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Citation: AIP Conference Proceedings **1527**, 363 (2013); doi: 10.1063/1.4803278
View online: http://dx.doi.org/10.1063/1.4803278
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1527?ver=pdfcov
Published by the AIP Publishing

Contribution of oxidized organic compounds to nanoparticle growth

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Abstract. Nucleation and subsequent growth of particles was studied in the CLOUD7 chamber experiment at Cern. Experiments were performed in varying concentrations of sulphuric acid, ammonia, dimethylamine and α-pinene, and using both ozone and hydroxyl radicals as oxidizers. Particle growth rates were determined at size ranges <1.5 nm, 1.5–3 nm, and >3nm. Comparison of the growth to the amount oxidized organics in the mass range 300–450 amu was made.

Keywords: Nucleation, Growth, α-pinene, Ozonolysis, Oxidized organics
PACS: 92.60.Mt, 82.70.Rr

INTRODUCTION

Nucleation and the growth of the nucleated aerosol particles are one of the key phenomena associated with the atmospheric aerosol system. Many field studies have shown that nucleation occurs frequently in the continental boundary layer and also in free troposphere [1]. The specific nucleation and growth mechanisms are currently a topic of very active research, and key compounds that have been identified to take part in these processes are sulphuric acid, ammonia, amines and various organic compounds and their oxidation products.

In atmospheric conditions it is typically observed that growth of the nucleated particles cannot be explained by the sulphuric acid concentration alone, but condensation of some other vapor or vapors is also needed. One candidate for these vapors are oxidation products of organic vapors. Various volatile organic compounds (VOCs) are emitted by vegetation, and in the atmosphere these VOCs are oxidized mainly by ozone, OH and NO_3 into lower volatility compounds that are able to condense on particles. From long-term observations at a boreal forest station in Central Finland, it has been observed that particle growth rates are clearly highest at summertime at the same time as emissions of VOCs are also largest during the year [2].

The CLOUD experiment is conducted at Cern using a 26 m^3 stainless steel chamber. The conditions and vapor concentrations inside the chamber can be carefully controlled [3]. The experiments presented in this work were performed during

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AIP Conf. Proc. 1527, 363-366 (2013); doi: 10.1063/1.4803278

CLOUD7 campaign in October–December, 2012. The nucleation and growth of new particles was studied in the presence of various trace gases, including sulphuric acid (concentration 10^6-10^7 cm^{-3}), ammonia (0-35ppt), dimethylamine (0-40 ppt) and α-pinene (0–1000 ppb).

DATA AND METHODS

The growth of the nucleated nanoparticles initially of size around 1.7 nm was followed with several instruments in the CLOUD7 campaign, starting from cluster sizes and continuing to several tens of nanometers, depending on the experimental conditions. Condensation particle counters with different cut-offs give the times when the concentrations are observed to rise, corresponding to particles growth above the detection limits of the instruments. Here we used data from Particle Size Magnifier (PSM) operated at a scanning mode [4]. The growth rate was determined from the appearance times of particles to different cut-off sizes of the PSM in the size range 1.3–3 nm. Particle growth can also be followed from measured number concentration size distributions. The Neutral cluster and Air Ion Spectrometer (NAIS) detects charged particles in the 0.8–42 nm size range and also neutral particles in the 2–42 nm size range [5]. The Scanning Mobility Particle Sizer measured size distributions in the size range 4–80 nm. From these size distribution data the peak of the nucleation mode can be followed, or the concentration maxima in the each of the size bins, and the particle growth rate is obtained by a linear least-squares fit to the data points of peak-size as function of time [6].

The chemical ionization atmospheric pressure interface time-of-flight mass spectrometer (CI-APi-TOF) was used to observe sulfuric acid and other acidic compounds. CI-APi-TOF consists of a high-resolution mass spectrometer and a chemical ionization inlet, where the chemical ionization occurs at atmospheric pressure via proton transfer between nitrate ions and its clusters and sulfuric acid. The nitrate ions are created by soft x-ray source.

RESULTS

Several nucleation and growth experiments were performed during CLOUD7 at varying conditions. α-pinene ($C_{10}H_{16}$) was used as a representative VOC compound. Pure ozonolysis of α-pinene was studied by removing OH radicals with addition of H_2 into the chamber. The OH oxidation products of α-pinene were studied by producing OH from the photolysis of nitrous acid HONO, and suppressing the chamber ozone concentration. Additional experiments were performed where both O3 and OH were present in the chamber. The monomers of oxidized organics (oxidation reaction products of α-pinene) were considered to be organic compounds between mass-to-charge values from 300 to 450 Th detected with the CI-APi-TOF. The high mass resolution of the instrument makes it possible to accurately determine atomic compositions of individual peaks in the mass spectra and thus identify compounds.

