Is the gas-particle partitioning in alpha-pinene secondary organic aerosol reversible?

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This paper discusses the reversibility of gas-particle partitioning in secondary organic aerosol (SOA) formed from α-pinene ozonolysis in a smog chamber. Previously, phase partitioning has been studied quantitatively via SOA production experiments and qualitatively by perturbing temperature and observing particle evaporation. In this work, two methods were used to isothermally dilute the SOA: an external dilution sampler and an in-chamber technique. Dilution caused some evaporation of SOA, but repartitioning took place on a time scale of tens of minutes to hours—consistent with an uptake coefficient on the order of 0.001–0.01. However, given sufficient time, α-pinene SOA repartitions reversibly based on comparisons with data from conventional SOA yield experiments. Further, aerosol mass spectrometer (AMS) data indicate that the composition of SOA varies with partitioning. These results suggest that oligomerization observed in high-concentration laboratory experiments may be a reversible process and underscore the complexity of the kinetics of formation and evaporation of SOA. Citation: Grieshop, A. P., N. M. Donahue, and A. L. Robinson (2007), Is the gas-particle partitioning in alpha-pinene secondary organic aerosol reversible?, Geophys. Res. Lett., 34, L14810, doi:10.1029/2007GL029987.

1. Introduction

Secondary organic aerosol (SOA) contributes a significant portion of organic aerosols in rural and urban areas [Seinfeld and Pandis, 1998]. SOA forms from the condensation of semi-volatile reaction products of gas-phase precursors. Current models treat this partitioning as a reversible process at equilibrium involving a fixed set of products [Odum et al., 1996; Pankow, 1994], but this assumption has not been tested and can create substantial uncertainty in SOA model predictions [Tsigeridis and Kanakidou, 2003]. To date, the lumped parameters used to describe gas-particle partitioning of SOA have been determined via yield experiments, in which progressively higher levels of precursors are added to a smog chamber [see, e.g., Presto and Donahue, 2006]. However, no one has directly investigated whether the phase partitioning during formation is the same as during evaporation. For example, oligomerization reactions may cause the partitioning to evolve with time or alter condensation and evaporation kinetics.

Temperature and concentration both influence the phase partitioning of semi-volatile organic matter. Volatility...
Figure 1. Comparison of gas-particle partitioning measured during dilution of α-pinene SOA (symbols) with a fit of yield data from traditional SOA experiments (solid line). Results are plotted in terms of the normalized aerosol mass fraction (AMF) and COA, calculated assuming a particle bulk density of 1 g cc⁻¹, as discussed in the text. The large symbols indicate the beginning and end equilibrium states with the smaller symbols showing the particles evolving after dilution. Each small symbol represents one SMPS scan (2 minutes for Experiment 1, 3.5 minutes for others). Error bars on COA represent uncertainty due to wall-losses in the chamber; AMF error bars are based on estimated uncertainty in the yield parameterization.

versus a dilution time of order 10 minutes and a mixing time of ~1 minute for the in-chamber technique. An advantage of the in-chamber approach is that it allows changes in the SOA to be observed over a period of hours to verify the system has returned to equilibrium.

[8] For both techniques, the level of dilution was determined by measuring the CO₂ mixing ratio [Lipsky and Robinson, 2005]. Approximately 15,000 ppmv of CO₂ was added to the chamber before each experiment. Dilution of SOA was performed approximately 30 minutes after the injection of α-pinene. This allowed for the complete oxidation of the α-pinene (shown by a peak in particle mass concentrations) and for the initial coagulation of fine particles (shown by stabilization of the median particle diameter).

[9] For both approaches, the evaporation of SOA was determined from particle size-distribution measurements taken with the SMPS. We calculate the volume fraction remaining (VFR):

\[
VFR = \frac{D_p,undiluted}{D_p,diluted} 
\]

where \(D_p,undiluted\) and \(D_p,diluted\) are the particle median mobility diameters just before and during the dilution process, respectively. The VFR is equal to the fraction of the particle mass remaining if the particles are spherical and their bulk density is constant, assumptions discussed in more detail below. We also calculated the VFR using a range of particle size percentiles (10th, 25th, median, 75th, etc.) which indicated that the entire size distribution shrunk uniformly.

[10] To determine whether phase partitioning is reversible, the results of dilution experiments were compared with previously published data from traditional SOA yield experiments. SOA yield is often expressed in terms of a normalized aerosol mass fraction—AMF = \(C_{OA}/\Delta C_{ROG}\), where \(C_{OA}\) (\(\mu g\ m^{-3}\)) is the mass concentration of organic aerosol formed by the oxidation of \(\Delta C_{ROG}\) (\(\mu g\ m^{-3}\)) of precursor. In this paper \(C_{OA}\) refers to the mass concentration as measured by the SMPS, with an assumed SOA density of 1 g cc⁻¹. The change in AMF with \(C_{OA}\) defines the SOA yield curve; it can be expressed using partitioning theory [Donahue et al., 2006],

\[
AMF = \sum_{i=1}^{n} \alpha_i \left( \frac{C_{i}^*}{C_{OA}} \right)^{-1} 
\]

where \(\alpha_i\) is the mass yield of semivolatile product i with effective saturation concentration \(C_{i}^*\). The set of \(\alpha_i\) and \(C_{i}^*\) are determined by fitting smog chamber data [Odum et al., 1996].

