

**Self-limited uptake
of α -pinene-oxide to
acidic aerosol**

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Self-limited uptake of α -pinene-oxide to acidic aerosol: the effects of liquid-liquid phase separation and implications for the formation of secondary organic aerosol and organosulfates from epoxides

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Abstract

The reactive uptake of α -pinene oxide (α PO) to acidic sulfate aerosol was studied under humid conditions in order to gain insight into the effects of liquid-liquid phase separation on aerosol heterogeneous chemistry and further elucidate the formation of secondary organic aerosol and organosulfates from epoxides. A continuous flow environmental chamber was used to monitor changes in diameter of monodisperse, deliquesced, acidic sulfate particles exposed to α PO at 30 and 50 % RH. In order to induce phase separation and probe potential limits to particle growth from acidic uptake, α PO was introduced over a wide range of concentrations, from 200 ppb to 5 ppm. Uptake was observed to be highly dependent on initial aerosol pH. Significant uptake of α PO to aerosol was observed with initial $\text{pH} < 0$. When exposed to 200 ppb α PO, aerosol with $\text{pH} = -1$ doubled in volume, and 6 % volume growth was observed at $\text{pH} = 0$. Aerosol with $\text{pH} = 1$ showed no growth. The extreme acidity required for efficient α PO uptake suggests that this chemistry is typically not a major route to formation of aerosol mass or organosulfates in the atmosphere. Partition coefficients (K_p) ranged from $0.2\text{--}1.6 \times 10^{-4} \text{ m}^3 \mu\text{g}^{-1}$ and were correlated to initial particle acidity and particle organic content; particles with higher organic content had lower partition coefficients. Effective uptake coefficients (γ) ranged from 0.4 to 4.7×10^{-5} and are much lower than recently reported for uptake to bulk solutions. In experiments in which α PO was added to bulk H_2SO_4 solutions, phase separation was observed for mass loadings similar to those observed with particles, and product distributions were dependent on acid concentration. Liquid-liquid phase separation in bulk experiments, along with our observations of decreased uptake to particles with the largest growth factors, suggest an organic coating forms upon uptake to particles, limiting reactive uptake.

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1 Introduction

The reactive uptake of volatile organic compounds (VOCs) by tropospheric aqueous aerosols has recently gained attention as a potential source of secondary organic aerosol (SOA) and organosulfate species (Ervens et al., 2011; Lim et al., 2010; McNeill et al., 2012; Volkamer et al., 2009; Sareen et al., 2010; Kroll et al., 2005; Nozière et al., 2010; Galloway et al., 2009; Liggio et al., 2005). Volatile compounds can react in the particle phase (e.g. hydrolyzing or oligomerizing) after uptake to form low-volatility products. Recently, interest has grown in reactive uptake for aerosols with significant water content (McNeill et al., 2012). Aqueous uptake and processing of organic matter may be important in explaining the extreme levels of oxidation ($O:C \geq 1$) observed in secondary organic aerosol (Lee et al., 2011; McNeill et al., 2012). The focus of this study is the reactive uptake of epoxides to acidic sulfate aerosol and understanding the effects of particle composition on acid-mediated reactive uptake.

Epoxides have been identified as potential SOA precursors in both laboratory studies and thermodynamic calculations, in particular through their ability to form organosulfates (OS) through acid-catalyzed ring opening (Iinuma et al., 2009; Lal et al., 2012; Minerath and Elrod, 2009; Paulot et al., 2009). Recent observations of OS in ambient samples have led to laboratory studies aimed at determining their formation mechanisms and organic precursors (Surratt et al., 2006, 2007, 2008; Lin et al., 2011; Hatch et al., 2011; Lal et al., 2012; Minerath et al., 2008, 2009; Minerath and Elrod, 2009; Darer et al., 2011; Hu et al., 2011; Perri et al., 2010). OS yields are known to depend on particle acidity and total aerosol volume (Surratt et al., 2007; Iinuma et al., 2009; Lal et al., 2012; Hu et al., 2011). In addition, while initial OS formation may drive uptake to aerosol, less-substituted OS or those with nearby electron-withdrawing groups may readily hydrolyze to diol compounds (Hu et al., 2011). Laboratory experiments have observed monoterpene-derived epoxide uptake to extremely acidic aerosol ($pH \sim 0$), but results at acidities above 0 and less than 7 have not been reported. We conducted

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experiments over a wide range of aerosol pH and α PO concentrations to explore the importance of epoxide uptake under ambient conditions.

Reactive uptake can be strongly affected by particle morphology and phase separation of particle organic and inorganic components. After liquid-liquid phase separation, a core-shell morphology with the organic phase coating the outer surface of the particle has been observed (Bertram et al., 2011; Smith et al., 2012; You et al., 2012). Such a morphology change is expected to impact aerosol heterogeneous chemistry by changing the surface composition from aqueous to organic (You et al., 2012). Zuend and Seinfeld also showed via calculations that liquid-liquid phase separation can dramatically impact gas-particle partitioning of semivolatile species (Zuend et al., 2010). Particles with significant water content may exist in several morphologies. These could include a fully mixed aqueous/organic particle, a phase separated aqueous core with an organic shell, and an aqueous phase partially engulfed by an organic phase (Smith et al., 2012). The organic-rich phase of phase-separated acidic particles may be proton-depleted, with the aqueous phase retaining the initial acidity (Reichardt, 1990; Pavia et al., 1999). In addition, uptake studies with bulk phase mimics of acidic sulfate aerosol particles (e.g. sulfuric acid solutions) do not replicate this complicated phase behavior and may only represent initial uptake rates to systems with low levels of organics. By studying uptake to both bulk solutions and particles over a range of organic content and acidities, we begin to elucidate the effects of particle morphology on uptake to acidic aerosol.

