Atmospheric oxidation of α-pinene: characterisation of chemical and physical properties of aerosols in chamber experiments

A contribution to subproject CMD

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Summary

Atmopheric oxidation of monoterpenes is considered as an important process in tropospheric ozone formation and secondary organic aerosols, but our understanding of products and, especially, particle phase oxidation products is still very limited. In this study, some first results from chamber experiments for the characterisation of α-pinene oxidation products in the gas and particle phase are presented.

Introduction

Various organic species are emitted to the atmosphere from vegetation. Biogenic hydrocarbons, especially monoterpenes play important role in the formation of secondary organic aerosols (SOA) by the oxidation process in the atmosphere. It has been estimated that they contribute a significant mass to the total aerosol mass in the troposphere, ranging from 30 to 270 Tg y^{-1} [Andreae and Crutzen, 1997].

The identification and quantification of reaction products from the oxidation process of terpenes in the gas phase has been receiving great attention over the past two decades. More recently, the aerosol formation during the oxidation process of terpenes in the atmosphere has been investigated [Pandis *et al.*, 1991; Zhang *et al.*, 1992; Hoffmann *et al.*, 1997]. Although this process is believed to be a major source of SOA in the troposphere only limited number of experiments have been carried out to understand the quantitative and chemical nature of the produced aerosol [Griffin *et al.*, 1999]. Therefore understanding the nature of these species in both gas and particle phases is essential step towards assessing the climatic importance of these species.

In this study, the reactions will take place in a 9 m^3 Teflon reaction chamber. The initial concentration of α-pinene will be 100 ppbV. Ozone will be produced by the photolysis of O$_2$ with Hg lamp and the concentration of ozone can be ranged up to 200 ppbV. The concentration of α-pinene will be determined by GC analysis and the concentration of ozone will be determined by absorption spectroscopy at the wavelength of 254 nm. Ammonium sulphate seed aerosols will be produced by a nebuliser and then dried with a diffusion drier prior to the entering the chamber. A bipolar charge neutraliser will be used to neutralise the dried seed aerosol. The size distributions of particles in the reaction chamber as a function of time will be measured by a differential mobility particle sizer (DMPS) and ultrafine differential mobility particle sizer (UDMPS). The samples will be collected with PTFE filter (0.47 mm diameter, 1 μm pore size) with a Berner type 5 stage cascade impactor. The samples will be analysed with GC-MS and CE in order to have more information of both soluble and insoluble species in the particle phase.

Objectives

The aim of this study is to investigate followings:

- The formation of organic acids and aerosols from the ozone oxidation of α-pinene.

- Particle phase concentrations of α-pinene oxidation products.

- The influence of oxidation products to the seed aerosols - modification of aerosol size distributions as a function of time

- The influence of temperature and humidity to the chemical and physical parameters of aerosols.

- A method development for the CE analysis of α-pinene oxidation products.

Activities and first results from chamber characterisation

The physical characterisation of a Teflon reaction chamber is taking place at IfT in Leipzig. The number and volume size distributions of seed aerosols in a reaction chamber as a function of time (without α-pinene and ozone presence) are measured and examples are shown in Figure 1 and 2, respectively. The peak diameter for the number size distribution, dN/dlogDp, (Figure 1) was found at 70nm when the seed aerosols were injected (0 hour) then the peak shifted gradually to the larger diameter (140nm after 24 hours). Also the number of particles decreased with time in all size ranges. Contrary to the peak diameter shift of dN/dlogDp, the peak shift of volume size distribution, dV/dlogDp, was not pronounced and only volume decreased in all size ranges. Also the decrease in volume with time was not so significant compared to the decrease in the number of particles. Smaller particles were possibly lost quickly due to coagulation with large particles or to the wall of the chamber but lost particles might have been supplemented by the coagulation of small particles.
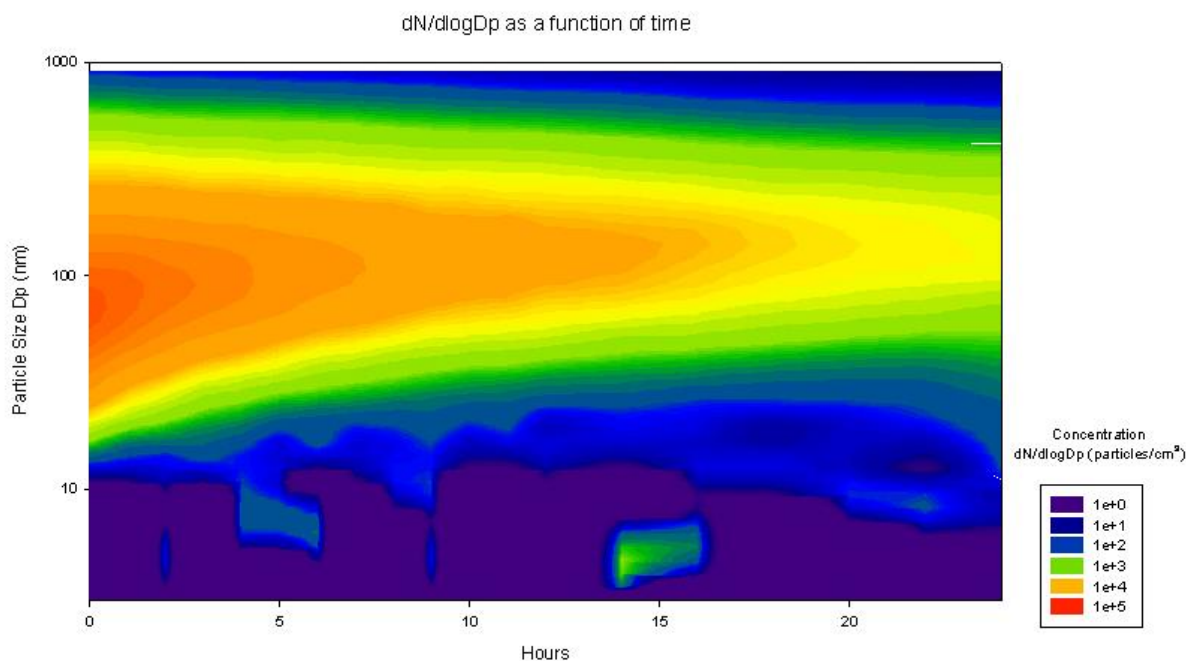

