Gas-phase oxidation of α-pinene: gaseous and particle products in chamber experiments

Yoshiteru Iinuma, Olaf Böge, Thomas Gnauck, Konrad Müller, and Hartmut Herrmann
Institut für Troposphärenforschung, Leipzig, Germany
http://www.tropos.de/

Introduction

Various organic species are emitted to the atmosphere from vegetation. Biogenic hydrocarbons, especially monoterpenes play an important role in the formation of secondary organic aerosols (SOA) initiated by their atmospheric oxidation. It has been estimated that they contribute a significant mass to the total aerosol mass in the troposphere, ranging from 30 to 270 ng/g PPN [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 also 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 conducted to understand the chemical nature of the produced aerosol [Griﬃn et al., 1999; Winterhalter et al., 2001]. Therefore understanding the nature of these species in both gas and particle phases is essential step towards assessing the climatic importance of these species.

Experimental Condition

Reactions were run in a 9 m3 Teflon reaction chamber. Figure 1 shows the experimental setup. The initial concentration of α-pinene was 16-48 ppbV. Concentration of ozone was determined by UV absorption at λ = 254 nm. Ammonium sulfate seed aerosols were produced by a nebulizer and then dried with a diffusion dryer prior to the entering the chamber. A bipolar charge neutraliser was used to neutralise the dried seed aerosol. The size distributions of particles in the reaction chamber as a function of time were measured by a differential mobility particle sizer (DMPS) and ultraﬁne differential mobility particle sizer (UDMPS). The seed aerosols and ozone are injected to the reaction chamber and mixed with a fan prior to the reaction with α-pinene. After deﬁning the initial concentrations of ozone and seed aerosols, α-pinene was injected and mixed for further 5 minutes with a fan. The samples were collected on a PTFE ﬁber (0.47 mm diameter, 1 mm pore size). Fibers were extracted in 3 mL of Milli-Q water for CE-MS analysis. A buffer system containing 3 mM ammonium acetate/10% methanol at pH 9.0 (adjusted by NH₄OH) was used. A fused silica capillary with internal diameter of 75 µm and total length of 50 cm was used for the separation by CE.

Results and discussion

Figure 2 and 3 show examples of increased aerosol mass (ΔM) and size distribution change as a function of time with and without seed aerosols, respectively. Increase in particle number, mass and mode diameter were observed shortly after α-pinene was injected for both with and without seed aerosols case. In the presence of seed aerosols, condensation of organic vapors or newly formed ionic particles on the existing particulate species causes increase in particle size and mass. In a non-seeded aerosol experiment, heat nucleation forms a signiﬁcant number of particles that then followed similar evolution of particle size and mass as a seeded experiment. A maximum in ΔM are reached about 3 hours after α-pinene injection for both cases. Particle size distributions for both cases were polydispersed but showed rather different characteristics. Although no clear explanation can be given without further characterization experiments, it may be due to the difference between a number of SSA in the time of the nucleation and the speed of coagulation during the evolution of particles. Preliminary experimental results suggest ΔM is strongly inﬂuenced by the initial experimental parameters and no clear relationship between each experimental parameter was observed from the results and further experiments are needed in order to understand the factor deciding ΔM and yield.

Figure 4 shows a typical electrophrogram. Only ﬁlter samples from experiments with seed aerosols were analyzed at this time. CE analysis showed that major water soluble ionic products in the particle phase were pinic acid, 10-hydroxy-pinonic acid, norpinic acid, pinonic acid relatively small concentration of nonanoic acid and possibly pralonic acid.

Table 1: Detection Limit

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration of Sample Injected (ng/ml)</th>
<th>Absolute Mass Injected (pg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinic Acid</td>
<td>6</td>
<td>0.23±0.08</td>
</tr>
<tr>
<td>Norpinic Acid</td>
<td>6</td>
<td>0.25±0.05</td>
</tr>
<tr>
<td>Pinonic Acid</td>
<td>85</td>
<td>3.9±0.02</td>
</tr>
<tr>
<td>Noronic Acid</td>
<td>59</td>
<td>2.7±0.3</td>
</tr>
</tbody>
</table>

Summary

In this study, some ﬁrst results from chamber experiments for the characterization of α-pinene ozonolysis products in the particle phase are presented. Evolution of particles (ΔM and dN/dlogDp) as a function of time are shown for both seeded and non-seeded experiments. Further experiments are planned in order to characterize aerosol formation and evolution from α-pinene ozonolysis. Oxidation products were analyzed by CE-MS and it is found that pinic acid, 10-hydroxy-pinonic acid, norpinic acid and pinonic acid to be major ionic species in the particle phase. CE-MS provides a fast and sensitive analysis for the identiﬁcation of ionic species from α-pinene ozonolysis products.

Future work

- Characterization of experimental parameter dependence of particle evolution: temperature, RH, concentration of α-pinene, ozone and seed aerosols properties
- Determination of gas/particle phase partitioning ratio
- The improvement of CE-MS technique
- Oxidation with 97% RH

Acknowledgements

Part of this project is supported by BMU within AFO2000 in the projects BIWA2000 and EFEU under contracts 07ATF25 and 07AFT47, respectively.

References