Figure 1 shows an example of a nucleation experiment in the presence of sulphuric acid, dimethylamine and α-pinene. The oxidation mechanism during this run was pure

ozonolysis. The particle growth below 2 nm can be followed from the time delays in the rise of particle concentrations measured by PSM at varying cut-off sizes (top panel), and in the larger sizes from the evolution of size distributions measured by NAIS (bottom panel). In this case the particle growth rates as function of particle size was determined to be 2.2 nm h^{-1}, 2.8 nm h^{-1} and 3.2 nm h^{-1} in size ranges <3nm, 3–7 nm and 7–15 nm. The increased growth rate of the larger particles is similar to many observations of atmospheric particle growth rates [2].

A detailed analysis of several nucleation experiments performed in varying vapor concentrations and using different oxidizers will be presented.

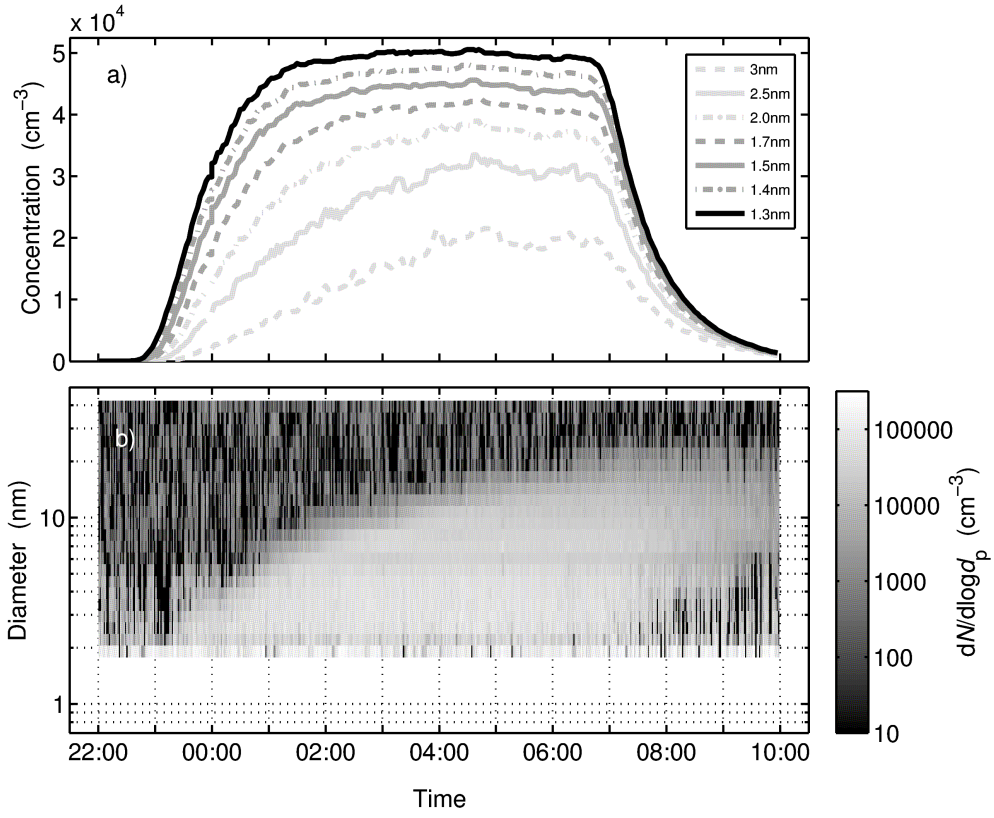

FIGURE 1. The total particle concentrations at different cut-off sizes measured with PSM (top panel), and particle number size distributions measured with NAIS (bottom panel).

ACKNOWLEDGMENTS

We would like to thank CERN for supporting CLOUD with important technical and financial resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC Seventh Framework Programme (Marie Curie Initial Training Network "CLOUD-ITN" no. 215072, MC-ITN "CLOUD-TRAIN" no. 316662, and ERC-Advanced "ATMNUCLE" grant no. 227463), the German Federal Ministry of Education and Research (project nos. 01LK0902A and 01LK1222A), the Swiss National Science Foundation (project nos. 200020_135307 and 206620_130527), the Academy of Finland (Center of Excellence

project no. 1118615), the Academy of Finland (135054, 133872, 251427, 139656, 139995, 137749, 141217, 141451), the Finnish Funding Agency for Technology and Innovation, the Nessling Foundation, the Austrian Science Fund (FWF; project no. P19546 and L593), the Portuguese Foundation for Science and Technology (project no. CERN/FP/116387/2010), the Swedish Research Council, Vetenskapsrådet (grant 2011-5120), the Presidium of the Russian Academy of Sciences and Russian Foundation for Basic Research (grants 08-02-91006-CERN and 12-02-91522-CERN), and the U.S. National Science Foundation (grants AGS1136479 and CHE1012293).

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