

A re-evaluation on the atmospheric significance of octanal vapor uptake by acidic particles: roles of particle acidity and gas-phase octanal concentrations

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Abstract

An electrodynamic balance was used to investigate the uptake of octanal vapor by single sulfuric acid droplets levitated under various relative humidity (RH) conditions and gas-phase octanal concentrations. In the high octanal concentration experiments (200–300 ppm), we observed that the organic mass yield depended on the acidity of the sulfuric acid droplets and significant uptake of octanal only occurred when the RH was about 10% (H_2SO_4 wt% \sim 64%). Furthermore, reversible partitioning of a portion of condensed organic compounds was observed after active dilution with octanal-free compressed air. This finding indicates the potential importance of repartitioning of condensed organics in affecting the organic mass fraction and chemical composition of atmospheric organic aerosols. When a relatively lower octanal concentration (700–900 ppb) was used, no significant uptake of octanal vapor by the sulfuric acid droplets was observed even at 10% RH with long exposure time (> 25 hrs). Our findings suggest that both particle acidity and gas-phase octanal concentration are the critical factors that influence the organic mass yield of levitated acidic droplets. Because of the severe conditions of low RH and high octanal conditions required to effect the reactions, the reactive uptake of aldehydes, especially those that have chemical structures and properties very similar to octanal, into acidic particles may not be an important pathway in secondary organic aerosol formation under actual atmospheric conditions.

Keywords: secondary organic aerosol (SOA), acid-catalyzed reaction, sulfuric acid, aldehyde, gas-particle partitioning

1 Introduction

Atmospheric aerosols have been found to exert pronounced effects on human health and the radiative balance of the earth's atmosphere and thus on the global climate (Dockery et al., 1993; Pöschl, 2005; IPCC, 2007). Organic aerosols are major constituents of atmospheric aerosols and their composition and properties change continuously throughout their atmospheric lifetime as a result of various physical and chemical aging processes (Kanakidou et al., 2005; Rudich et al., 2007). In addition to the large uncertainties about the emissions inventories of primary organic aerosols (POA) as well as the gas-phase precursors of secondary organic aerosols (SOA), our poor understanding of the chemical aging processes of organic aerosols also limits the accuracy and reliability of current global climate modeling (Kanakidou et al., 2005).

While the literature predominately describes SOA formation as a photooxidation process involving gas-phase organic precursors followed by the partitioning of gas-phase products into the particle phase, the heterogeneous reactions between gas-phase and particle-phase materials have been recognized as another vital chemical aging process of organic aerosols in the last decade. A number of recent laboratory studies have focused on investigating the aging of particulate organics in the presence of gas-phase oxidants (e.g., Bertram et al., 2001; Rudich, 2003; Molina et al., 2004; Zahardis and Petrucci, 2007, George et al., 2007). These oxidative aging processes modify the composition of organic aerosols as well as their hygroscopicity, cloud condensation nuclei (CCN) activity and density (e.g., Katrib et al., 2005; Petters et al., 2006; Shilling et al., 2007; Lee and Chan, 2007ab). In addition, reactive uptake of volatile organics, especially carbonyl compounds, into preexisting acidic particles has been proposed to further explain the huge abundance of SOA in the atmosphere (Jang et

al., 2004), but their potential atmospheric importance is still under debate based on the existing particle mass yield/growth data, mechanistic and kinetic information obtained from laboratory studies (Jang et al., 2001; Esteve and Nozière, 2005; Kroll et al., 2005; Zhao et al. 2005; Liggio and Li, 2006; Casale et al., 2007) and thermodynamic (Barsanti and Pankow, 2004) and kinetic calculations (Ervens and Kreidenweis, 2007).

Jang et al. (2002) firstly proposed the significance of acid-catalyzed reactions of volatile carbonyl compounds, such as glyoxal and octanal, in SOA formation. On the basis of a series of chamber and flow reactor experiments, Jang and coworkers concluded that the presence of sulfuric acid particles catalyzes the reactions of most carbonyl compounds to form low-vapor-pressure products in the aerosol phase and hence markedly increases the SOA mass production, via various mechanisms including hydration, aldol condensation, acetal/hemicetal formation (in the presence of alcohols) and polymerization (Jang and Kamens, 2001; Jang et al., 2003ab; 2005). However, Kroll et al. (2005) did not observe any significant aerosol growth due to reactive uptake of most carbonyls that they investigated (e.g., formaldehyde, 2,4-pentanedione, octanal, etc.), which is in contrast with the findings reported by Jang and coworkers. In Kroll et al.'s work, single exception was glyoxal but they found that large glyoxal uptake is due to the high ionic strength of inorganic seed particles instead of particle acidity. Furthermore, Zhao et al. (2005) reported that octanal was physically absorbed by sulfuric acid without undergoing irreversible reactions although they observed irreversible reactive uptake of 2,4-hexadienal. The inconsistencies reported in the literature suggest the need of further investigation of the importance of acid-catalyzed reactions of carbonyl compounds under atmospheric conditions.

