Gas-Phase Measurements of Oxidized Organic Compounds Generated by a Potential Aerosol Mass (PAM) Reactor using Acetate Chemical Ionization High-Resolution Time-of-Flight Mass Spectrometry

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We present gas-phase measurements of laboratory generated oxidized organic compounds using acetate chemical ionization mass spectrometry (Acetate-CIMS). This relatively new detection scheme uses acetate ions ($CH_3C(O)O^-$) to initiate proton transfer reactions with trace organic and inorganic acids with gas-phase acidities higher than that of acetic acid (Veres *et al*, 2008; Bertram *et al*, 2011). This technique has been used in conjunction with recently developed aerosol inlets to study secondary organic aerosol in both the field and laboratory (Yatavelli *et al*, 2009, 2012).

Here, we present acetate-CIMS spectra of oxidized organic vapors generated from the ozonolysis of α-pinene and photooxidation of α-pinene, isoprene, and naphthalene in a Potential Aerosol Mass (PAM) flow reactor over multiple days of equivalent atmospheric OH oxidation (Lambe *et al*, 2011). By taking advantage of the high-resolution capabilities of the Tofwerk HToF on the CIMS, we are able to explore the elemental composition of the oxidized organic vapors as a function of OH exposure and precursor. Such vapors are of interest because low volatility organics have been implicated in aerosol nucleation processes (Riipinen *et al*, 2012).

Within the range of our measurements, we investigate commonly used metrics for oxidation level such as the average oxygen to carbon (O/C) ratio, carbon oxidation state (OS_c), and carbon number (C_n) of the oxidized vapors relative to C_n of the precursor. Figure 1 shows O_{sc} as a function of C_n of oxidized vapors produced from the ozonolysis of α-pinene, referred to here as a Kroll diagram (Kroll *et al*, 2011). Average O/C ratios and OS_c values typically range from 0.7 to 1.1 and -0.1 to 0.9, respectively, across the entire simulated OH exposure.

To gain insight into the relative acidity of these oxidized organic vapors, we compare acetate-CIMS spectra with NO_3-CIMS spectra obtained for the same systems in the laboratory and for ambient measurements obtained during the Southern Oxidant and Aerosol Study (SOAS) at the forest supersite in Centreville, AL. The NO_3-CIMS method is specific to species with gas-phase acidities higher than that of nitric acid, thus producing spectra that represent a subset of the acetate-CIMS spectra.

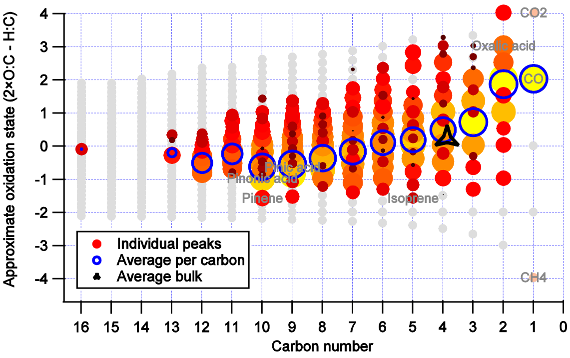

Figure 1: Kroll diagram of oxidized organic vapors produced from the ozonolysis of α-pinene.

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