

Surfactants from the gas phase may promote cloud droplet formation

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Clouds, a key component of the climate system, form when water vapor condenses upon atmospheric particulates termed cloud condensation nuclei (CCN). Variations in CCN concentrations can profoundly impact cloud properties, with important effects on local and global climate. Organic matter constitutes a significant fraction of tropospheric aerosol mass, and can influence CCN activity by depressing surface tension, contributing solute, and influencing droplet activation kinetics by forming a barrier to water uptake. We present direct evidence that two ubiquitous atmospheric trace gases, methylglyoxal (MG) and acetaldehyde, known to be surface-active, can enhance aerosol CCN activity upon uptake. This effect is demonstrated by exposing acidified ammonium sulfate particles to 250 parts per billion (ppb) or 8 ppb gas-phase MG and/or acetaldehyde in an aerosol reaction chamber for up to 5 h. For the more atmospherically relevant experiments, i.e., the 8-ppb organic precursor concentrations, significant enhancements in CCN activity, up to 7.5% reduction in critical dry diameter for activation, are observed over a timescale of hours, without any detectable limitation in activation kinetics. This reduction in critical diameter enhances the apparent particle hygroscopicity up to 26%, which for ambient aerosol would lead to cloud droplet number concentration increases of 8–10% on average. The observed enhancements exceed what would be expected based on Köhler theory and bulk properties. Therefore, the effect may be attributed to the adsorption of MG and acetaldehyde to the gas-aerosol interface, leading to surface tension depression of the aerosol. We conclude that gas-phase surfactants may enhance CCN activity in the atmosphere.

atmospheric chemistry | VOCs | indirect effect

The reactive uptake of volatile organic compounds (VOCs) by wet aerosols is a potentially important source of organic matter (OM) (1–3). The α -dicarbonyl species glyoxal and methylglyoxal (MG), along with acetaldehyde and other carbonyl-containing species, belong to this class; they are absorbed by wet aerosol particles (or cloud droplets) and undergo aqueous phase reactions to form low-volatility secondary organic aerosol (SOA) (2, 4–6). The impacts of these processes on aerosol cloud condensation nuclei (CCN) activity and cloud droplet formation are highly uncertain at this time. Few studies have focused on the impact of SOA generated in the aqueous phase on aerosol CCN activity (7–9). It was recently shown that the formation of SOA via the condensation of low-volatility VOC oxidation products, which are generally less hygroscopic than deliquescent inorganic salts, can affect the CCN activity of the seed aerosol (10–15). SOA generated through aqueous-phase chemistry is likely to be highly oxygenated and surface-active, hence making it strongly CCN-active (6, 16, 17). Some of the VOC precursors themselves, including MG and acetaldehyde, are also surface-active (6, 16, 17).

We studied the changes in the CCN activity of acidified ammonium sulfate seed aerosols upon exposure to gas-phase MG or acetaldehyde. Both these organics are surface-active molecules and they also form surface-active material in aerosol bulk (6, 16, 17). A continuous-flow streamwise thermal gradient CCN chamber

(CFSTGC) was used downstream of a 3.5-m³ Teflon reaction chamber or an aerosol flow tube to determine the cloud-forming potential of these aerosols after various exposure times. The critical dry diameters observed for each experiment as a function of instrument supersaturation are compared with the pure, non-acidified (NH₄)₂SO₄ control to demonstrate the effect of the organics. A decrease in critical activation diameter at a given critical supersaturation indicates enhancement in CCN activity, and vice versa. We find that, on the timescale of hours, MG and/or acetaldehyde exposure enhances CCN activation beyond what is expected from Köhler theory predictions based on bulk properties. We attribute this enhancement to the surface adsorption of these VOCs from the gas phase to the aerosol interface. The uptake of relatively insoluble, volatile organic gases by atmospheric aerosol particles may lead to an enhancement in cloud droplet formation and points to an unaccounted-for mechanism for augmenting CCN activity. This study proposes the idea that volatile organics in the atmosphere may act as a reservoir of surfactants that can be taken up by aerosol particles and augment their CCN activity.