2 Experimental methods

2.1 Smog chamber setup

All chamber experiments were conducted in a $\sim 3.5 \text{ m}^3$ Teflon chamber as shown in Fig. 1. The chamber is run in steady-state operation with a constant gas flow of 13 Lpm for a chamber residence time of about 4 h, and in practice stable conditions were

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reached between 3 and 4 h. This is consistent with previous static chamber studies of epoxides and similar aerosol acidity, particle concentration, and α PO concentration that indicate reactive uptake reaches steady state after about 2 h (Lin et al., 2011; linuma et al., 2009). Prior to each experiment, the bag was rinsed with de-ionized water and flushed with dry nitrogen to remove any material present on the chamber walls. All chamber experiments were conducted at approximately 50 % RH and 25 °C, except for experiments with a particularly high particle acidity of pH = -1, which were run at 30 % RH. A hygrometer (Vaisala) was used to monitor the humidity and temperature of the chamber. The conditions for each experiment are listed in Table 1; also shown are the results of each experiment to be discussed below.

The bag was filled with a combination of three flows: humidified nitrogen, ammonium sulfate/sulfuric acid aerosol in nitrogen, and α PO in nitrogen. The final humidity was adjusted by combining a nitrogen flow that passed through a water bubbler filled with de-ionized water and a second flow of dry nitrogen. The total humid-nitrogen flow was 11 Lpm. An atomizer (TSI-3076) produced seed particles by atomizing a 0.2 M $(\text{NH}_4)_2\text{SO}_4$ with a nitrogen flow rate of 2 Lpm. Particle acidity was altered by adjusting the ratio of $\text{H}_2\text{SO}_4 : (\text{NH}_4)_2\text{SO}_4$ in the atomizing solution. In order to achieve precise growth measurements, the atomizer output was size-selected at 150 nm using a DMA operating at a 8 : 0.8 sheath to sample flow (Lpm) ratio. Particle concentrations in the bag were in the range of 1000–3000 cm^{-3} . α PO (Sigma Aldrich, > 97 %) vapor was injected at variable concentrations by passing nitrogen over liquid α PO held at varying temperature, which was controlled using a cold finger setup. To run below ambient temperatures, the cold finger was immersed in a dewar filled with either ice (0 °C) or an NaCl/ice bath (-20 °C). The concentration of the α PO delivered from the cold finger was calibrated in a separate set of experiments with a custom-built chemical ionization mass spectrometer using $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ as the reagent ion. See Sareen et al. for a description of the instrument and its operation (Sareen et al., 2010). α PO was detected as the protonated molecule at m/z 153 ($\text{C}_{10}\text{H}_{16}\text{O} + \text{H}^+$), its water cluster ($\text{C}_{10}\text{H}_{16}\text{OH}^+ \cdot \text{H}_2\text{O}$) at m/z 171, and the protonated dimer ($2 \cdot \text{C}_{10}\text{H}_{16}\text{O} + \text{H}^+$) at m/z 205.

2.2 Chamber operation

Data from a typical experiment are shown in Fig. 2. After a stable initial diameter is achieved for the seed particles, in this case ~ 150 nm pure sulfuric acid particles at 50 % RH, the α PO flow was initiated. After ~ 30 min lag period, particles are observed at larger diameters. After injecting α PO for roughly 4 h, the particles in the chamber attain a stable output diameter.

2.3 Bulk uptake studies

2.3.1 Gas phase uptake to bulk surfaces

The phase behavior and diffusivity of α PO reactive uptake products were observed in additional experiments in which gas-phase α PO was taken up by bulk aqueous sulfuric acid samples. 4 vials with 10 mL of sulfuric acid of varying concentration in water (10, 3, 1, and 0.1 M) and 1 vial with 3 mL of pure α PO were placed beneath a large inverted beaker. This created a sustained exposure of the acid surface to the room temperature vapor pressure of gas-phase α PO (0.819 torr, 25 °C). Vials after 18 h of α PO exposure are shown in Fig. 3a. In the 10 M acid solution, a light-red layer was formed at the solution surface within several hours and continued to thicken with longer α PO exposure. The 3 M solution became slightly cloudy, and none of the other solutions formed visible products from α PO exposure. The top and bottom layer of the acid solutions were extracted with a pipette, and the UV-Vis absorbance spectra of these fractions were measured. Digital photographs of the 10 M reaction vials were used to monitor the depth of this colored layer with time and estimate the aqueous-phase diffusion coefficient of α PO. Control experiments in which the acid solutions were exposed to ambient laboratory air under the trapped beaker in the absence of α PO resulted in no color change.

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2.3.2 Slow addition of liquid α PO to bulk acid solution

To deliver a larger volume fraction of α PO, 3 mL of liquid α PO was slowly added at $750\mu\text{Lh}^{-1}$ to 3 mL of sulfuric acid solutions with a syringe pump to achieve a 50% volume fraction of α PO after 3 h. For both the 10 M and 3 M acid concentrations, visible phase separation occurred; the vial with 10 M acid is shown in Fig. 3b.

3 Results and discussion

3.1 Uptake of α PO to particles: effect of α PO concentration and particle acidity

The volume-growth factor, defined as the ratio between the final and initial volumes (V_f/V_i), increased with the gas-phase α PO concentration. These results are displayed in Fig. 4 and Table 1 for experiments for several particle acidities. High particle acidity and gas-phase α PO concentration resulted in very high growth factors and particle organic content. For particles with $\text{pH} \sim -0.5$ and 5 ppm α PO, the growth factor is greater than 2 and the organic fraction of the particle, $(V_f/V_i - 1)/V_f$ reaches nearly 50%.