[11] The solid line in Figure 1 shows the traditional α-pinene ozonolysis SOA yield curve derived by fitting a compilation of literature data. The fit used in this work is a slight update of an earlier fit [Presto and Donahue, 2006] to account for the modestly higher initial concentrations in our experiments.

3. Dynamics of Evaporation

[12] In this section we compare the results from the two dilution approaches to investigate the dynamics of SOA evaporation. Since we did not measure the gas-phase α-pinene concentrations we cannot directly calculate the AMF for our experiments. Therefore, in order to compare our data with the yield data as compiled by Presto and Donahue [2006], we assigned an initial AMF using the total chamber \(C_{OA}\) (mass in suspension and on chamber walls, discussed below) and the fit described above. The initial point thus falls, by definition, on the traditional yield curve. The subsequent (post-dilution) AMF values are calculated by scaling the initial AMF value with the measured VFR.

[13] Figure 1 shows that essentially no change in particle volume was observed for experiments with the external dilution sampler. These experiments diluted a single population of chamber SOA by up to a factor of 80, which should have evaporated roughly two-thirds of the SOA based on the traditional yield curve. Potential explanations for the observed lack of evaporation are insufficient system residence time, interactions between the aerosol and the walls of the dilution sampler or the influence of oligomerization on the volatility of the SOA. All of these explanations seem problematic. Experiments have shown single-component particles of individual species present in α-pinene SOA to evaporate in 4–26 seconds [Bilde and Pandis, 2001], which is shorter than the ~30 second residence time of our system. Experiments with combustion-generated aerosol show no evidence of bias due to wall interactions [Lipsky and Robinson, 2006]. Irreversible partitioning implies total and rapid oligomerization, which seems unlikely given that these experiments were performed with fresh SOA, an OH scavenger, and without acidic seed particles.
The second approach to dilution—in-chamber dilution—allows us to measure the evaporation over a period of hours. Figure 2 shows a time series of VFR from an in-chamber dilution experiment. The shaded box shows the period during which the SOA was actively diluted by a factor of 25; during this time about 60% of the mass that ultimately evaporated from the particles was lost. The particles then continued to evaporate (shrink) for another 2.5 hours after active dilution was stopped. The ultimate change in the mass-weighted median mobility diameter was from 235 nm to 200 nm during this experiment. The slowing of the evaporation rate after active dilution may be due to a reduction in the evaporative driving force as the gas- and particle-phase concentrations of semivolatile material approach equilibrium. The delay of several minutes between the onset of dilution and the initial response of particle median diameter may be partly due to the mixing time in the chamber (~1 minute). However, such a delay is also consistent with the data from the dilution sampler experiments. All in-chamber dilution experiments show a similar behavior.

Figure 2. Time series of measured VFR during in-chamber dilution of α-pinene SOA. The shaded region shows the period during which chamber contents were actively diluted by a factor of 25. Horizontal lines indicate the amount of evaporation that took place during and after active dilution. Inset shows particle size distributions immediately preceding dilution (point A) and near the end of the experiment (point B); mass-weighted median diameter was used to calculate VFR.

The change in VFR is not due to wall interactions or changing particle density. For example, control experiments without dilution show a gradual increase in $D_{p,\text{median}}$ presumably caused by coagulation or preferential deposition of smaller particles in the chamber [Presto et al., 2005]. SMPS total particle volume calculated assuming spherical particles and AMS total organic mass were strongly correlated in all experiments (linear correlation $R^2 = 0.995$), indicating that the particle density (and water content) remains essentially constant during dilution and supporting the use of VFR to quantify SOA evaporation.

Our experiments clearly show that dilution causes some of the SOA to evaporate, but that the evaporation rate is much slower than expected, especially relative to condensation rates observed in yield experiments. Applying the framework used to analyze TDMA data [Bilde and Pandis, 2001] to the average particle shrinkage rate during active dilution shown in Figure 2 suggests an uptake coefficient of order 0.001 to 0.01 (a value of 1 is generally assumed). The evaporation rate observed here is much slower than that of single-component aerosols [Bilde and Pandis, 2001]. This difference could be due to mixture effects in the organic solution or to decomposition of weakly bound oligomers. Although our experiments only consider fresh SOA, some oligomerization occurs immediately [Gao et al., 2004] with further oligomerization over time [Kalberer et al., 2004]. Oligomerization likely influences evaporation kinetics. Interactions of semivolatile material with chamber walls (discussed in more detail below) may also influence the evaporation rate. For example, the particles on the walls might evaporate more slowly than suspended particles. However, this would depress vapor concentrations and thus accelerate evaporation of suspended particle mass, the opposite of what was observed here. In addition, the vast majority of the particle mass is in suspension during dilution in most of the experiments.

