Investigation of realistic long term isoprene atmospheric photooxidation in simulation chamber

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Isoprene (2-methyl-1,3-butadiene, C_5H_8) is one of the most abundant non-methane hydrocarbons emitted into the troposphere. Its annual global emission has recently been estimated in the range of 440 to 660 TgC (1). Because of its large concentrations and high reactivity with the hydroxyl radical (OH), isoprene can have a strong influence on tropospheric photochemistry. It has been determined recently that isoprene also plays a role in secondary organic aerosol (SOA) formation in the ambient atmosphere even if isoprene leads to low SOA yields. The aim of the present work was to study isoprene photooxidation with OH radical in order to investigate its oxidation products and resulting aerosol production. A special care was taken to the realism of the experiment: light source, NOx level, OH source and aging time (around 10 hours).

To do so, experiments were performed in CESAM chamber at LISA, specifically designed to investigate multiphase processes with a highly realistic irradiation compared to solar radiation (2). Connected to the chamber, a large panel of instruments was used to monitor the gas-phase and the particulate phase during experiments. Gas-phase composition was analysed in-situ via a Fourier Transform Infrared Spectrometer (FTIR) and a Proton Transfer Reaction Mass Spectrometer (PTR-TOF-MS) as well as NO_x and O₃ analyzers. A Scanning Mobility Particle Sizer (SMPS, diameter range 20-800 nm) measured SOA size distributions and total concentrations inside the chamber. An Aerodyne aerosol mass spectrometer (TOF-AMS) was also used to investigate aerosol composition. In each experiment, around 500 ppb of isoprene was injected in the chamber before irradiation. During all the experiment, a very low continuous flow of NO was injected in order to mimic atmospheric emission and maintain oxidation rate, thanks to its propagating role. It therefore allowed us to investigate not only isoprene chemistry but also the fate of its products. Some experiments were carried out with initial ammonium sulfate seed aerosols.

The major gas-phase oxidation products of isoprene we measured, in low NO conditions, are formaldehyde, methacrolein and methyl vinyl ketone identified as first-generation products, and also methylglyoxal and peroxyacyl nitrates (PAN and MPAN), identified as second-generation products. NO₂ to NO ratios, yields of all measured oxidation products and carbon budget were calculated. In all experiments, we noted a SOA production at the end of isoprene oxidation i.e. exhibiting a clear secondary products type growth. The gas-phase composition as well as the aerosol yields obtained during these experiments have been compared to results simulated by an explicit 0D photochemical box model (including around 20000 reactions). The goal of this work was to assess whether or not the processes contained in current chemical mechanisms enable to reproduce observations in the gas-phase.

References

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