Figure 1: Contour plot of seed aerosol dN/dlogD as a function of time. T=290K, RH<10%
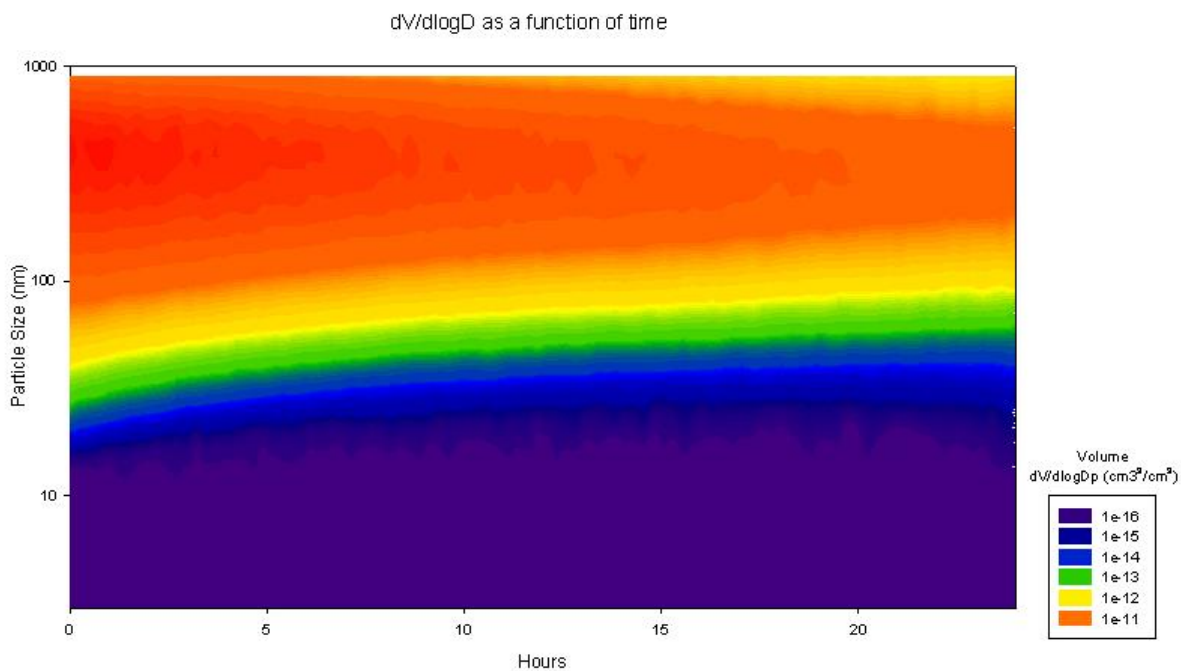
Figure 2: Contour plot of seed aerosol dV/dlogD as a function of time. T=290K, RH<10%

CE analytics

Standards of pinic, pinonic, norpinic and norpinonic acids were tested on a CE in order to find the optimal condition for the CE analysis of α-pinene oxidation products. The buffer containing p-aminobenzoate (20 mmol l^{-1}), NaOH (resulting in a pH 9.6), and diethylenetriamine (8 mmol l^{-1}) showed the best separation and sensitivity for this buffer combination. Excellent linear response is found from all standard. Figure 3 shows an example of electropherogram for the standard of α-pinene oxidation products.
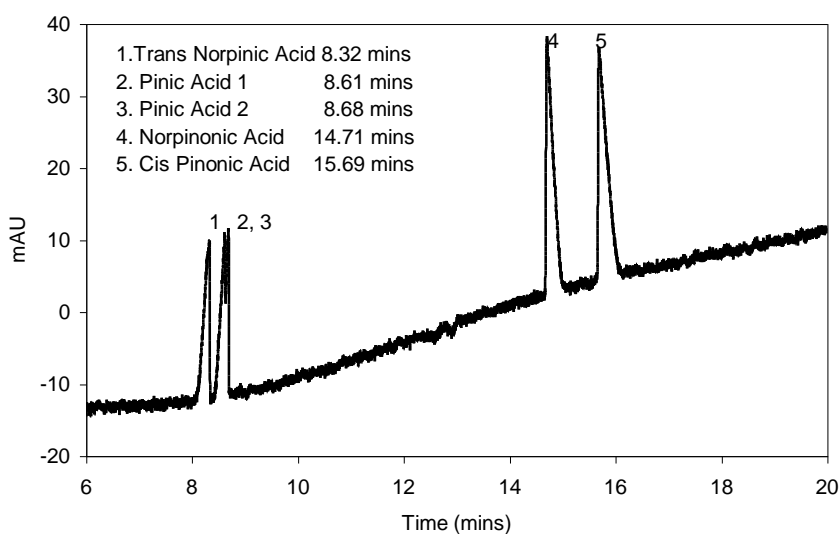
Figure 3: Example of electropherogram for the standard of α-pinene oxidation products (100 μM, ref. λ=254nm).

The reason for the split peak of pinic acid may be due to the optical isomer in the standard as the both peaks show almost identical response.

Some first measurements of the physical and chemical properties of particles from the oxidation of α-pinene will be presented.

References

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