles formed in these reactions were studied in real time using an on-line ion trap mass spectrometer with an atmospheric pressure chemical ionization (APCI) source. Here, APCI in the positive ion mode enables the detection of quasi-molecular ions ([M+H]+) of the formed SOA. Organic peroxydes containing a hydroperoxy group could be identified in the particle phase, showing a characteristic loss of m/z 34 (H2O2) in their MS/MS-spectra. Figure 1 shows the on-line APCI(+) mass spectra of a protonated hydroperoxid product (MW: 172Da) derived from the α-pinene/ozone reaction.

Figure 1. On-line APCI(+)-MS² fragment spectra of a protonated hydroperoxid product (MW: 172Da) derived from the α-pinene/ozone reaction

Figure 2. Proposed peroxy structure observed in the reaction of α-pinene with ozone