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Aerosol Nucleation and Growth in a Mixture of Sulfuric Acid / Alpha-Pinene Oxidation Products at the CERN CLOUD Chamber

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Abstract. The role of α-pinene in aerosol nucleation and growth was investigated using the CERN CLOUD chamber, a nano scanning mobility particle sizer (nanoSMPS) and several condensation particle counters (CPCs) with different diameter cut-offs. Different oxidation conditions for α-pinene – OH· vs. ozone oxidation – were considered to investigate their contributions to particle nucleation and growth. Results from the latest CERN experiment from fall 2012 (CLOUD 7) are presented.

Keywords: aerosol nucleation, aerosol growth, alpha-pinene, oxidized organics, CLOUD
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INTRODUCTION

Aerosol nucleation has been observed at many different locations and altitudes under varying atmospheric conditions (Kulmala et al., 2004). It is well known that aerosol nucleation and the growth of newly nucleated aerosols by condensation affects the properties of atmospheric aerosols and hence eventually influences the Earth's climate. However, aerosol nucleation and growth are not yet fully understood. Earlier studies of the CLOUD (**C**osmics **L**eaving **OU**tdoor **D**roplets) chamber have shown that at cold temperatures ambient observations can be explained by ternary nucleation of water (H_2O), ammonia (NH_3) and sulfuric acid (H_2SO_4). However, at warmer temperatures, additional aerosol precursors are needed to understand the nucleation and growth rates observed in the field (Kirkby et al, 2011).

For this reason the latest CLOUD experiment focused on the role of organics in aerosol nucleation and growth. For this purpose numerous experiments with α-pinene were conducted at the CERN CLOUD chamber. Different oxidation conditions for α-pinene were examined and aerosol nucleation and growth with different mixtures of

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sulfuric acid and α-pinene oxidation products were investigated. Several instruments were used (see Table 1) to gain as much information as possible from these complex experiments. The presented results focus on nucleation and growth rates and are derived from the nano scanning mobility particle sizer (nanoSMPS) and several condensation particle counters (CPCs).

TABLE 1. Selection of CLOUD 7 instrumentation for analysis of nucleation and growth rates

Output	Instrumentation
nucleation and growth rates	nano scanning mobility particle sizer (nanoSMPS), condensation particle counter (CPC) and laminar diffusion tube (LDT)
sulfuric acid concentration	chemical ionization mass spectrometer (CIMS) and chemical ionization atmospheric pressure interface time of flight mass spectrometer (CI-APi-TOF)
α -pinene concentration	proton-transfer-reaction mass spectrometer (PTR-TOF)
organics concentration	CI-APi-TOF and APi-TOF (atmospheric pressure interface - time of flight - mass spectrometer)

METHODS

Experimental Setup

α-pinene oxidation experiments were performed using the CERN CLOUD chamber, which allows to conduct experiments very close to atmospheric conditions and with a very low contaminant background. Chamber conditions were set to a relative humidity of 38% and a temperature of 5°C. Atmospheric concentrations of SO_2, O_3, HONO, H_2O and α-pinene were established in the chamber as shown in Table 2.

TABLE 2. Experimentally relevant gases and their range of set concentrations. Contaminant ammonia (NH_3) and dimethylamine (DMA) concentration were below the detection limit.

Chamber Gases	Minimum Concentration	Maximum Concentration
SO_2	0.5 ppbv	70 ppbv
O_3	below detection limit	25 ppbv
HONO	below detection limit	2 ppbv
α-pinene	100 pptv	1600 pptv

Oxidation of α-pinene was achieved using: (1) OH· radicals, (2) ozone with OH· scavengers (pure ozonolysis) and (3) OH· and ozone. H_2 was used as OH· scavenger with a concentration of 0.1%. In addition, SO_2 was present in the chamber as a precursor of sulfuric acid. To enable photochemical reactions, a UV light source with optical fibers was used to provide the necessary light intensity. To further enhance the intensity of UV light, a UV light saber could additionally be installed inside the chamber.

To investigate the effect of OH·, α-pinene was oxidized by photochemical reactions (producing OH· via HONO + hυ → OH· + NO) initiated by the UV fiber system in the chamber. For this experiment no O_3 was injected into the chamber to avoid ozonolysis.

In the absence of OH· radicals, pure ozonolysis of α-pinene was observed. For this purpose O_3 and the OH· scavenger H_2 were injected into the chamber.

For the determination of the aerosol number concentration TSI CPCs 3010 and 3776 were used with 50% cut-off diameters of approximately 12 nm and 2.5 nm, respectively. In addition, the LDT was used to assess the particle number concentration by varying the make-up flow for the sampling line and, thus, the 50% cut-off diameter. For measuring the aerosol particle number size distribution between 5 and 80 nm a nanoSMPS was used. Chamber conditions were either charged or neutral. Ion concentrations of around 3000 cm^{-3} were achieved using CERN's proton synchrotron. Neutral conditions were possible using a strong HV field cage (30 kV), which removes all charged particles in the chamber.

Data Analysis

The analysis of nucleation and growth rates includes data from the nanoSMPS, TSI CPC 3776 and LDT. Growth rates were retrieved from the nanoSMPS (for particle sizes larger than 5 nm) and LDT (for particle sizes below 5 nm). Nucleation rates were determined using the TSI CPC 3776 concentration. Further analysis will include a correction for CPC efficiency and loss mechanisms such as diffusion in the CPC sampling line and wall losses in the CLOUD chamber (see Riccobono et al., 2012).

RESULTS

For all oxidation conditions, aerosol nucleation and growth have been observed and investigated. An example of a pure α-pinene ozonolysis experiment with several subsequent nucleation events can be seen in Figure 1, showing exclusively the effect of ozonolysis.

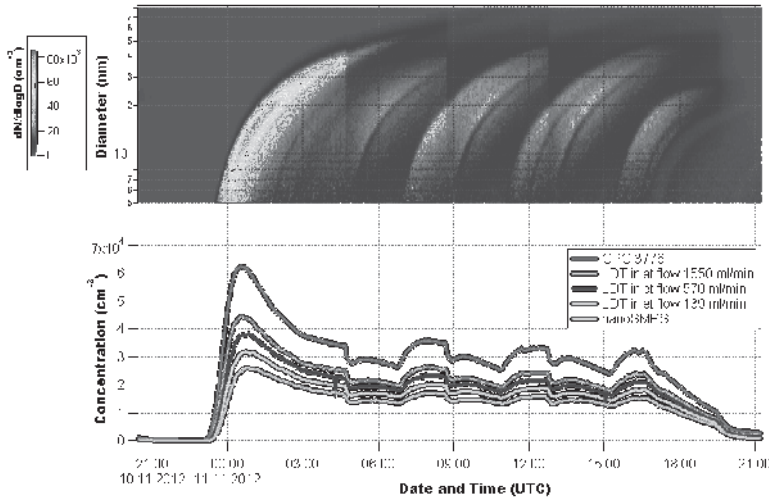

FIGURE 1. NanoSMPS particle size distribution of a nucleation and subsequent growth (top), and the aerosol concentration as measured by the TSI CPC 3776, the LDT with different flows, and nanoSMPS (bottom), for a pure ozonolysis experiment. Sharp decreases in the aerosol concentration yield from applying the cleaning field, removing all charged particles.

OUTLOOK

Nucleation and growth rates will be presented as a function of the concentrations of sulfuric acid and oxidized organics. Additionally, differences between the oxidation conditions will be emphasized. Further analysis will also include a consideration of the possible influence of ions compared to neutral conditions.

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