In this study, an electrodynamic balance (EDB) was used to investigate the reactions between octanal vapor and single levitated sulfuric acid droplets. The EDB has been shown to be very useful in examining particle hygroscopicity because it is very sensitive to any changes in particle mass in response to changes in the surrounding air (Peng et al., 2001; Choi and Chan, 2002). This feature also makes the EDB an ideal tool to directly measure the mass yield (or loss) of levitated particles when they interact with gas-phase reactants (Lee and Chan, 2007ab). The ability to levitate single particles for extended periods of time allows investigation of complex reactions, such as ozonolysis of organic acids at ozone concentrations relevant to atmospheric conditions. Another distinct advantage of the EDB in the current study is that the octanal vapor supply can be easily cut off after a certain period of exposure to examine whether any reversible partitioning of condensed organic materials occurs after purging with octanal-free compressed air, which has been considered in both laboratory experiments and model predictions of SOA formation (Pankow, 1994; Grieshop et al., 2007; Robinson et al., 2007). This additional information may help us understand the relative importance of physical and reactive uptakes of octanal vapor by sulfuric acid droplets. Furthermore, single particle Raman spectroscopy was also used to probe the changes in chemical compositions of the levitated sulfuric acid droplets (Ling and Chan, 2007; Lee et al., 2008). The experiments were conducted under different relative humidity (RH) conditions (10–50%) and gas-phase octanal concentrations (both ppb and ppm levels). The objectives of this study were 1) to determine the effects of laboratory conditions, including particle acidity and gas-phase octanal concentrations, on the organic mass yield of SOA and 2) to shed light on the atmospheric importance of the acid-catalyzed reactions of aldehydes in SOA formation.

2 Experimental methods

2.1 Generation of inorganic seed particles

A small amount of diluted sulfuric acid solution was introduced into a piezoelectric particle generator (Uni-Photon Inc., NY., USA, Model 201). By applying electric pulses to the droplet generator, solution droplets (~20–40 μm) were generated and charged by passing them across a metal induction plate before they entered into the electrodynamic balance (EDB). Single sulfuric acid droplets were levitated and held stationary with proper adjustments of the combination of AC and DC electric fields inside the EDB. A similar procedure was used to prepare ammonium sulfate (>99%, Sigma-Aldrich) particles in the control experiments.

2.2 Generation of octanal vapor

The octanal vapor was generated by passing RH-controlled compressed air over an octanal reservoir. To determine the gas-phase concentration, octanal vapor was trapped using volatile organic carbon (VOC) adsorption tubes (SKC sorbent tube) and subsequently quantified using a combination of thermal desorption (Perkin Elmer, Automated Thermal Desorber Turbo Matrix ATD) and gas chromatography-mass spectroscopy (Perkin Elmer, Clarus 500). The calibration curve was constructed by evaporating a known amount of octanal at about 50°C and then collected by a VOC adsorption tube. The octanal concentrations ranged from approximately 200 to 300 ppm in the high octanal concentration experiments. In the low and medium octanal concentration experiments, the particles were exposed to octanal vapor with concentrations about 700–900 ppb and 5–7 ppm, respectively, for more than 25 hrs.

2.3 The electrodynamic balance and mass yield measurements

The principle of the EDB has been well documented (Davis, 1997) and therefore is not described in detail here. In brief, a charged particle with about a 20–40 μm diameter is trapped at the null point of the cell through a combination of DC and AC electric fields surrounding the particle. Assuming that there is no loss of charge, the mass of the particle is proportional to the applied DC voltage. Any relative mass change in the particle due to any physical (e.g., evaporation or condensation of water in response to the changes in ambient RH) or chemical changes is determined by recording the DC voltage required to balance the weight of the particle. This makes the EDB as an ideal tool to measure particle hygroscopicity and mass yield (or loss) caused by chemical reactions (Lee and Chan, 2007ab).

In this study, the sulfuric acid droplets were first equilibrated at specific RH conditions and then the relative mass changes of the levitated particles caused by physical uptake of organics and/or heterogeneous reactions were monitored at 1–2 hr intervals over a whole period of octanal exposure. The experimental results are presented here in the form of mass ratios (m_t/m_0), which is the ratio of the particle mass at a given octanal exposure time, m_t , to the initial particle mass, m_0 . The weight percentage of sulfuric acid in the levitated droplets at specific RH conditions was predicted using the Aerosol Inorganics Model (AIM) (Clegg et al., 1998). The RH inside the EDB was adjusted by mixing a stream of saturated air and another of dry air at controlled flow rates. The overall experimental error in the mass ratios was within 1% for droplets, and the error in the determination of RH was estimated to be $\pm 1\%$ at RH = 40–80%.

2.4 Raman spectroscopy of single levitated particles

We measured the Raman scattering of levitated particles undergoing heterogeneous reactions for aerosol composition (functional group) analyses. In this study, we used a Raman spectroscopy system similar to that used in our previous study (Lee et al., 2008). It consisted of a 5 W argon ion laser (Coherent I90-5) and a 0.5 m monochromator (Acton SpectraPro 500) attached to a CCD (Andor Technology DV420-OE), which was integrated with the EDB system. The 514.5 nm line of an argon ion laser with output power between 25–50 mW was used as the source of excitation. A pair of lenses, which matched the $f/7$ optics of the monochromator, was used to focus the 90° scattering of the levitated droplet in the EDB onto the slit of the monochromator. A 514.5 nm Raman notch filter was placed between the two lenses to remove the strong Rayleigh scattering. A 300 g/mm grating of the monochromator was selected. The integration time of each spectrum was 30 s (30 frames, each with an accumulation time of 1 s). The resolution of the spectra obtained was about 6 cm^{-1} . All measurements were made at ambient temperatures of 22–24 °C.

