

Chemical composition studies of laboratory-made α -pinene SOA by NMR

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Understanding atmospheric processes such as chemical transformations, nucleation, cloud formation, scattering and absorption of solar radiation, contributing to climate change and human health effects, requires studies at a molecular level. The application of nuclear magnetic resonance (NMR) spectroscopy to the structural analysis of atmospheric samples remains rather uncommon. Some work has been done for ambient samples and laboratory organic aerosol where NMR has proven to be a valuable tool (e.g. Finessi et al. 2012, Maksymiuk et al. 2009, Duarte et al. 2008).

Our work was focused on monoterpene secondary organic aerosol (SOA) formation and analysis by NMR, in order to study reactive intermediates which are often lost during long residence times and sample preparation or analysis by common analytical tools like liquid chromatography (LC), and to complement information about aerosol chemical composition and formation mechanism. Since these compounds are unsaturated or reactive, they are rapidly transformed into other compounds by the oxidizing atmosphere. The non-volatile oxidation products like highly oxidized organic peroxides, organic acids, aldehydes serve as condensation nuclei and can provide functionality for particle growth. The mechanism of how organic molecules take part in the first steps of nucleation and growth of new particles has been the focus of several studies in recent years but no conclusive results have yet been obtained.

In order to study monoterpene chemistry related to the atmosphere, SOA from α -pinene ozonolysis was generated in a house-made 30.5 L flow reactor, collected and analysed by ¹H, ¹³C-NMR and HPLC-MS. Although NMR is low-sensitivity instrumentation, with our experimental set up we were able to collect sufficient amounts of SOA to make a chemical composition assessment. Variability in sampling time and residence time allowed us to study labile compounds and compounds involved in particle aging.

¹H-NMR spectra of α -pinene SOA at different residence times revealed the same major signals corresponding to identical compounds (Figure 1.). The major signals were identified as pinic, pinonic and terpenylic acid (compared with ¹H-NMR and ¹³C-NMR spectra of standards). The differences between aged SOA occurred in the composition of minor compounds, and in reciprocal ratio of signals. In expanded ¹H-NMR spectra plenty of protons attributed to aldehydes, hydro peroxides, double bonds and protons to electron-poor sp³ carbon or heteroatoms were recognized. Several of these compounds are reactive enough to be transformed during

the sampling process. They were recorded only in short time samples, whereas others appear only in samples with longer residence times, thus on more aged particles. The major compound composition determined by ¹H-NMR and HPLC-MS of aged particles is compared in Table 1. Particle aging is related to a decrease of pinic acid, pinonic acid and pinonaldehyde, and an increase in terebic acid.

Figure 1. ¹H-NMR spectra of α -pinene SOA at 40 s, 100 s and 165 s residence time.

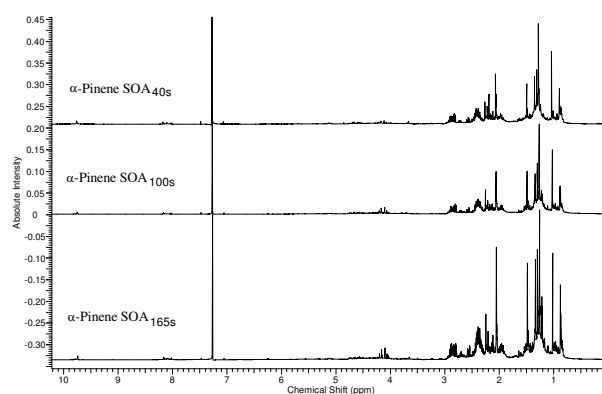


Table 1. Comparison between chemical composition of aged particles

SOA- α -pinene constituent*	T _{Residence} , s		
	40 s	100 s	164 s
Pinic acid	1.56	1.22	0.82
Pinonic acid	0.61	0.58	0.56
Terebic acid	0.10	0.18	0.24
Pinonaldehyde	0.38	0.29	0.27

* Concentrations expressed as relative ratio to terpenylic acid

These experiments allowed us to recognize major compounds on particles and the most labile compounds, which are involved in the mechanistic pathway of monoterpene oxidation and particle formation. Still, additional experiments are required in order to make full structural identification of these intermediates.

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