Results and Discussion

Fig. 1 summarizes the results of the CCN activation experiments showing the change in critical activation diameters compared with pure (NH₄)₂SO₄ for the various conditions tested. Fig. S1 contains the supersaturation vs. activation diameter plots for each individual condition). After 3 min of exposure to 250 parts per billion (ppb) MG in the flow tube experiments (particle concentration $1.5 \pm 0.3 \times 10^5 \text{ cm}^{-3}$), there is a negligible change in aerosol CCN activity. However, when aerosols ($9.7 \pm 0.3 \times 10^5 \text{ cm}^{-3}$) are exposed to MG for longer periods in the chamber (3–5 h), their CCN activity is enhanced considerably. For the conditions considered, MG reduces the critical activation diameters of the inorganic seed aerosol on average by $6.36 \pm 0.05\%$ at the supersaturations studied (0.2–1.0%). Acetaldehyde is another VOC which has been shown to depress surface tension in bulk aqueous ammonium sulfate solutions (6). Chamber experiments similar to those carried out with MG were conducted using 250 ppb acetaldehyde at an exposure time of 5 h. Acetaldehyde

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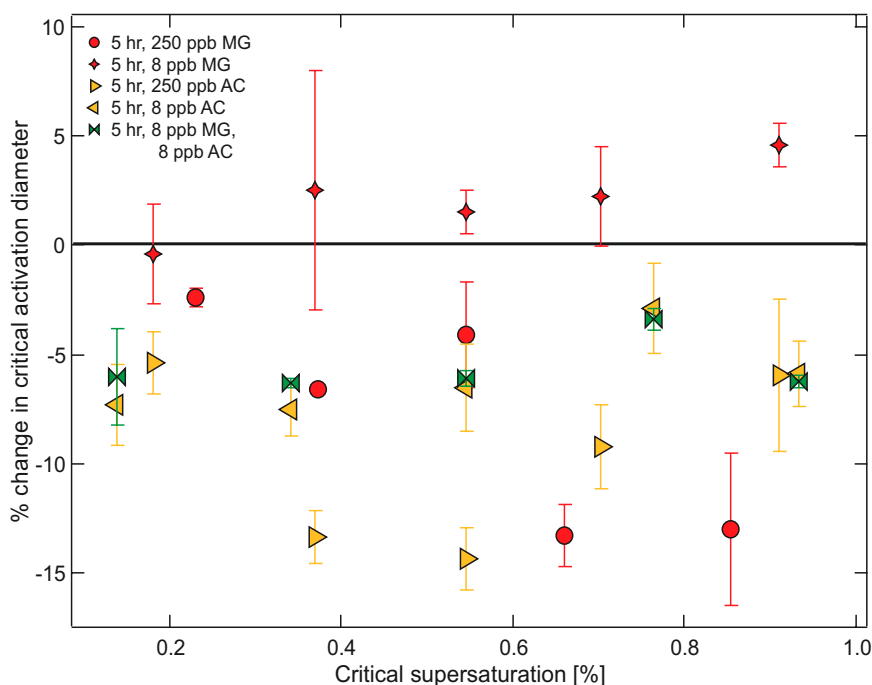


Fig. 1. CCN activity data. Humidified $(\text{NH}_4)_2\text{SO}_4$ aerosols were exposed to gas-phase MG or acetaldehyde in a 3.5-m^3 Teflon reaction chamber. The critical dry diameters observed for each experiment as a function of instrument supersaturation are compared with the $(\text{NH}_4)_2\text{SO}_4$ control to demonstrate the effect of organics. A decrease in critical activation diameter at a given critical supersaturation indicates enhancement in CCN activity, and vice versa. The data shown here are the results for $(\text{NH}_4)_2\text{SO}_4$ particles exposed to 250 and 8 ppb MG for 5 h, particles exposed to 250 and 8 ppb acetaldehyde for 5 h, and finally particles exposed to a mixture of 8 ppb MG and 8 ppb acetaldehyde for 5 h.

enhances CCN activity even more than MG, reducing the critical activation diameters on average by $9.68 \pm 0.04\%$.