2.5 Light scattering pattern measurements

The laser-illuminated light scattering pattern of the levitated particles was monitored and captured through the window of the EDB using a microscope (5× objective and 20× eyepiece) coupled with a digital camera (Nikon Coolpix 990). A He-Ne laser with a wavelength of 632.8 nm was used as the illuminating source. The laser beam passed through the levitated particle from the bottom of the EDB and the microscope was positioned at an angle of 90° with respect to the laser beam. The light scattering image was first focused so that two clear light spots could be observed via the eyepiece of the microscope. After that, the eyepiece was

removed to obtain the laser-illuminated light scattering pattern (the particle image was actually out of focus). If the levitated particle was a homogeneous droplet, then the light scattering pattern included some sharp horizontal lines, with the number of horizontal lines depending on the particle size. If the levitated particle contained solids or crystalline materials or had an irregular coating, then the light scattering pattern became irregular and fluctuated (Lee and Chan, 2007b). Parsons et al. (2006) and Olsen et al. (2006) also used a similar experimental approach to study the nucleation of levitated droplets.

3 Results and Discussion

In the current study, the uptakes of octanal vapor by single levitated sulfuric acid droplets were investigated under various RH conditions and octanal vapor concentrations using the EDB. On the basis of the observations from the high octanal concentration experiments, we first consider the effect of particle acidity on the organic mass yield of levitated sulfuric acid droplets. Second, we provide evidence of reversible partitioning of particle-phase organic materials. Last, the effect of gas-phase octanal concentration on the organic mass yield is discussed for the case of sulfuric acid droplets that equilibrated at 10% RH.

3.1 Effects of particle acidity on the organic mass yield in the high octanal concentration experiments

Figures 1a, b and c show the relative mass changes of sulfuric acid droplets as a function of exposure time (first 10 hrs) in the high octanal concentration experiments (200–300 ppm) at 10%, 30% and 50% RH, respectively. These octanal concentrations were much higher than

typical atmospheric concentrations of carbonyl compounds, which are normally in ppb level. Significant uptakes of octanal vapor were observed in the sulfuric acid droplets equilibrated at 10% RH and their masses appreciably increased by about 20–70% of their original mass. The variation in organic mass fractions was probably due to differences in particle size and fluctuations in octanal concentrations between each individual experiment in Figure 1a. For the case of 30% RH, the masses of the sulfuric acid droplets slightly increased by about 2–3%. When the sulfuric acid droplets were exposed to octanal vapor at 50% RH, no significant particle mass changes were observed. Ammonium sulfate ((NH₄)₂SO₄) aqueous droplets equilibrated at 50% RH were exposed to octanal vapor as control experiments. Figure 1d shows that the masses of supersaturated (NH₄)₂SO₄ droplets remained almost unchanged after 10 hrs of octanal exposure at 50% RH, indicating that both physical and reactive uptakes of octanal vapor were insignificant in (NH₄)₂SO₄ aqueous droplets even at very high octanal concentrations.

The Raman spectra of the levitated (NH₄)₂SO₄ droplets before and after octanal exposure were almost identical as shown in Figure 2a, which further confirms that there was no significant uptake of octanal vapor by the supersaturated (NH₄)₂SO₄ droplets at 50% RH. In contrast, sulfuric acid droplets equilibrated at 10% RH had strong fluorescence signals that masked all the Raman signals as shown in Figure 2b, which is commonly observed in Raman spectra of sulfuric acid solutions especially with high concentrations when a small amount of organic contaminants exist (Hegglin et al., 2002). Although the strong fluorescence signals make it difficult to identify the functional characteristics of the condensed organic materials, the fluorescence signal increases in intensity as a function of octanal exposure (Figure 2b), indicating the gradual formation of fluorescence products. Furthermore, distortion in the light scattering pattern was observed after the reactions at 10% RH as presented in Figure 3a and

3b, suggesting that the levitated droplet had inhomogeneous configuration. The organics probably formed non-uniform or partially coating on the surface of the sulfuric acid droplets (see discussion below). On the other hand, the light scattering patterns of the supersaturated $(\text{NH}_4)_2\text{SO}_4$ droplets remained unchanged after exposure to octanal (Figure 3c and 3d).

Our direct particle mass measurements clearly illustrate that the uptakes of octanal vapor by sulfuric acid droplets strongly depend on the RH of the surrounding air under such a high octanal concentrations. Since sulfuric acid is very hygroscopic in nature, the RH inside the EDB can directly influence the water content of the levitated droplets and consequently their acidity. Based on the AIM model (Clegg et al., 1998), we determined the initial weight percentage of sulfuric acid in the levitated droplets to be about 64, 50, and 43% when they are equilibrated at 10%, 30% and 50% RH, respectively. Obviously, the organic mass yield increased with the particle acidity and the organic fraction markedly increased when the weight percentage of sulfuric acid reached 64%. Garland et al. (2006) studied the acid-catalyzed reaction of hexanal vapor on sulfuric acid droplets. The partial pressure of hexanal ranged from 0.004 to 0.009 atm in their experiments, which are also much higher than typical ambient levels. They showed that increasing the weight percentage of sulfuric acid leads to more organic materials being incorporated into the droplets.