The clear trend of increased uptake with particle acidity indicates that α PO only forms SOA under conditions of reactive uptake. This is consistent with the relatively low aqueous solubility of α PO (219 mgL^{-1} or roughly 0.02% by mass). Previous measurements have also shown α PO uptake to be strongly dependent on particle acidity (Surratt et al., 2006, 2007; Lin et al., 2011; Iinuma et al., 2009; Lal et al., 2012). Iinuma et al. ran experiments with acidic ($\text{pH} = 0$) and neutral aerosol, but only observed uptake at $\text{pH} = 0$ (Lal et al., 2012). Surratt and co-workers also observed a strong pH dependence for the reactive uptake of isoprene-derived epoxides, with greater uptake at low pH, consistent with acid-catalyzed reactions driving uptake to aerosol (Lin et al., 2011).

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3.2 Partitioning coefficients

To quantify the partitioning of a gas-phase component to the aqueous aerosol, we use an effective partitioning coefficient, $K_{p,\text{eff}}$ ($\mu\text{g m}^{-3}$):

$$K_{p,\text{eff}} = \frac{\Delta C_{p,\text{tot}}}{C_g \times C_{p,\text{tot}}} \quad (1)$$

5 where $\Delta C_{p,\text{tot}}$ is the increase in total particle mass concentration from gas uptake, C_g is the mass concentration of organic precursor in the gas phase, and $C_{p,\text{tot}}$ is the total particle mass concentration, all expressed in ($\mu\text{g m}^{-3}$). The partitioning coefficient is shown as a function of particle growth factor in Fig. 5. A value of $2.8 \times 10^{-4} \text{ m}^3 \mu^{-1} \text{ g}^{-1}$ was measured by linuma et al. under conditions of 50 ppb αPO , $4 \times 10^{-6} \text{ cm}^3 \text{ m}^{-3}$ seed
10 concentration, and particles with pH = 0 (linuma et al., 2009). We measured $K_{p,\text{eff}}$ under similar conditions and 200 ppb αPO to be between $0.4\text{--}1 \times 10^{-4} \text{ m}^3 \mu^{-1} \text{ g}^{-1}$. This is in good agreement given measurement uncertainty and the observed increase in uptake coefficient with lower αPO concentration.

As shown in Fig. 5, the partitioning coefficient decreases with increasing growth factor. In other words, as the organic fraction of the particle becomes greater, the affinity of αPO for the particle decreases. The trend of uptake with growth factor suggests that changes in particle composition and/or morphology upon αPO uptake play a major role
15 in determining αPO partitioning to acidic particles.

3.3 Uptake of αPO to bulk solutions

20 The uptake of αPO to bulk sulfuric acid solutions was strongly pH-dependent. The reactive uptake of αPO by the 10 M H_2SO_4 solution was made evident by the formation of a red layer at the top of the solution. When left to sit over 48 h, this layer darkened and grew thicker. UV-Vis spectrophotometry confirms the formation of strongly light-absorbing products at high solution acidities and that this chemistry is reversible upon

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dilution with water (see Supplement). The change in thickness of the red layer over time allowed an estimate of the diffusivity for the reactive uptake products of α PO. After 45 h the products formed a layer roughly 1.5 cm thick. Fick's law (Eq. 2) gives a relationship between diffusivity, D , the distance traveled in a given direction, x , and the elapsed time, t :

$$D = \frac{x^2}{2t} \quad (2)$$

The diffusivity of the reaction products is calculated to be $9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This value is similar to that of glucose in water (Gladden and Dole, 1953), and does not indicate particularly low diffusivity.

Liquid–liquid phase separation was observed at higher mass loadings of α PO. Using a syringe pump, liquid α PO was slowly injected to the surface of sulfuric acid solutions. The flow rate was set to give a similar volume-addition rate of α PO to the acid solution as was observed in the particle uptake experiments, doubling the solution volume over 3 h. Phase separation occurred for both the 10 and 3 M sulfuric acid solutions, but the organic phase in the 3 M solutions was not colored, consistent with our other bulk experiments. The α PO concentration in a solution or particle will affect the product distribution, because a higher organic concentration will favor oligomerization. Lal et al. observed a change in the product distribution in bulk studies of the mixed liquids with different α PO:acid mass ratios, suggesting that the concentration of organics at the bulk surface or in a particle affects the product distribution (Lal et al., 2012). Standard organic synthesis has shown that, at least in bulk sulfuric acid solutions, the hydrolysis products involve opening of the 4-member ring in α PO (Coelho et al., 2012). This is not likely to be reversible and retains a double bond that will allow for further reaction. The estimation of relatively fast diffusion rates in these systems and the decreased K_p values at high-mass loading experiments suggest that products of α PO uptake will saturate the particle volume and then phase separate with increased loading to form a coating around the particle's inorganic core.

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3.4 Loss of water upon drying

Particles were dried after organic uptake in order to get more information about their phase/morphology. The results from drying are shown in Table 1 and also Fig. 6 as diameter growth vs. the fraction of water lost from the particle. The fraction of water lost is calculated as:

$$F_{\text{loss}} = \frac{V_{\text{wet}} - V_{\text{Dry}}}{V(\text{H}_2\text{O})_{\text{RH,wet}} - V(\text{H}_2\text{O})_{\text{RH,Dry}}} \quad (3)$$

where V_{wet} and V_{Dry} are the particle volumes before and after the drier, and $V(\text{H}_2\text{O})_{\text{RH,Wet}}$ and $V(\text{H}_2\text{O})_{\text{RH,Dry}}$ are the volumes of water at the RH conditions before and after the drier. The volumes of water can be predicted from the efflorescence and deliquescence curves for sulfuric acid and ammonium sulfate (Seinfeld and Pandis, 2006b). We observe a clear trend in the fraction of the total particle-water lost with the increase in particle diameter. Greater particle diameter growth (i.e. a thicker organic coating) led to decreased water loss from the particles. This suggests that the organic component of the particle inhibited evaporation.

