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# Evolution of $\alpha$ -Pinene Oxidation Products in the Presence of Varying Oxidizers: Negative APi-TOF Point of View

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**Abstract.** Laboratory experiments conducted in the frame of the CLOUD project at CERN investigated the oxidation of  $\alpha$ -pinene oxidation products in a carefully controlled environment and with different oxidation conditions: 1) pure ozonolysis (with the use of an hydroxyl radical ( $\cdot$ OH) scavenger), 2) ozonolysis without use of a scavenger, and 3) pure  $\cdot$ OH oxidation using nitrous acid (HONO) to produce  $\cdot$ OH. The anions and negatively charged clusters present in the chamber were analyzed and their chemical composition compared for the different oxidation pathways.

**Keywords:** atmospheric nucleation, charged clusters, APi-TOF,  $\alpha$ -pinene, ozonolysis, hydroxyl radicals, chamber experiments

**PACS:** 36.40.Wa,36.40.-c,82.33.Tb,82.80.Rt,92.60.Mt

## INTRODUCTION

$\alpha$ -Pinene is a representative compound of monoterpenes — a class of biogenic volatile organic compounds — and has been extensively studied, due to its important secondary organic aerosol (SOA) formation potential [1, 2, 3, 4]. It can be oxidized by hydroxyl radicals ( $\cdot$ OH), the most important oxidizing species of the atmosphere, and also by ozone ( $O_3$ ) due to the double-bond present in its structure. The products of  $\alpha$ -pinene oxidation have been the focus of many studies in the last decades [5, 6, 7, 8]. Ozonolysis yields  $\cdot$ OH, so that pure ozonolysis oxidation products can only be identified if an  $\cdot$ OH-scavenger has been used. Products from pure  $\cdot$ OH-oxidation have been studied in details as well [9, 10, 11]. Recently, Ehn et al. [12] reported highly oxidized compounds found in ambient air and during chamber experiments from online measurements.

The project CLOUD investigates new particle formation processes under controlled conditions close to atmospherically ones [13]. This study presents nucleation events from sulfuric acid ( $H_2SO_4$ ) and  $\alpha$ -pinene oxidation products from the point-of-view of negative atmospheric pressure interface time-of-flight (APi-TOF) mass spectrometer. It allows to investigate the chemical composition of the ions present in the chamber and of the charged clusters formed, that have a diameter smaller than 2 nm.

## EXPERIMENTAL

The CLOUD chamber is a 26 m<sup>3</sup> reactor used to investigate new particle formation processes simulating various atmospherically relevant conditions [13]. The temperature can be precisely controlled ( $\pm 0.01$  K), as well as relative humidity ( $\pm 0.1$  %). Trace gases levels can be introduced and monitored at very low and atmospherically relevant levels (ppbv and below). Contaminants levels are usually extremely low. The chamber volume can be illuminated by a ultraviolet fiber system to trigger photo-oxidation [14]. Additionally, one of the main feature of the chamber is the possibility to control the ion concentration using a pion beam from the CERN Proton Synchrotron (PS), simulating the intensity of galactic cosmic rays (GCR) at different altitudes. Neutral conditions can also be achieved using a clearing electric field to get rid of the natural GCR reaching the chamber when the pion beam is not used. Comparison between charged and neutral runs can disentangle the charged from the neutral effects on nucleation rates.

In order to investigate the different oxidation paths of  $\alpha$ -pinene ( $\cdot\text{OH}$  and  $\text{O}_3$ ) during the early stages of particle formation, the following different measurement conditions were used:

1. ozone ( $\text{O}_3$ ) only, using hydrogen ( $\text{H}_2$ ) as a  $\cdot\text{OH}$ -scavenger
2.  $\cdot\text{OH}$  only, produced by photolysis of nitrous acid (HONO)
3.  $\text{O}_3$  without use of  $\cdot\text{OH}$ -scavenger, thus combined  $\cdot\text{OH}$  and  $\text{O}_3$  oxidation

$\alpha$ -Pinene levels ranged from 0 to 1600 pptv and  $\text{SO}_2$  levels ranged from 1.5 to 70 ppbv, while ammonia, amines and other organic contaminants were only present at background levels. The experiments were performed at 38 % RH and 278 K. An extensive suite of state-of-the-art instrumentation is used to carefully analyze the new particle formation events from the particle size point of view, but also monitoring the chemical composition of the gas phase and the newly formed particles. This work focus on the results of the anions composition analysis measured with an API-TOF mass spectrometer used with negative polarity. This instrument was recently developed to retrieve the chemical composition of atmospheric ions and clusters [15]. This study presents the measurements performed with negative polarity to analyze anions present in the chamber and negatively charged clusters. Unlike other studies from the bulk chemical composition of SOA, early stage of particle formation involving oxidized organic compounds are reported here.

## RESULTS AND DISCUSSION

The high-resolution analysis allowed by the TOF mass analyzer provides chemical formula of the formed products from the different oxidation conditions. Therefore important organic compounds binding to sulfate ions can be identified for example. This is necessary to propose mechanistic pathways involving the different oxidizers.

With the presented experiment design, it is possible to disentangle which oxidation products are formed by  $\cdot\text{OH}$  or  $\text{O}_3$  oxidation. As a more realistic simulation, runs with both species present were performed. Compounds formed by the common action of both oxidizers are expected to be found only with these conditions. This may obviously

influence as well the formation of compounds resulting from "pure" oxidation from one or the other oxidizer.

These results represent only the negative part of ion-mediated nucleation and has to be completed by its positive counterpart, as well as by neutral formation of new particles, which was reported to be dominant in the troposphere [16]. These results have therefore to be put in perspective of measured (charged) nucleation rates. Comparison with instruments measuring the chemical composition of neutral clusters [17] allows to understand the effect of charge on the oxidation mechanisms.

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