3.2 Formation of low volatility products and reversible partitioning of condensed organic materials in the high octanal concentration experiments

To examine whether the organic materials accumulated in the particles evaporated back into the gas phase when the octanal was no longer supplied, the EDB was purged with octanal-free compressed air after the reactions took place for about 10 hrs. At 30% RH, no significant

changes in particle mass were observed during the purging period as shown in Figure 1b, indicating that the formed organic materials were non-volatile and the overall uptake process was irreversible under ambient temperatures. In contrast, a dramatic drop in particle mass was observed in the first two hours of purging for the case of 10% RH and over 50% of the condensed organic materials ultimately evaporated back into the gas phase (Figure 1a). The remaining organic mass fractions ranged between 10% and 25% after the whole period of purging but were larger than those obtained from the 30% RH condition (~2–3%). This observation clearly demonstrates the formation of low volatility products that tends to remain in the particle-phase at 10% RH condition as well as the reversible partitioning of a portion of particle-phase organic materials under octanal-free environment.

When we consider the uptake behavior of octanal vapor at 10% RH, we find that the organic mass of the levitated droplets increased slowly during the first 5–6 hrs of exposure as shown in Figure 4. More rapid organic mass gains were observed in the latter period of exposure (6–10 hrs), an approximately two-fold or higher increase in the uptake rate was observed. We attribute the change in the overall uptake rate to the significant enhancement of the physical uptake process as reaction proceeds. Our hypothesis is that the physical uptake of octanal vapor is limited at the beginning of exposure because octanal has high vapor pressure (on the order of 10^{-4} atm) and extremely low solubility in aqueous solutions. However, under low RH conditions (e.g., 10% RH), once the octanal molecules physically adsorb onto the sulfuric acid droplets, the high acidity catalyzes the formation of less-volatile organic compounds, which have a stronger tendency to remain in the particle phase than has octanal. The overall uptake process of octanal vapor is therefore predominantly driven by the chemical reactions in the first 5–6 hrs (Figure 4).

Since octanal and reaction products are immiscible with 64 wt% of sulfuric acid as observed in our bulk investigation (Li et al., 2008), the acid-catalyzed reaction of octanal was expected to occur in the organic-aqueous interface instead of inside the solution droplet. As the hydrophobic products accumulate on the surface of sulfuric acid droplets, the chemical properties of the droplets, such as the mass accommodation coefficient and hydrophilicity, are modified accordingly (Donaldson and Vaida, 2006), favoring the condensation growth (physical uptake) of octanal, which becomes the main contributor of the overall uptake process in the latter period of exposure. Most of the octanal is expected to be adsorbed onto and/or absorbed into the levitated droplets between 6 and 10 hrs, which was reflected by the rapid mass enhancement as shown in Figure 4. As there may be insufficient reaction time for all octanal to undertake the reaction in the organic-aqueous interface to form low volatility products, a portion of octanal was rapidly evaporated into the gas phase after active dilution with compressed air, which can explain the partial repartitioning of particle-phase organics as shown in Figure 1a. Some volatile/semi-volatile products (if any) may also escape to gas phase during the purging period but their contribution to the overall evaporative loss is expected to be very small since the acid-catalyzed reactions of octanal not likely generate high volatility products.

The absorptive gas-particle partitioning of SOA formed from the condensation of semi-volatile oxidation products of gas-phase precursors has been considered as a reversible process at equilibrium in the current models (e.g. Pankow, 1994; Odum et al., 1996). However, Tsigaridis and Kanakidou (2003) pointed out that substantial uncertainty in SOA predictions is potentially because of the incomplete repartitioning of particle-phase organics due to the heterogeneous reactions or other physical processes that result to low volatility products. Similar to the current study, partial repartitioning of condensed organic matter was

experimentally verified in some recent studies on POA and SOA formation. For instance, Grieshop et al. (2007) investigated the reversibility of gas-particle partitioning in SOA formed from α -pinene ozonolysis in a smog chamber using the isothermal dilution approach. Their results demonstrated that only a portion of SOA formed from α -pinene ozonolysis repartitions reversibly when active dilution reduces the gas-phase concentration of semi-volatile organic species and the SOA composition varies systematically with partitioning based on their aerosol mass spectrometer data. Robinson et al. (2007) presented diesel exhaust data measured at different levels of atmospheric dilutions. In that work, the POA emission factor decreased with increasing dilution ratios because of the evaporation of semi-volatile organic compounds to maintain the phase equilibrium. Their observation also suggests that the repartitioned primary organics are probably oxidized and re-condensed into the particle phase, consequently enhancing SOA formation.

3.3 Effects of gas-phase octanal concentration on organic mass yield

Although we observed the dependence of organic mass enhancement on acidity and the reversible partitioning phenomenon in the high octanal concentration experiments, it is particularly important to determine if a significant organic mass yield can be obtained under more realistic atmospheric carbonyl concentrations. For this reason, the cases of relatively lower octanal concentrations (700–900 ppb) and highly acidic sulfuric acid droplets (64 wt% at 10%RH) were also investigated in the current study. After 25 hrs of low octanal exposure at 10% RH, insignificant changes in particle mass were observed (Figure 5), indicating that both physical and reactive uptakes were not important under such low octanal concentrations. The same conclusion was drawn when the medium octanal concentration (5–7 ppm) was used as shown in Figure 5.