MG and acetaldehyde have been observed in both marine and continental environments (18–23). The gas-phase MG, acetaldehyde, and particle concentrations used in the experiments described above exceed typical atmospheric concentrations [urban: 10^4 cm^{-3} , 2.5 ppb MG, 4 ppb acetaldehyde (24, 25); wet-season Amazon: 10^2 cm^{-3} , 0.125 ppb MG (18, 26), 0.5 ppb acetaldehyde (27)]. Chamber experiments conducted at lower acetaldehyde and particle concentrations ($2.58 \times 10^4 \text{ cm}^{-3}$, 8 ppb acetaldehyde) with a 5-h residence time showed a depression in critical activation diameters by $6.01 \pm 0.02\%$ at the supersaturations studied (Fig. 1). However, experiments conducted at low MG and particle concentrations ($1.78 \times 10^4 \text{ cm}^{-3}$, 8 ppb MG) showed CCN activity approaching that of ammonium sulfate.

Table 1 lists the average apparent hygroscopicity parameter κ [calculated from the CCN activity data following Petters and Kreidenweis (28) and following the convention that $\sigma = \sigma_{\text{water}}$] for each experiment. [Fig. S2 shows the change in κ compared

with $(\text{NH}_4)_2\text{SO}_4$, and a statistical analysis of the data is shown in Table S1.] For the 3-min MG flow tube experiments, the κ -values (0.63 ± 0.18) are consistent with pure $(\text{NH}_4)_2\text{SO}_4$. Particles exposed for longer timescales, however, show an increase in κ [beyond that of pure $(\text{NH}_4)_2\text{SO}_4$] with increasing supersaturation. Exposure to 250 ppb MG in the chamber increases the apparent hygroscopicity from ~ 0.6 to ~ 1.0 . Particles exposed to 250 ppb acetaldehyde become substantially more hygroscopic than pure ammonium sulfate, with κ -values ranging from 0.62 to 1.00 (the highest observed κ -value for the 8 ppb exposure experiments was 0.88).

Such shifts in hygroscopicity could lead to important enhancements in cloud droplet number concentrations (CDNC). Simulations using the GEOS-Chem and National Aeronautics and Space Administration-Global Modeling Initiative models coupled with the cloud droplet adjoint framework of Karydis et al. (29) were conducted to understand the stratus cloud CDNC response to a hypothetical 20% increase in hygroscopicity (reflecting what was observed in the 8-ppb acetaldehyde exposure experiments). Fig. 2 shows that these global models predict that CDNC increases on average by 10%, and by as much as 20% over continental regions. Given that marine stratocumulus clouds are strong climate forcers and are sensitive to CCN concentration changes, a 10% increase in CDNC (from the effect of gas-phase surfactants) would be important. To the extent that liquid water is not affected, such a CDNC perturbation could lead to roughly a 3.1% decrease in cloud droplet effective radius. This could change shortwave cloud albedo by up to 0.8% (30), which if globally relevant would exert a $-0.4\text{-W}\cdot\text{m}^{-2}$ radiative cooling. Although not all strati are expected to be affected and manifest this cooling, this simple calculation illustrates the potential impact of this phenomenon on calculations of shortwave cloud forcing.

Given that organics generally exhibit more than twofold lower κ than $(\text{NH}_4)_2\text{SO}_4$ (28), the aerosol surface tension must be lower than that of pure water to explain the increase in κ that

Table 1. Hygroscopicity parameter κ values for the different chamber and flow-tube experiments for MG and acetaldehyde

Experiment	Average κ
$(\text{NH}_4)_2\text{SO}_4$	0.60 ± 0.18
5 h, 250 ppb MG	0.81 ± 0.24
3 h, 250 ppb MG	0.74 ± 0.22
3 min, 250 ppb MG	0.63 ± 0.18
5 h, 8 ppb MG	0.55 ± 0.16
-3 min, 8 ppb MG	0.59 ± 0.18
5 h, 250 ppb AC	0.81 ± 0.24
5 h, 8 ppb AC	0.72 ± 0.22
5 h, 8 ppb AC, 8 ppb MG	0.71 ± 0.19

AC, acetaldehyde; MG, methylglyoxal.

