**Heterogeneous oxidation of organic aerosols by OH, and comparison to gas-phase condensation**

*N. Campbell, Department of Chemistry and Biochemistry, UC San Diego – SIO 217D WI14 Course Project*

Oxidative aging of organic atmospheric aerosols is crucial in determining their chemical and physical properties and understanding potential climate and health effects, yet is poorly constrained in the literature. Due to the wide range of organic species present in aerosols, select classes of reactions are chosen for laboratory studies, one being heterogeneous oxidation by OH radicals. Recent publications have investigated heterogeneous OH oxidation of both reduced and oxidized organic species (Kessler, S. H. et al., 2012; Che, D. L. et al., 2010). The hydroxyl radical is one of the most important species in the atmosphere, as it is a highly unstable species that, in the presence of NOx, reacts with hydrocarbons to generate tropospheric ozone (Smith, J. D. et al., 2009). The work presented here addresses potential changes in number and mass concentrations resulting from heterogeneous OH oxidation of citric acid and squalane particles, and compares to shifts expected as a result of formic acid gas-phase condensation onto organic aerosols.

Ambient SMPS size distributions (Figure 1) from Look Rock, TN during the summer 2013 Southern Oxidant and Aerosol Study (SOAS) were averaged and heterogeneous reaction with hydroxyl radicals simulated for two types of organic aerosols, citric acid and squalane. Several simplifying assumptions were made: 1) the particles are homogeneous, 2) the entire particle volume is available for reaction, 3) only hydrogen atoms located on carbon atoms are available for abstraction by OH, 4) particle density remains constant, even after reaction with OH, and 5) the number of reactions occurring on the particles can be equated to the number of hydrogen atoms lost, which can subsequently be equated to the number of oxygen atoms gained by the particle. As demonstrated in Figure 2, heterogeneous OH reaction does not alter number distributions for either citric acid or squalane particles. Similar figures can be constructed for mass concentration before and after reaction. The absence of change in mass concentration as a result of reaction is consistent with results reported by Kessler et al.; although particle composition (often described by the O/C ratio) may change as a result of oxidative aging, overall mass remains constant (Kessler, S. H. et al., 2012). While squalane shows an increasing O/C ratio over time, citric acid, does not. This may be attributed to the fact that citric acid initially starts with a high O/C ratio, and the incorporation of additional oxygen species likely does not change the ratio significantly.

 An aerosol condensation model was employed to understand changes in particle number and mass concentrations over time resulting from vapor condensation as opposed to heterogeneous reaction. Aerosol size distribution model parameters were modified to represent ambient SMPS size distributions (Figure 1) from Look Rock, TN as closely as possible. Important constants and calculated values used in this model include the vapor pressure of formic acid (11.16 torr), the diffusivity of formic acid in air (0.129 cm2s-1, based on theoretical data from Gibson, L. T. et al., 1997), the mean molecular speed of formic acid (calculated by Eq. 1), and the Knudsen number for formic acid (calculated using Eq. 2).

$$Mean speed= \sqrt{\frac{8RT}{πMW\_{formic acid}}} (Eq. 1)$$

$$Knudsen number=2\frac{λ}{D\_{p}} where λ= \frac{3\*Diffusivity}{Mean speed} (Eq. 2)$$

Some assumptions were made: 1) the atmospheric formic acid concentration was assumed to be 19 pptv, as suggested by 1994 data for Riverside, CA (Lawrence, J. E. and Koutrakis, P., 1994), 2) the accommodation coefficient was assumed to be unity, and 3) the temperature and altitude at which condensation occurs were assumed to be 273 K and 1 km, respectively. The condensation of formic acid to particles was modeled for size distributions from June and July of 2013 (Figures 3 and 4, respectively) over a 96-hour period. As can be seen in both figures 3 and 4, the number distribution shifts as a result of formic acid condensation. In figure 3, there is a slight narrowing of the distribution and a shift towards particles of a larger diameter; in figure 4, there is a noticeable narrowing of the condensation mode as particles grow to approach the accumulation mode. This lack of increase in total number concentration, in conjunction with a narrowing of the distribution, is a signature of condensational growth in aerosol distributions, and is thus expected for populations where condensation is the only relevant process. Unlike total number concentration, the total mass concentration does increase as a result of condensation (figures not shown). For the distributions represented, where there are only two aerosol modes (condensation and accumulation) present, the condensation mode experiences the largest fractional mass increase, but the accumulation mode experiences the largest absolute mass increase.