By incorporating our findings from the high octanal concentration experiments with those the more realistic experiments, we suggest that gas-phase octanal concentration is a critical factor, in addition to the particle acidity, that influences the organic mass fraction of levitated acidic droplets. In our previous study, we investigated heterogeneous reactions between octanal vapor and deposited sulfuric acid droplets using a reaction flow cell and offline GC-MS characterization. A similar conclusion on the effect of gas-phase organic concentration on SOA formation was drawn (Li et al. 2008). In that study, none of the accretion reaction products, which have relatively high molecular weight and low vapor pressure, were detected even at RH less than 1% if ~900 ppb of octanal vapor was employed in the gas-particle experiments. In addition, at 30% RH (H_2SO_4 wt% ~ 50%), no accretion reaction products were observed after exposing the deposited sulfuric acid droplets to ~20 ppm of octanal vapor whereas cyclotrimerization products were dominant in the bulk experiments under these acidic conditions. The discrepancy between the bulk and the gas-particle experiments is probably due to the limited availability of octanal in the deposited sulfuric acid droplet experiments. This observation suggests the need to re-examine the reaction mechanisms proposed in the literature that is based on bulk experiments.

Some previous laboratory studies also investigated the uptake of octanal vapor using different techniques and their conclusions are somewhat controversial. Kroll et al. (2005) reported negligible growth when mixed ammonium sulfate/sulfuric acid droplets were exposed to 500 ppb of octanal vapor at RH approximately equal to 50% in their smog chamber experiments. Zhao et al. (2005) examined the heterogeneous uptake of octanal vapor on a 60–85 wt% sulfuric acid solution using an octanal concentration on the order of 10^{-1} ppm. They found that octanal was physically absorbed by sulfuric acid without undergoing an irreversible

reactive uptake process. These results are generally in a good agreement with our observations. Furthermore, Barsanti and Pankow (2004) considered the thermodynamics of the accretion reactions of octanal, including hydration, aldol condensation, acetal/hemicetal formation and polymerization, and they also concluded that all these accretion reactions are not thermodynamically favored either in the real atmospheric environment or in the experimental conditions used by Jang and Kamens (2001). On the contrary, Jang and coworkers reported a significant growth in sulfuric acid droplets in a number of carbonyl compounds including octanal under various RH conditions, aldehyde concentrations and inorganic seed particle compositions (Jang and Kamens, 2001; Jang et al., 2003ab; 2005). Even at a relatively low octanal concentration (~230 ppb at 20% RH), they observed significant aerosol growth (Jang et al., 2005). It is obvious that further research is needed to understand the discrepancies between these studies.

3.4 Kinetic analysis

Aldol condensation has been suggested as one of the most important reactions of aldehydes in acidic solution and the reaction mechanisms can be found in Casale et al. (2007). Ervens and Kreidenweis (2007) investigated if aldol condensation might contribute to SOA formation by aliphatic aldehydes based on kinetic calculations using Equations 1 and 2. Assuming the rate limiting step in the aldol condensation is the particle phase reaction between the aldehyde and their corresponding enolization form, the reaction rate can be calculated as follows.

$$\frac{d[\text{aldehyde}]_p}{dt} = -\frac{k_{aldol}}{K_{enol}}[\text{aldehyde}]_p^2 \quad (1)$$

where k_{aldol} is a second-order aldol condensation rate constant and K_{enol} is an enolization equilibrium constant of aldehyde. If all reacted aldehyde molecules produce SOA mass, which is probably an overestimate, the SOA formation rate as a function of a gas-phase aldehyde concentration can be calculated by assuming equilibrium between the particle-phase and gas-phase aldehyde and applying Henry's Law constant, H , as shown in Equation (2).

$$\frac{d[SOA]_p}{dt} = \frac{k_{aldol}}{K_{enol}} (H[aldehyde]_g)^2 \quad (2)$$

In this kinetic analysis, the initial formation rate of SOA mass observed in Figure 4 is assumed to be predominately caused by the formation aldol condensation products in our high octanal concentration experiments (200–300 ppm at 10% RH). This assumption is supported by the chemical characterization of our recent gas-particle experiments using sulfuric acid deposited particles exposed to ~20 ppm of octanal vapor at 10% RH or below (Li et al., 2008). Hence, the initial slopes (from 0 to 5 hrs of octanal exposure in Figure 4) can be used to estimate the initial SOA formation rate in Equation 2. By using Equation 3, the kinetic data obtained in the high octanal concentration experiments can be used to test whether the contribution of aldol condensation of octanal is significant on SOA formation under 900 ppb of octanal vapor and 10% RH condition. The values of k_{aldol} , K_{enol} and H would not affect the accuracy of our estimations.

$$\left(\frac{\Delta(m_{t1} / m_0)_{200 \text{ ppm}}}{\Delta(m_{t2} / m_0)_{900 \text{ ppb}}} \right) = \frac{([aldehyde]_{200 \text{ ppm}})^2 t_1}{([aldehyde]_{900 \text{ ppb}})^2 t_2} \quad (3)$$

According to Figure 4, after 5 hrs (1.8×10^4 s, t_1) of 200 ppm octanal exposure at 10% RH, the changes in mass ratio ($\Delta(m_{t1}/m_0)_{200\text{ppm}}$) is approximately ranged from 0.05 to 0.13. Hence, the time required (t_2 , in which $\Delta(m_{t1}/m_0)_{200\text{ppm}} = \Delta(m_{t2}/m_0)_{900\text{ppb}}$) for yielding 5–13 wt% of SOA on the sulfuric acid droplets at about 900 ppb of octanal vapor and 10% RH condition is about 10^9 second (years), which is consistent with our experimental observations that no significant SOA yields at such octanal concentration and RH. Ervens and Kreidenweis (2007) used Equation 2 with the kinetic parameters (k_{aldol} , K_{enol} and H) available in the literature to perform the kinetic calculation. They reported that the time required to produce 1 ng of SOA m^{-3} via aldol condensation of hexanal and octanal is about 10^{10} second, which is in agreement with our kinetic analysis. On the basis of our kinetic analysis, aldol condensation of octanal is not an efficient process for significant transfer of organic material into atmospheric aerosols.

