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Evolution of Alpha-Pinene Oxidation Products in the Presence of Varying Oxidizers: CI-APi-TOF Point of View

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Abstract. Alpha-pinene oxidation was studied in the CERN CLOUD chamber under near atmospheric conditions using varying levels of different oxidizers (i.e., O_3, HO_x and NO_x with differing gas mixture compositions) in the presence and absence of UV-radiation, SO_2 and additional organic traces; ammonia (NH_3) and dimethylamine (DMA). The oxidation products and their evolution due to aging in the chamber were studied using a novel CI-APi-TOF technique, with the nitrate ion (NO_3^-) based chemical ionization (CI) scheme. We aimed to the results that would indicate how different oxidizing pathways lead to different product distributions in the product clusters detected.

Keywords: Chemical ionization mass spectrometer, alfa-pinene oxidation, oxidized organics.
PACS: 92.60.Mt

EXPERIMENTAL

The experiments were conducted in the CERN CLOUD-chamber (Cosmics Leaving Outdoor Droplets) [1, 2] using the CI-APi-TOF (Chemical Ionization Atmospheric Pressure interface Time-of-Flight) mass spectrometer [3]. The schematics of the chamber, the mass spectrometer and the experiments are presented in Figure 1.

The CI-APi-TOF instrument and its application to atmospheric cluster measurement have been described previously [3, 4]. Briefly, the APi consist of an atmospheric pressure inlet that is connected to differentially pumped chambers containing quadrupole ion guides and an ion lens focus system (Figure 1). The sample air is ionized using chemical ionization with different charge transfer reagents. The ionized sample is then detected and separated according to its mass to charge ratio in a high-resolution time-of-flight mass spectrometer. In the CLOUD experiments, the instrument was tuned to detect different product clusters with varying cluster compositions, using the nitrate ion (NO_3^-) as the charge transfer ion. The use of nitrate ion as a charge transfer reagent enables efficient detection of clusters

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containing sulphuric acid and oxidized organics, and hence, is an ideal method for studying new particle formation in the CLOUD chamber measurements.

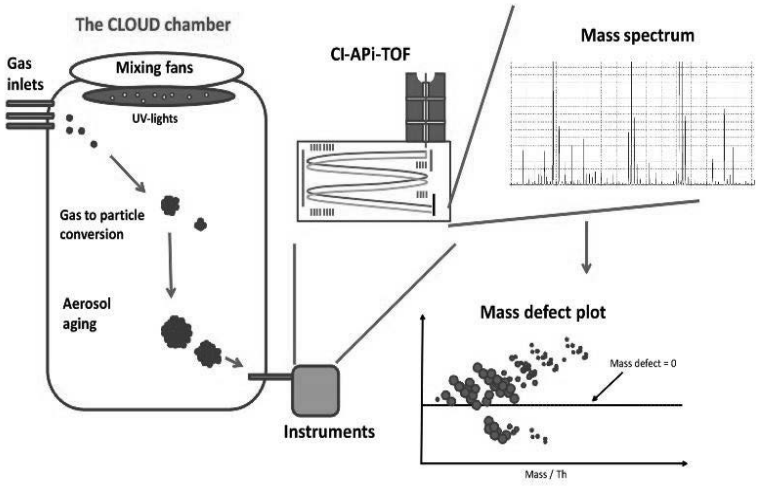

FIGURE 1. Schematic description of the experiments. Shown are the CLOUD chamber [1, 2], the CI-APi-TOF used to measure the cluster mass spectra [3] and illustrative examples of the spectra observed and the mass defect plot extracted from the spectral data.

In these experiments, alpha-pinene oxidation and its potential for new particle formation were investigated in the presence and absence of different levels of varying oxidizers and trace gases, *i.e.*, O_3, HONO (= OH and NO radical source), NH_3, DMA and SO_2. As some secondary reactions in the reaction system are potential additional OH-sources (*e.g.*, O_3 + alpha-pinene), in some of the measurements molecular hydrogen (H_2) was added to the gas mixture to scavenge the produced secondary OH-radicals. This was mainly done in order to enable the separation of the effects caused by different oxidizers; ozonolysis reactions only, OH reactions only, or both at the same time. Comparison of these experiments can provide valuable insight into the mechanisms of these processes.

The experiments were conducted under three significantly differing experimental conditions: under (1) *neutral*, (2) *charged* and (3) *galactic cosmic ray* conditions. Under the *neutral* conditions, the particle formation was studied with an electric field applied across the chamber, equipped to remove any charged species from the chamber, and hence, to exclude ion-induced nucleation. In the *charged* experiments, the particle formation in the chamber was studied under steady bombardment of a charged pion beam from the CERN proton cyclotron. Under *galactic cosmic ray* conditions, the chamber is irradiated by natural cosmic rays emerging from outer space. The *neutral* experiments measure the extent of neutral nucleation, whereas the *charged* and the *galactic cosmic ray* experiments measure both, the extent of neutral nucleation together with the ion-induced nucleation. These three different set of experiments were chosen to learn more about ambient atmospheric nucleation processes, which include neutral-neutral nucleation, ion-induced nucleation, and in addition, nucleation due to galactic cosmic rays. All of these different processes are thought to be omnipresent in the Earth´s atmosphere, but with varying importance depending on, for example, on the altitude and on the trace gases present.

RESULTS

The extent of alpha-pinene oxidation and the products formed were found to depend on the levels of oxidizers and trace gases present, as well as on the prevailing experimental conditions. The dependences are directly observed in the measured mass spectra, as different bands of detected compounds appear in the spectrum as a result of aging and conditioning of the reaction mixture in the CLOUD chamber (see schematic example in Figure 1). The strengths of these bands and the apparent identities of the molecules and clusters detected were found to evolve according to the aging and experimental conditions.

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