Separation of the particles into water-rich and organic-rich liquid phases is suggested by our bulk-phase studies. This is consistent with recent studies by Bertram et al. which showed phase separation for particles of ammonium sulfate and organic compounds that have atomic O : C ratios of less than 0.7, and product studies of $\alpha\text{PO} + \text{H}_2\text{SO}_4$ suggest material with O : C of 0.2–0.5 is formed (Lal et al., 2012; Iinuma et al., 2009; Coelho et al., 2012). In their studies, Bertram et al. observed a core-shell morphology for phase separated particles, with the organic phase on the outside. Inhibition of water loss from particles with high organic content is consistent with slow diffusion of water out of the particle through the organic-rich phase of the particle. The observed trend in water loss highlights the importance of phase separation in predicting the effects of RH on particle mixing state and water uptake/loss.

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3.5 Uptake coefficients

The dynamic uptake of gases to the particle surface is determined by the uptake coefficient. It characterizes the collision efficiency for uptake of an organic molecule to a surface. Assuming a set timescale to grow to the final diameter, we can estimate this parameter, and then compare this value to previous measurements and values for similar cases. Our experiments do not directly yield the timescale to reach the final growth factor, because the experimental timescale is determined by the time to reach steady state in the continuous-flow chamber. We can use the estimate of ~ 1.5 h. from the batch reactor experiments of linuma et al. as a guide (linuma et al., 2009). Assuming a constant particle density, there is a simple relation between the mass flux and molecular collision with a particle that yields the uptake coefficient:

$$\Delta D_p = \frac{\gamma \omega C_{\text{gas}} MW_{\text{gas}}}{4\rho} \Delta t \quad (4)$$

where ΔD_p is the change in particle diameter, γ is the uptake coefficient, ω is the molecular speed, C_{gas} is the condensing species' gas-phase concentration, MW_{gas} is the molecular weight of the condensing species, ρ is the particle density, and Δt is the duration of condensation. As a first approximation we can use this relation to calculate an average uptake coefficient during the course of an experiment. Using the timescale from linuma et al. we calculate uptake coefficients between 1 and 50×10^{-6} . These values, shown in Fig. 7, are particularly low for reactive uptake of organics. Lal et al. have measured uptake coefficients for α PO to bulk sulfuric acid surfaces to be 4.6×10^{-2} , and uptake coefficients for other reactive organics are in the range of 1×10^{-3} (Lal et al., 2012; Liggió et al., 2005). The absorbing phase in the previous studies of α PO to bulk solution does not reach high volume fractions of organics, so these measurements might reflect only initial uptake of α PO to particles, before accumulation (or without the presence) of organic material. Our low values for the effective uptake coefficients show that the uptake coefficient depends on the volume fraction of

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organics and decreases as the particle accumulates organic material. Since α PO uptake is driven by reaction with acid in the aqueous phase, this is again consistent with the formation of an organic-rich phase at the gas-aerosol interface.

4 Conclusions

We have demonstrated via bulk and aerosol chamber measurements that the reactive uptake of α PO to acidic aerosol is self-limiting due to liquid-liquid phase separation at high organic loadings. Both the effective partition coefficients and uptake coefficients decreased for particles with higher volume fractions of organics, and inhibited water loss was observed at high organic loadings. In experiments using bulk solutions, phase separation was observed for solutions with high volume fractions of α PO and its reaction products. Similar effects are possible for aqueous aerosol SOA formation in other systems with O : C ratios < 0.7 (and therefore liquid-liquid phase separation is predicted) (Bertram et al., 2011). In scenarios where isoprene epoxydiols or glyoxal dominate uptake to the aerosol aqueous phase, the O : C ratio is expected to be > 0.7 , so this effect may not limit SOA formation via those pathways (McNeill et al., 2012). However, more experimental evidence is needed to confirm this prediction.

To date, studies have only shown uptake of monoterpene-derived epoxides at an aerosol pH of zero. Our results support this fact and show that even at an aerosol pH of 1.0, no observable uptake occurred for α PO. This suggests that under typical ambient conditions, significant formation of monoterpene-derived SOA or organosulfate compounds is not likely to occur. Both our observations of complex phase behavior and pH dependent product formation suggest that flow tube measurements of epoxide uptake to bulk solutions may only apply to particles with low organic content and equivalent acidity, and that particle organic content strongly affects product yields/identities.

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Supplementary material related to this article is available online at:
[http://www.atmos-chem-phys-discuss.net/13/7151/2013/
acpd-13-7151-2013-supplement.pdf](http://www.atmos-chem-phys-discuss.net/13/7151/2013/acpd-13-7151-2013-supplement.pdf).