4 Conclusions and atmospheric implications

In this study, we observed two phenomena in the high octanal concentration experiments (200–300 ppm). First, we found that the organic mass yield depends on the acidity of the sulfuric acid droplets and significant uptake of octanal can be only observed when the RH inside the EDB is equilibrated at about 10% (H_2SO_4 wt% \sim 64%). Some possible mechanisms of acid-catalyzed reactions of aldehyde have been proposed in the literature (e.g. Jang et al., 2002; Garland et al., 2006; Liggió and Li, 2006). Although the mechanisms of heterogeneous acid-catalyzed reactions of aldehyde still remain uncertain based on the existing laboratory measurements, thermodynamic and kinetic calculations (Barsanti and Pankow, 2004; Casale et al., 2007; Ervens and Kreidenweis, 2007; Li et al., 2008), it is reasonable that our observed

organic mass yield (after purging) is mainly caused by the formation of high molecular weight products with relatively low vapor pressure.

Second, we have evidence to show the occurrence of partial reversible partitioning of condensed organic compounds under active dilution of octanal-free compressed air at 10% RH. In the atmosphere, the continuous uptake and release of volatile/semi-volatile organics probably occur throughout the particles' lifetime as the gas-phase concentrations of organic species vary continuously. In addition, the current study and some recent studies (Grieshop et al., 2007; Robinson et al., 2007) demonstrated that the phenomenon of partial reversible partitioning should be considered in the POA/SOA prediction model and laboratory studies of organic aerosol formation, especially when a relatively high gas phase concentration of organics is employed to compensate for a short exposure time. Otherwise, the predicted and the measured organic aerosol yield caused by the heterogeneous processes may be overestimated.

Although the octanal concentration in the low concentration experiments (700–900 ppb) is higher than typical atmospheric concentrations, there was no significant uptake of octanal vapor by the sulfuric acid that equilibrated even at 10% RH and a long exposure time (> 25 hrs). Since sulfuric acid droplets equilibrated at 10% RH can provide sufficient acidity to facilitate reactive uptake in the high octanal concentration experiments, the gas-phase octanal concentration is another critical factor that influences the organic mass fraction of levitated acidic droplets. On the basis of the experimental observations and kinetic analysis reported here, we conclude that the uptake of octanal vapor by sulfuric acid droplets is only important under the condition when both a high gas-phase octanal concentration and highly acidic particles exist at the same time. These two criteria may be also applicable to the case of other

carbonyl compounds, especially those that have chemical structures and properties very similar to octanal.

The significant enhancement of octanal uptake in the latter period of exposure (at 10% RH and 200–300 ppm octanal) is another observation that requires further discussions. This change in uptake is probably due to the accumulation of hydrophobic organic products, which significantly enhances the condensation of volatile/semi-volatile hydrophobic organics, such as octanal in this study, onto the levitated sulfuric acid droplets. This observation implies that heterogeneous chemical processes are a potentially important pathway for incorporating hydrophobic organics into hydrophilic aerosols, and hence modifying the physical uptake properties of volatile/semi-volatile hydrophobic organics of atmospheric aerosols. Although this hydrophilic-to-hydrophobic conversion may not happen under real atmospheric conditions for the case of octanal as reported here, some gas-phase biogenic organics (e.g., isoprene, α -pinene, etc.) and their photooxidation products (e.g., pinoaldehyde) possibly react with acidic particles under atmospheric conditions to facilitate such conversion (Liggio and Li, 2006; Liggio et al., 2007; Surratt et al., 2007). Furthermore, physical uptake enhancement may be important to affect the atmospheric gas-phase and heterogeneous chemistry as the volatile/semi-volatile hydrophobic organics would have a higher tendency to partition into the particle phase and subsequently react with atmospheric oxidants or reactants.

