α-Pinene: Because it is so interesting!

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Canonical systems have value because they allow a comprehensive test of our understanding; we keep studying α-Pinene Secondary Organic Aerosol (SOA). It is the gift that keeps on giving. There is abundant evidence that volatility matters in the formation of SOA – that is almost tautological, as volatility is the tendency of compounds to leave the condensed phase. Put another way, a very large flux of organic compounds collides with ambient particles, and only a very small fraction sticks. Our objective is to understand which ones stick, why, and how long they stay stuck.

The simplest hypothesis was put forward by Odum. Compounds stick because they are formed in the gas phase with low volatility. They can then condense to form a (more or less ideal) mixture in an amorphous (not necessarily liquid) phase. This explains the well-defined, rising mass yields with rising aerosol concentration observed in smog chambers. It clearly holds for primary organic aerosol (POA), which ironically is still often represented as non-volatile pieces of grit. Considerable evidence exists, however, that SOA can be more complicated. First, there is long-standing evidence indicating formation of association products (oligomers) with mass fractions possibly exceeding 50%. Second, ambient oxidized organic aerosol (OOA) is much more oxidized than SOA typically formed in smog chambers. Finally, there is growing evidence that organic aerosols exist with a huge range of viscosity (it is really diffusivity that matters), potentially including such low diffusivity that particles might never come into equilibrium on any practical timescale, equivalent to waiting for pitch to drip.

We have explored all of these issues with a (probably not ideal) mixture of experiments and modeling. We conduct single-particle mingling experiments in which aerosols of different composition (often isotopically labeled) are combined and observed with single-particle mass spectrometery as they mix via gas-phase (Marcolli) exchange. We observe particle bounce via delayed collection in our mass spectrometer. We observe mass equilibration on various timescales after isothermal dilution and small stepwise temperature changes. Finally, we have developed a dynamical version of the volatility basis set including a dimerization pathway that describes the various behaviors we observe.