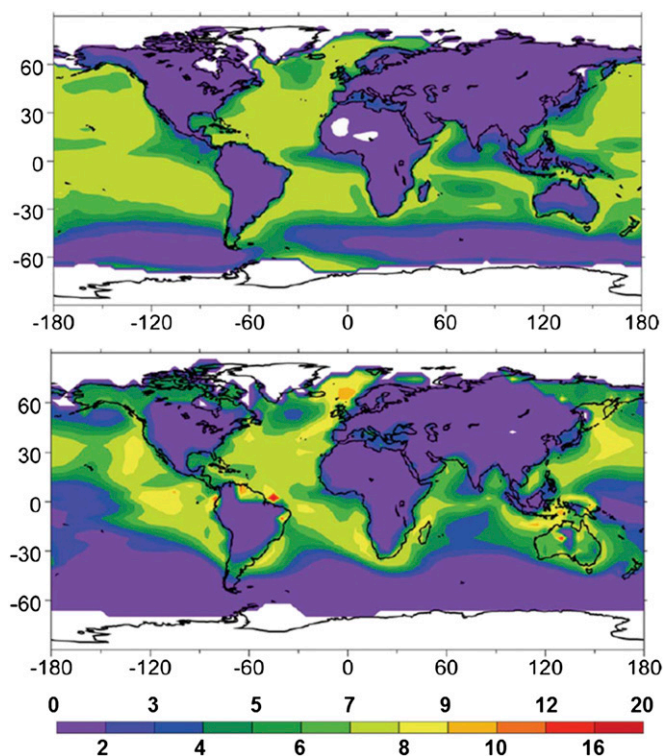


Fig. 2. Stratus cloud CCN response (%) to an aerosol κ increase of 20%. Results are shown for the GEOS-CHEM (Upper) and NASA-GMI (Lower) models coupled with the cloud droplet adjoint framework of Karydis et al. (29). For a 40% (60%) perturbation in κ , multiply legend by a factor of 2 (3). CCN changes were calculated by multiplying the direct sensitivity of CCN to κ , $\partial\text{CCN}/\partial\kappa$ (computed by the adjoint method) with the κ -perturbation, as CCN responds linearly to κ for this range of variation. For more information on the simulations, see ref. 29.

we observe (31) at higher supersaturations. As another way of expressing this, the observed critical supersaturation in our experiments (S_c) deviates somewhat from the power-law dependence on dry diameter (d_d) predicted by simple Köhler theory ($S_c \sim d_d^{-1.5}$); power-law exponents range from -1.28 for the 5-h experiments to -1.51 for 3-min exposures (Table S2). This is indicative of surfactants being present, as particles activating at higher supersaturations (i.e., smaller particles) tend to be more concentrated in surfactants at the critical wet diameter, resulting in a greater surface tension reduction than in particles which activate at lower supersaturations. This is applicable when surface-bulk partitioning of organics does not fully compensate for surface tension depression (32), and if surfactants are in equilibrium with the bulk and gas phase.

Köhler theory analysis (KTA) (33) was used to infer the extent of surface tension depression (with respect to water) in the particles. The relative abundance of the organic and inorganic components was obtained from water-soluble organic carbon (WSOC) analysis and ion chromatography of aqueous extracts of filter samples (by pumping down the chamber for ~ 14 h following an exposure experiment with 250 ppb MG and 5-h residence time). KTA suggests that MG and its reaction products suppress the surface tension of the aerosols to $65.1 \pm 0.8 \text{ dyn-cm}^{-1}$ compared with $72.55 \text{ dyn-cm}^{-1}$ for water. MG and acetaldehyde have low effective Henry's Law constants compared with that of glyoxal (34). In accord with the observations of Kroll et al. (3), we observed negligible particle growth when inorganic seed particles with a diameter of 150 nm were size-selected using a differential mobility analyzer (DMA, TSI) and exposed to MG

in the chamber (Fig. S3). This suggests that the surface-active organic species in this study reside at the gas-aerosol interface and induce the significant effects on CCN activity observed mainly by altering the properties of the particle surface. This is consistent with the observation by Jayne et al. that acetaldehyde uptake by liquid water droplets on short timescales is pH-dependent and exceeds predictions based on bulk-phase parameters (35).