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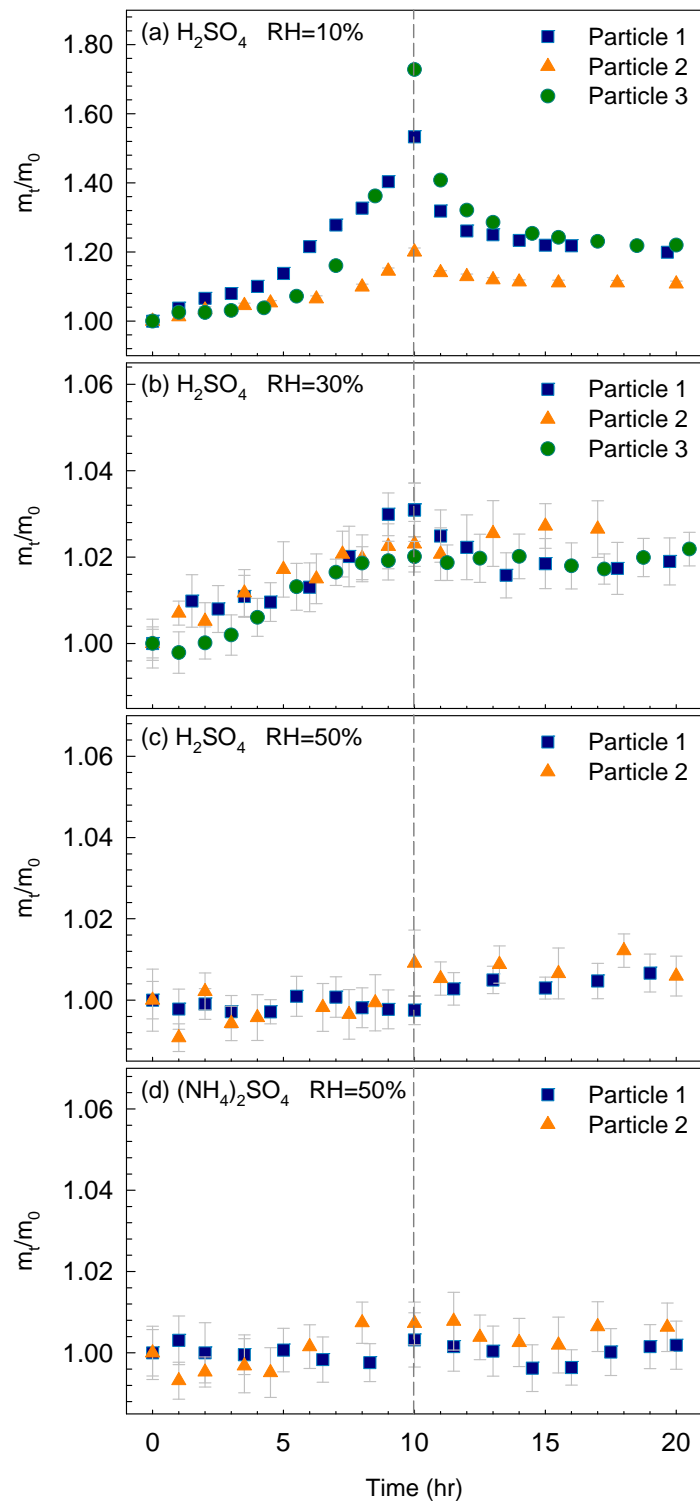