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References

- Bertram, A. K., Martin, S. T., Hanna, S. J., Smith, M. L., Bodsworth, A., Chen, Q., Kuwata, M., Liu, A., You, Y., and Zorn, S. R.: Predicting the relative humidities of liquid-liquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon elemental ratio of the organic component, *Atmos. Chem. Phys.*, 11, 10995–11006, doi:10.5194/acp-11-10995-2011, 2011.
- Coelho, J. V., de Meireles, A. L. P., da Silva Rocha, K. A., Pereira, M. C., Oliveira, L. C. A., and Gusevskaya, E. V.: Isomerization of \pm -pinene oxide catalyzed by iron-modified mesoporous silicates, *Appl. Catal. A-Gen.*, 443–444, 125–132, doi:10.1016/j.apcata.2012.07.030, 2012.
- Darer, A. I., Cole-Filipiak, N. C., O'Connor, A. E., and Elrod, M. J.: Formation and stability of atmospherically relevant isoprene-derived organosulfates and organonitrates, *Environ. Sci. Technol.*, 45, 1895–1902, doi:10.1021/es103797z, 2011.
- Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.*, 11, 11069–11102, doi:10.5194/acp-11-11069-2011, 2011.
- Galloway, M. M., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H., and Keutsch, F. N.: Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions, *Atmos. Chem. Phys.*, 9, 3331–3345, doi:10.5194/acp-9-3331-2009, 2009.
- Gladden, J. K. and Dole, M.: Diffusion in supersaturated solutions. II. Glucose solutions, *J. Am. Chem. Soc.*, 75, 3900–3904, doi:10.1021/ja01112a008, 1953.

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Hatch, L. E., Creamean, J. M., Ault, A. P., Surratt, J. D., Chan, M. N., Seinfeld, J. H., Edger-
ton, E. S., Su, Y., and Prather, K. A.: Measurements of isoprene-derived organosulfates in
ambient aerosols by aerosol time-of-flight mass spectrometry – Part 2: Temporal variability
and formation mechanisms, *Environ. Sci. Technol.*, 45, 8648–8655, doi:10.1021/es2011836,
2011.

Hu, K. S., Darer, A. I., and Elrod, M. J.: Thermodynamics and kinetics of the hydrolysis of
atmospherically relevant organonitrates and organosulfates, *Atmos. Chem. Phys.*, 11, 8307–
8320, doi:10.5194/acp-11-8307-2011, 2011.

Iinuma, Y., Boge, O., Kahnt, A., and Herrmann, H.: Laboratory chamber studies on the formation
of organosulfates from reactive uptake of monoterpene oxides, *Phys. Chem. Chem. Phys.*,
11, 7985–7997, doi:10.1039/b904025k, 2009.

Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.:
Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl
compounds, *J. Geophys. Res.-Atmos.*, 110, doi:10.1029/2005jd006004, 2005.

Lal, V., Khalizov, A. F., Lin, Y., Galvan, M. D., Connell, B. T., and Zhang, R.: Hetero-
geneous Reactions of Epoxides in Acidic Media, *J. Phys. Chem. A*, 116, 6078–6090,
doi:10.1021/jp2112704, 2012.

Lee, A. K. Y., Herckes, P., Leaitch, W. R., Macdonald, A. M., and Abbatt, J. P. D.: Aqueous OH
oxidation of ambient organic aerosol and cloud water organics: formation of highly oxidized
products, *Geophys. Res. Lett.*, 38, L11805, doi:10.1029/2011gl047439, 2011.

Liggio, J., Li, S.-M., and McLaren, R.: Reactive uptake of glyoxal by particulate matter, *J. Geo-
phys. Res.*, 110, D10304, doi:10.1029/2004jd005113, 2005.

Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its
role in secondary organic aerosol (SOA) formation, *Atmos. Chem. Phys.*, 10, 10521–10539,
doi:10.5194/acp-10-10521-2010, 2010.

Lin, Y.-H., Zhang, Z., Docherty, K. S., Zhang, H., Budisulistiorini, S. H., Rubitschun, C. L.,
Shaw, S. L., Knipping, E. M., Edgeron, E. S., Kleindienst, T. E., Gold, A., and Surratt, J. D.:
Isoprene epoxydiols as precursors to secondary organic aerosol formation: acid-catalyzed
reactive uptake studies with authentic compounds, *Environ. Sci. Technol.*, 46, 250–258,
doi:10.1021/es202554c, 2011.

McNeill, V. F., Woo, J. L., Kim, D. D., Schwier, A. N., Wannell, N. J., Sumner, A. J.,
and Barakat, J. M.: Aqueous-phase secondary organic aerosol and organosulfate forma-

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tion in atmospheric aerosols: a modeling study, *Environ. Sci. Technol.*, 46, 8075–8081, doi:10.1021/es3002986, 2012.

Minerath, E. C. and Elrod, M. J.: Assessing the potential for diol and hydroxy sulfate ester formation from the reaction of epoxides in tropospheric aerosols, *Environ. Sci. Technol.*, 43, 1386–1392, doi:10.1021/es8029076, 2009.

Minerath, E. C., Casale, M. T., and Elrod, M. J.: Kinetics feasibility study of alcohol sulfate esterification reactions in tropospheric aerosols, *Environ. Sci. Technol.*, 42, 4410–4415, doi:10.1021/es8004333, 2008.

Minerath, E. C., Schultz, M. P., and Elrod, M. J.: Kinetics of the reactions of isoprene-derived epoxides in model tropospheric aerosol solutions, *Environ. Sci. Technol.*, 43, 8133–8139, doi:10.1021/es902304p, 2009.

Nozière, B., Dziejczak, P., and Córdova, A.: Inorganic ammonium salts and carbonate salts are efficient catalysts for aldol condensation in atmospheric aerosols, *Phys. Chem. Chem. Phys.*, 12, 3864–3872, 2010.

Paulot, F., Crouse, J. D., Kjaergaard, H. G., Kurten, A., St. Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected epoxide formation in the gas-phase photooxidation of isoprene, *Science*, 325, 730–733, 2009.

Pavia, D., Lampman, G., and Kriz, G.: *Organic Laboratory Techniques*, 3 edn., Brooks/Cole, Pacific Grove, CA, 1999.