If the total uptake of MG to the particles is described by Henry's Law, then based on an effective Henry's Law constant of $H^* = 3.2 \times 10^4 \text{ M-atm}^{-1}$ (34), and experimental surface tension data for aqueous bulk MG solutions (16) (which is an upper limit in surface tension change given that bulk-surface repartitioning will mitigate some of the surfactant impacts on κ), the surface tension of the particles exposed to 250 ppb MG at the moment of activation is predicted to be $72.02 \text{ dyn-cm}^{-1}$. This leads to a very small predicted change in κ (2.2% increase relative to pure ammonium sulfate). A similar calculation for acetaldehyde, which has a Henry's Law constant 2 orders of magnitude lower than that of MG (34), predicts an insignificant change in κ (0.01% increase). If surface-bulk repartitioning of the solute had been dominant, it would have depressed hygroscopicity further compared with the pure inorganic. Romakkaniemi et al. modeled a similar system, specifically the reactive uptake of gas-phase MG to $(\text{NH}_4)_2\text{SO}_4$ aerosol, allowing aqueous-phase OH oxidation to take place (36). They predicted that total reactive uptake of surface-active species into the aqueous phase may be enhanced by surface-bulk partitioning, especially for small particles, beyond what would be predicted based on Henry's Law alone. The significant differences between the model system of Romakkaniemi et al. and our study are that (i) the additional driving force for uptake of the aerosol-phase OH reaction with the organics is absent in our experiments, and (ii) they assume equilibrium between the gas, surface, and bulk. The fact that we observe a much greater enhancement in κ than predicted solely based on Henry's Law, and that no chemical change in the bulk or surface composition will induce a Raoult effect that increases κ beyond that of pure $(\text{NH}_4)_2\text{SO}_4$, suggests that surface adsorption plays a significant role in determining the aerosol surface tension and thus CCN activity (1, 37).

To confirm that changes in bulk hygroscopicity cannot explain the κ -enhancements seen in the chamber data, we analyze the CCN activity of atomized aqueous filter extracts to quantify hygroscopicity of the bulk material in the aerosol. The data are summarized in Table S3. By comparing this hygroscopicity to that of the chamber aerosol, we can deduce changes related to surface processes and nonequilibrium phenomena occurring in the chamber. Aerosolized filter extracts show similar CCN activity to that of pure $(\text{NH}_4)_2\text{SO}_4$, but much less than that of particles exposed to MG in the aerosol chamber for 3–5 h (Fig. S4). Similar results to the filter extracts were observed for aerosols formed by atomizing bulk aqueous solutions of 3.1 M $(\text{NH}_4)_2\text{SO}_4$ and 0.5 M MG 24 h after mixing (previously shown to exhibit significant surface tension depression) (16). Aerosols formed from atomized solutions of 0.5 M MG and/or 0.5 M acetaldehyde and Millipore water exhibit decreased CCN activity compared with pure $(\text{NH}_4)_2\text{SO}_4$, typical of pure organic aerosols ($\kappa = 0.12 \pm 0.04$) and drastically different from the observed chamber aerosol hygroscopicity (Fig. S5). This supports the notion that surface adsorption of MG and acetaldehyde (not present in the atomized solution experiments) is key to the CCN enhancement seen in the particles sampled directly from the chamber, as the hygroscopicity of aerosol generated from bulk solutions never exceeds that of the pure salt.

