2.159 Influence of Relative Humidity on the Heterogeneous Oxidation of Secondary Organic Aerosol.

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Abstract:

While relative humidity (RH) has a substantial impact on particle phase, the impact of RH on heterogeneous oxidation of complex organic particles, such as secondary organic aerosol (SOA), is not well established. We have experimentally characterized how the heterogeneous oxidation by OH radicals of SOA produced from dark a-pinene ozonolysis depends on RH. At high RH (~ 89%) there is substantial loss of particle volume (~60%) at an equivalent atmospheric OH exposure of 3 weeks. In contrast, at low RH (RH = 25%) there is little mass loss (<20%) at the same OH exposure. Mass spectra of the SOA particles were measured using a vacuum ultraviolet aerosol mass spectrometer (VUV-AMS). The mass spectra observed at low RH overall exhibit minor changes with oxidation and negligible further changes at high OH exposures, indicating limited impact of oxidation on the average particle composition. In contrast, the mass spectra observed at high RH exhibit substantial, rapid and continuous changes as a function of OH exposure. Further, at high RH clusters of peaks in the mass spectra exhibit unique decay patterns, suggesting different responses of various species to oxidation. We developed a model of heterogeneous oxidation that accounts for particle phase to understand the origin of the difference in aging between the low and high RH experiments. RH-dependent differences in diffusivity (i.e. phase) of the SOA alone can explain the difference in compositional change but cannot explain the difference in mass loss. Instead, the difference in mass loss is attributable to RH-dependent differences in the OH uptake coefficient and/or the net probability of fragmentation within the condensed phase, with either or both larger at high RH compared to low RH. These results illustrate the important impact of relative humidity on the fate of SOA in the atmosphere.