Perri, M. J., Lim, Y. B., Seitzinger, S. P., and Turpin, B. J.: Organosulfates from glycolaldehyde in aqueous aerosols and clouds: laboratory studies, *Atmos. Environ.*, 44, 2658–2664, doi:10.1016/j.atmosenv.2010.03.031, 2010.

Reichardt, C.: *Solvents and solvent effects in organic chemistry*, VCH Weinheim, Basel, Switzerland, 1990.

Sareen, N., Schwier, A. N., Shapiro, E. L., Mitroo, D., and McNeill, V. F.: Secondary organic material formed by methylglyoxal in aqueous aerosol mimics, *Atmos. Chem. Phys.*, 10, 997–1016, doi:10.5194/acp-10-997-2010, 2010.

Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics*, 2 edn., Wiley, Hoboken, New Jersey, 2006.

Smith, M. L., Bertram, A. K., and Martin, S. T.: Deliquescence, efflorescence, and phase miscibility of mixed particles of ammonium sulfate and isoprene-derived secondary organic material, *Atmos. Chem. Phys.*, 12, 9613–9628, doi:10.5194/acp-12-9613-2012, 2012.

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- Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for organosulfates in secondary organic aerosol, *Environ. Sci. Technol.*, 41, 517–527, doi:10.1021/es062081q, 2006.
- 5 Surratt, J. D., Lewandowski, M., Offenberg, J. H., Jaoui, M., Kleindienst, T. E., Edney, E. O., and Seinfeld, J. H.: Effect of acidity on secondary organic aerosol formation from isoprene, *Environ. Sci. Technol.*, 41, 5363–5369, doi:10.1021/es0704176, 2007.
- Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W.,
- 10 Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, *J. Phys. Chem. A*, 112, 8345–8378, doi:10.1021/jp802310p, 2008.
- Volkamer, R., Ziemann, P. J., and Molina, M. J.: Secondary Organic Aerosol Formation from Acetylene (C_2H_2): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase, *Atmos. Chem. Phys.*, 9, 1907–1928, doi:10.5194/acp-9-1907-2009, 2009.
- 15 You, Y., Renbaum-Wolff, L., Carreras-Sospedra, M., Hanna, S. J., Hiranuma, N., Kamal, S., Smith, M. L., Zhang, X., Weber, R. J., Shilling, J. E., Dabdub, D., Martin, S. T., and Bertram, A. K.: Images reveal that atmospheric particles can undergo liquid–liquid phase separations, *P. Natl. Acad. Sci. USA*, 109, 13188–13193, doi:10.1073/pnas.1206414109, 2012.
- 20 Zuend, A., Marcolli, C., Peter, T., and Seinfeld, J. H.: Computation of liquid-liquid equilibria and phase stabilities: implications for RH-dependent gas/particle partitioning of organic-inorganic aerosols, *Atmos. Chem. Phys.*, 10, 7795–7820, doi:10.5194/acp-10-7795-2010, 2010.

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Table 1. Summary of experimental conditions.

Expt. #	1	2	3	4	5	6	7	8	9	10
pH ^a	−1	−1	−0.5	−0.5	−0.5	0	0	0	1	1
α PO (ppm)	5	1	5	1	0.2	5	1	0.2	5	1
Initial Diameter (nm)	160	146	163	155	147	170	165	165	175	170
Growth Factor ^b	2.55	1.93	1.92	1.48	1.23	1.44	1.1	1.06	0	0
Fraction water lost ^c	–	0.34	0.24	0.58	0.76	0.54	–	–	–	–
Init. water content ^d (vol/vol)	33%	33%	58%	58%	58%	46%	46%	46%	41%	41%

^a pH values calculated using atomizing solution.

^b Ratio of final to initial particle volume: V_f/V_i .

^c See results and discussion.

^d From thermodynamic data (Seinfeld and Pandis, 2006).