Figure 1

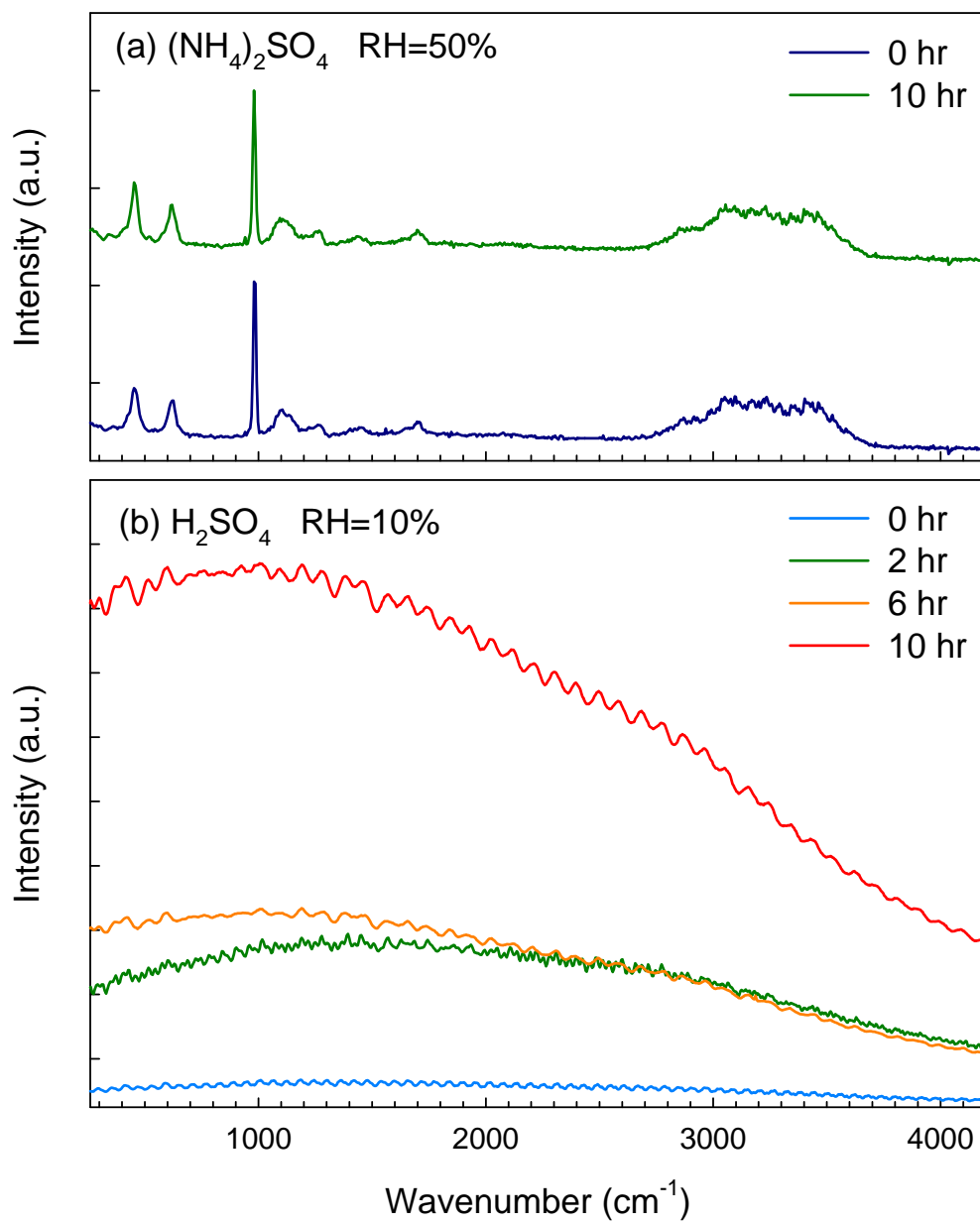


Figure 2

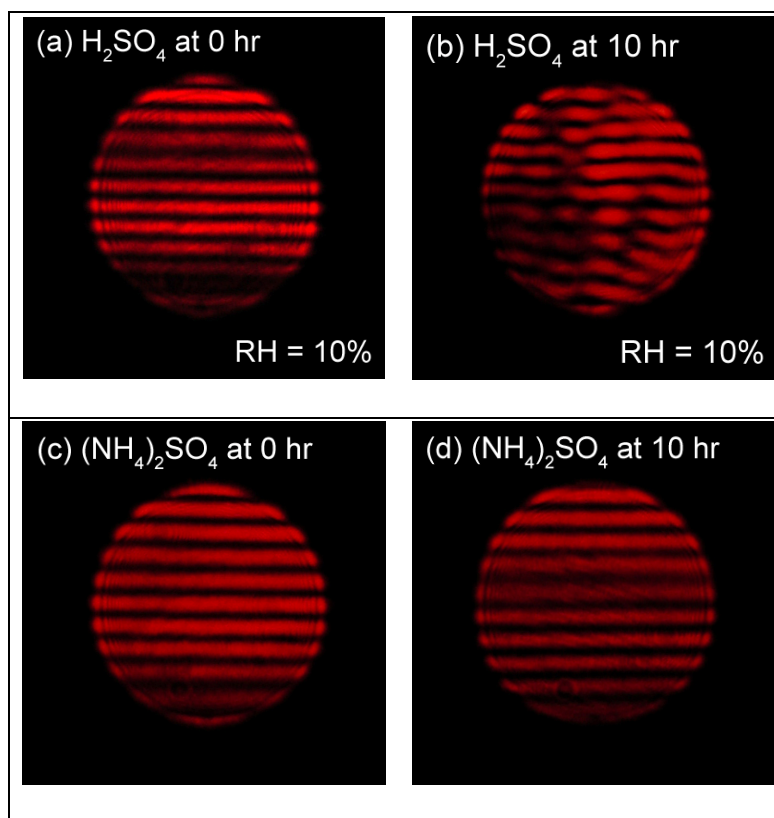


Figure 3

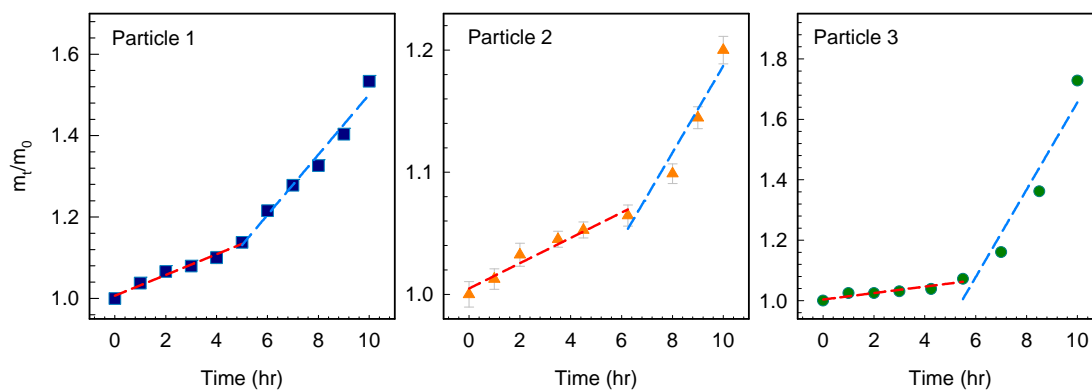


Figure 4

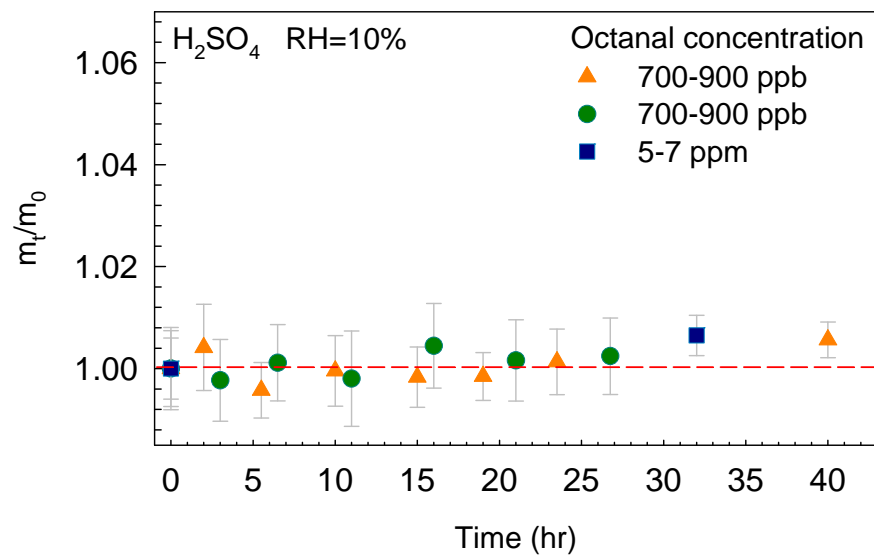


Figure 5