Modeling Aerosol Formation in α-pinene Oxidation Experiments: Impact of Non-Ideality of the Aerosol Mixture

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I. Introduction

The previously published BOREAM model[1] was developed to describe α-pinene oxidation. It has the following characteristics:

- The first oxidation steps of α-pinene are treated explicitly by theoretical calculations. Oxidation by OH, O₃, and NOₓ is considered.
- Second-generation oxidation products are lumped together to semiempirical or generic compounds.
- Partitioning to the aerosol phase is described kinetically.
- Non-idealities are corrected for each product, using a UNIFAC approach.
- The partitioning of this class of compounds is described by the activity coefficients included in the model.

II. Simulations without water uptake: impact of activity coefficients

When water condensation is allowed, the mass yield increases with relative humidity (RH). As equilibrium between gas and condensed phase is achieved quite rapidly, the molar fraction of water in SOA tends towards RH.

- The increase is due to both water uptake, and an increase in organics.
- At lower to medium RH, the increase in total mass yield is mainly due to an increase in organics.
- At higher RH (60%), the two become comparable.
- Reason: due to the water uptake, also the other aerosol compounds must increase to maintain the equilibrium.

III. Simulations with water uptake: ideal case

Water uptake can influence partitioning through changes in total mass Mᵣ, molar mass MWᵣ, and activity coefficient γᵢ.

Impact on SOA yield and mean molecular mass:

- The impact on the mass yields is very minor (a few % increase), to virtually non-existent in most cases.
- The mean molecular SOA mass is almost unchanged (not shown).
- Reason: the mean of the activity coefficient is close to unity.

Impact on composition:

- For most experiments, the relative error on particular phase species concentration is small but significant.
- The low VOC Presto experiments, the error can exceed to 40%.
- Reason: at low SOA masses, the equilibrium is closer to the gas phase, and the particulate phase is more sensitive to variations in activity coefficient.

IV. Impact of non-ideality on water uptake

The non-ideality lowers the mass yield for the higher RH cases.

- Water uptake is suppressed due to an activity coefficient γᵢ < 1.
- Subsequently, the uptake of organics is lowered due to a lower water content.
- For both the Hansen and the Magnusen parametrization, the effect is much stronger compared to the Raatikainen parametrization.

V. Testing phase separation effects (Work in progress)

We're investigating the above described systems at varying RH for phase-splitting effects. So far, no evidence of phase-splitting has been found.

VI. Conclusions

- For dry α-pinene oxidation experiments, the impact of non-ideality on SOA yield is unimportant.
- Water uptake enhances partitioning of organic molecules.
- Water uptake is affected by non-ideality, depending on the exact UNIFAC parametrization, in the order: ideal > Raatikainen > Hansen ≈ Magnusen.
- At high RH (60-90%), ideal calculations grossly overestimate the yield compared to non-ideal calculations.
- Preliminary results: Phase separation effects do not seem to occur in SOA purely from α-pinene oxidation products, even at high relative RH. This is in agreement with results of Chang and Pankow[15].

References