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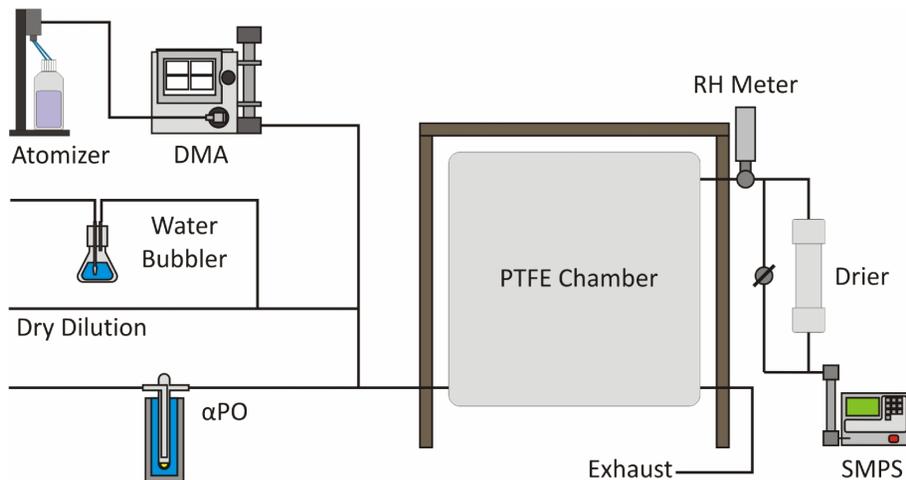
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**Fig. 1.** Schematic of the continuous flow experimental chamber setup.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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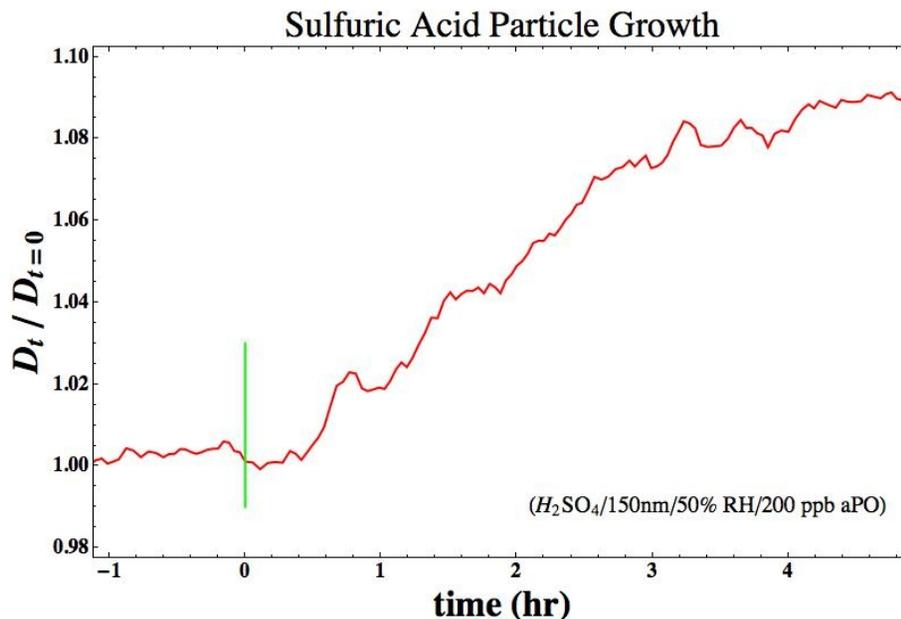


Fig. 2. Change in diameter of 150 nm sulfuric acid aerosol particles at 50 % RH due to uptake of α PO (200 ppb) during the approach to steady state in the continuous-flow chamber. See text for details.

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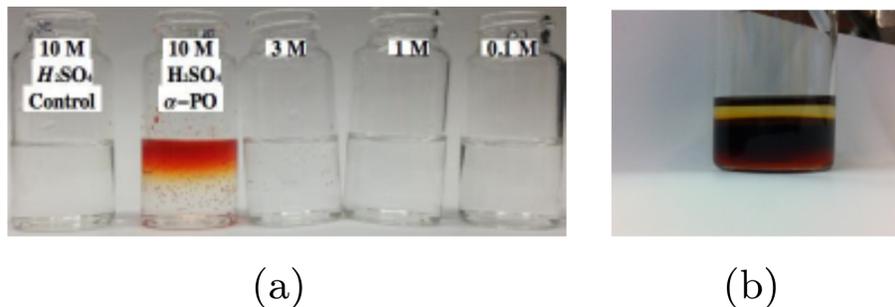


Fig. 3. (a) Photograph of reaction vials after 19 h of gas-phase uptake to α PO to acid solutions of (second on left to right) 10, 3, 1, and 0.1 M. At the far left is a control vial of 10 M acid not exposed to α PO. **(b)** Photograph of a reaction vial with slow addition of liquid α PO ($750 \mu\text{L h}^{-1}$) to 10 M acid solution.

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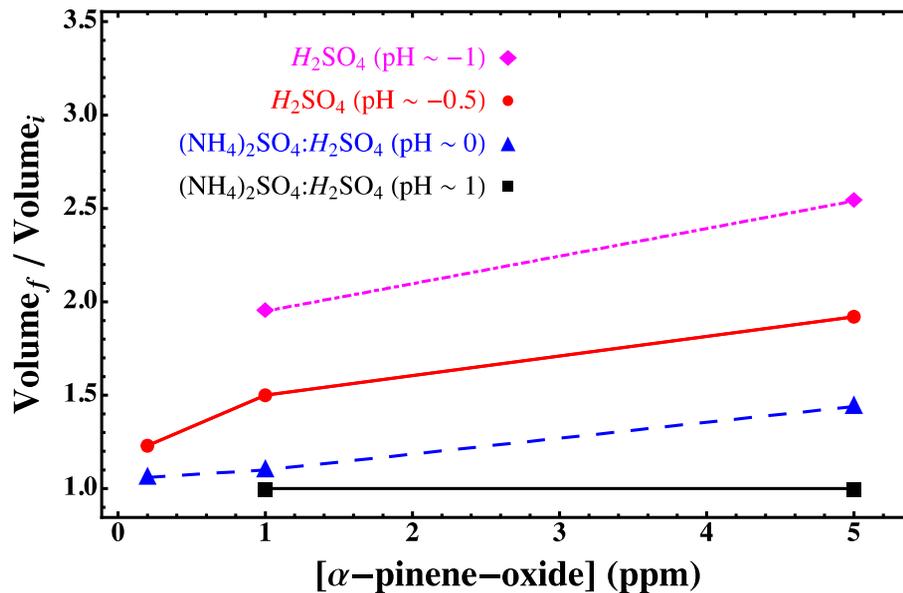


Fig. 4. Effect of acidity and α PO concentration on the growth factor of acidic sulfate particles (pH -1 : magenta diamonds, pH -0.5 : redcircles, pH 0 : blue triangles, pH 1 : black squares). Growth due to α PO uptake increases with acidity and α PO concentration.