4. Reversibility of Partitioning

In this section, we compare the results from the dilution experiments to the traditional SOA yield curve shown in Figure 1 to assess whether the gas-particle partitioning is reversible. Interpretation of partitioning data from smog chamber experiments is complicated by deposition of particles to the chamber walls. The key question is whether these deposited particles remain in equilibrium with the gas phase. The available evidence, in the form of multi-injection SOA experiments to constrain wall-loss partitioning behavior (E. Weitkamp et al., Organic aerosol formation from photochemical oxidation of diesel exhaust, submitted to Environmental Science and Technology, 2007), strongly suggests that they do. Therefore, we assume that all condensed-phase mass, both in suspension and that which has been deposited to the walls, evaporates at the same rate as that in suspension. Using VFR to quantify SOA evaporation minimizes errors due to wall-losses because chamber wall-losses have much smaller impacts on the particle size distribution than on the total suspended mass. The total mass in the particle phase (total $C_{OA}$) is the measured suspended mass plus the estimated aerosol mass deposited on the walls. The mass on the walls is calculated assuming a first-order wall loss rate and scaling the mass on the chamber walls using the VFR of the suspended particles to account for evaporation.

Figure 1 compares the results from three in-chamber dilution experiments to the traditional yield curve. In all cases, the equilibrium partitioning of the SOA after dilution agrees well with that observed during the traditional SOA-yield experiments. Therefore, given sufficient time, partitioning of fresh α-pinene SOA is reversible in this $C_{OA}$ range.

5. SOA Partitioning and Composition

The AMS was used to investigate changes in particle composition during both SOA formation and evaporation.

Figure 2 shows the period during which the SOA was actively diluted by a factor of 25; during this time about 60% of the mass that ultimately evaporated from the particles was lost. The particles then continued to evaporate (shrink) for another 2.5 hours after active dilution was stopped.
The authors would like to acknowledge the assistance of Gabriella Englehart in running SOA experiments. This research was supported by the EPA STAR program through the National Center for Environmental Research (NCER) under grants R832162 and RD-83108101. It has not been subject to EPA’s required peer and policy review, and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred.

Figure 3. Changes in SOA composition measured using an AMS. (a) Time series of the fractional contributions to the total AMS organic signal of ions at m/z 43, 44, 55 along with larger fragments (shown scaled up by a factor of 10) at m/z 91, 100, 109 and 139 (left-axis) and of the wall loss-corrected AMS organic aerosol concentration (right-axis). (b) Fractional contribution of ions at m/z 44 versus C_{OA} (based on SMPS data assuming $\rho = 1$ g cc$^{-1}$). Lines in Figure 3b are shown to guide the eye along trajectory during particle formation (black) and evaporation (grey).

[20] The fractional contributions of all the target AMS m/z co-vary with C_{OA}, with the exception of m/z 139. The relative contributions of some mass fragments increase while others decrease with changing C_{OA}. These changes were observed with both increasing C_{OA} via α-pinene addition and decreasing C_{OA} via dilution. Therefore, the composition of the SOA changes with partitioning.

[21] Figure 3b plots the fractional contribution from m/z 44 in terms of the total C_{OA}; m/z 44 contributes a larger fraction of the total organic signal at lower C_{OA}, indicating more polar components contribute a larger fraction of the SOA at low C_{OA}. Conceptually this makes sense since the more polar components of SOA likely have lower saturation vapor pressures and therefore condense preferentially at lower C_{OA}. This sort of behavior has been observed previously in traditional yield experiments [Zhang et al., 2006].

[22] The reversibility of the changes in composition can be evaluated by comparing the AMS data from the formation and dilution portions of the experiment. For example, the m/z 44 data shown in Figure 3b reveal a modest increase in the fractional contribution with time. Therefore, changes in composition due to partitioning may not be completely reversible.

6. Conclusion

[23] This work demonstrates a new method to investigate the gas-particle partitioning of SOA formed in a smog chamber. The results show that SOA from α-pinene ozonolysis repartitions reversibly upon dilution, but on a much longer time scale than has been observed in single-component aerosols of similar sizes. We hypothesize that the surprisingly slow evaporation rate may be due to some mixture effect or decomposition of weakly bound oligomers, but we cannot determine the mechanism from our data. Regardless of the mechanism, the relatively slow equilibration rate may influence behavior of SOA in the atmosphere and certainly affects interpretation of laboratory SOA data [An et al., 2007].

[24] The composition of aerosols also varies systematically with partitioning. At lower C_{OA}, more polar components appear to dominate the aerosol, while other products become more prevalent at higher concentrations when more volatile species will condense. Clearly, SOA composition must be considered concentration-dependent, as more-or less-volatile components partition with concentration or temperature changes.

[25] Our experiments only considered higher concentration conditions which are commonly encountered in smog chambers. They are at the upper end of atmospheric concentrations. The experiments also only considered relatively fresh SOA. Both of these parameters may influence the reversibility of gas-particle partitioning.

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