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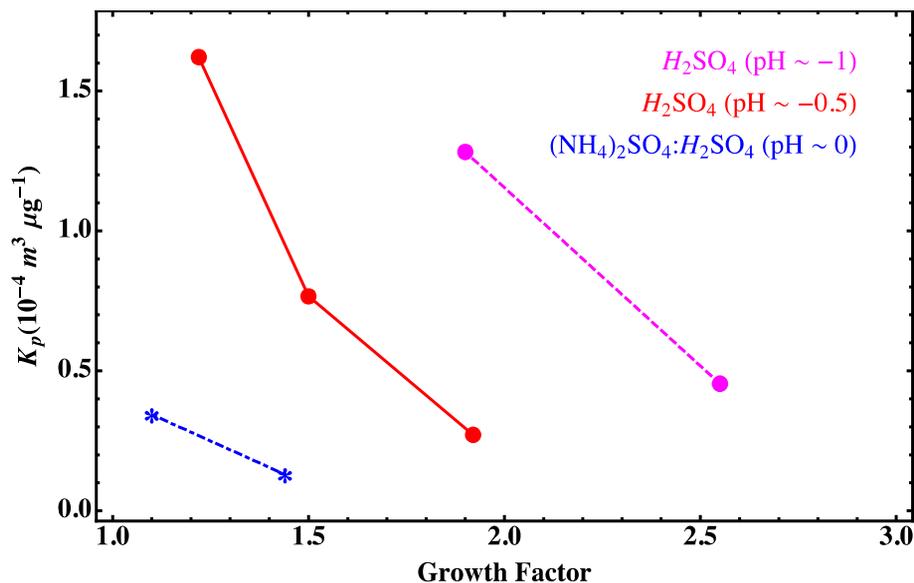


Fig. 5. Effective partitioning coefficients as a function of particle growth factor. Data are shown for three particle pH levels: -1 (magenta, dashed, circles), -0.5 (red, solid, circles), 0 (blue, dot-dashed, asterisks). Partitioning coefficients increase with increasing particle acidity and decrease with increasing growth factor.

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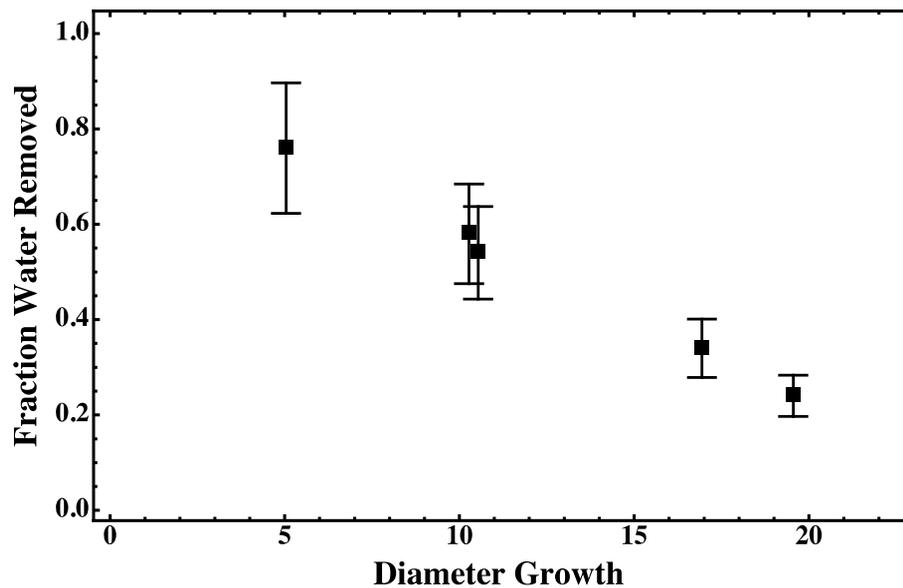
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**Fig. 6.** Fraction of water removed from particles after uptake of α PO vs. diameter growth.

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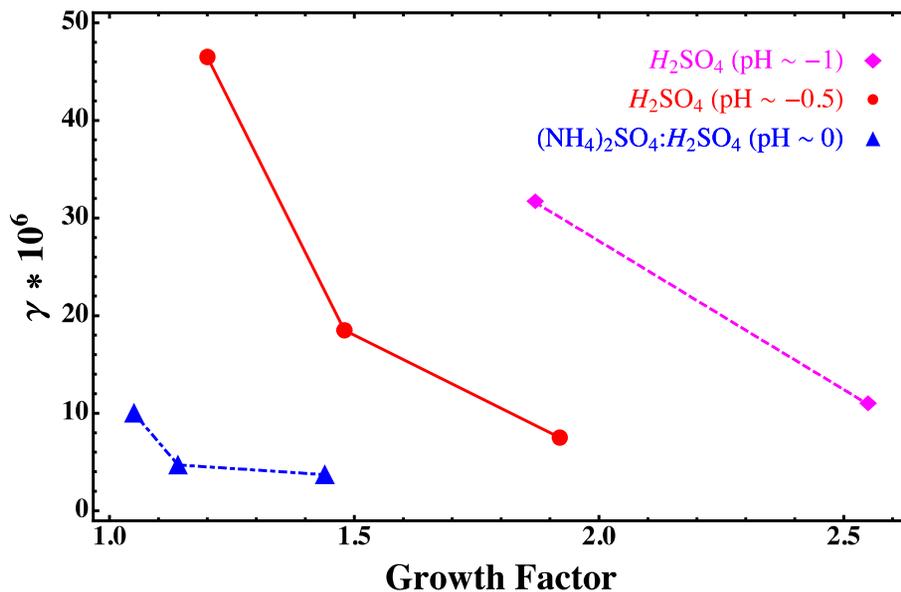


Fig. 7. Uptake coefficient dependence on growth factor for particles in the pH range -1 to 0 . Calculated pH values for the seed aerosol are -1 (diamonds), -0.5 (circles), and 0 (triangles).

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