Comparing our results for the flow tube and chamber exposure studies suggests that a timescale of $3 \text{ min} < \tau < 3 \text{ h}$ is required for surface modification and the concomitant enhancement in CCN activity. This could suggest a slow approach to adsorption equilibrium, or that formation of oligomers in the near-surface

region is required. Hydration of MG in the aqueous phase occurs on a timescale of ~ 1 s (38). The timescale of MG self-oligomerization reactions is on the order of hours (16) in saturated ammonium sulfate solutions (full details of the timescale analysis are given in [Supporting Information](#)). Recent studies of acetaldehyde and MG mixtures in bulk ammonium sulfate solutions showed that cross-reactions between the two organics lead to greater surface tension depression than predicted based on the single-species isotherms (6). To represent a more atmospherically relevant environment, the combined effect of these aldehydes was also studied in the chamber; $2.33 \times 10^4 \text{ cm}^{-3}$ acidified ammonium sulfate were exposed to 8 ppb each MG and acetaldehyde for 5 h. These experiments showed similar CCN enhancement to the low-concentration acetaldehyde experiments. Unlike the bulk experiments of Li et al. (2011), no synergistic effect due to the mixed organics was observed. This suggests that the mechanism of surface tension depression is different in the bulk system vs. the aerosols, and that the formation of oligomer cross-products may be more important to surface tension depression in the bulk system.

The possibility of phase separation when the particles enter the dryer/CFSTGC setup can be ruled out based on a number of factors: the aerosol was acidified, preventing complete drying, thereby, preserving the gas–liquid interface. Additionally, particle growth in the dry distribution was not observed; hence, the amount of organic material is small and this reduces the chances for a phase separation. The state behavior of the particles at higher and lower relative humidities is also predictable, suggesting that two-phase separation is unlikely ([Supporting Information](#)).

The wet diameter profiles of the activated droplets formed by the particles exposed to MG and/or acetaldehyde at all timescales studied are similar to that of pure $(\text{NH}_4)_2\text{SO}_4$. These observations rule out the possibility of a kinetic barrier to water uptake to these particles on the timescale of the CCN measurements (39). However, the barrier action of a surfactant film toward the uptake of gas-phase species to the particle depends on the identity of the penetrating gas-phase molecules. Hence, a barrier effect for the uptake of trace gases (with implications for aerosol heterogeneous chemistry) is a question for future study.

Conclusions

We report here the results of chamber experiments conducted to study how the uptake of two VOCs in the atmosphere, MG and acetaldehyde, on acidified $(\text{NH}_4)_2\text{SO}_4$ seed aerosols can affect their CCN activity. At 250 ppb, both organics individually enhanced CCN activity. At more atmospherically relevant concentrations of 8 ppb, acetaldehyde depressed the critical activation diameters, whereas no change was seen with MG. A mixture of the two organics at lower concentrations showed comparable augmentation in CCN activity to 8 ppb acetaldehyde alone. These enhancements are beyond what are expected due to Henry's Law alone and can be attributed to surface adsorption and nonequilibrium partitioning between the gas and aerosol phases. Based on the maximum enhancements seen in our experiments, a similar surfactant effect occurring in the atmosphere may increase calculated average CDNC by 8–10%, thus affecting predictions of shortwave cloud albedo. Note that droplet closure studies in polluted ambient clouds (e.g., refs. 40–42) do not account for surfactant adsorption effects but require an assumption of water uptake coefficient γ that is considerably lower ($\gamma = 0.03$ – 0.06) than theoretical expectations or in situ CCN activation experiments ($\gamma = 0.2$ – 1.0) (43–49). This discrepancy in uptake coefficient elevates CDNC in ambient clouds by up to 20% (41), consistent with the magnitude of the surfactant effects observed in our study. Therefore, although surfactant adsorption effects on droplet number have not been identified in ambient aerosol to date, the aforementioned discrepancy in water uptake coefficient may be a direct consequence of it. To demonstrate that the observed effects occur in

the atmosphere, future field studies in regions with high VOC concentrations should be conducted by exposing $(\text{NH}_4)_2\text{SO}_4$ seed aerosols to ambient air in an aerosol chamber and using similar CCN and filter analyses to those done in our laboratory chamber experiments. Alternatively, particles under stable equilibrium with supersaturated water vapor can be suspended using an electrodynamic balance (50), and then exposed to the organic gas-phase precursors to examine whether nucleation is induced in accord with our measurements. Finally, exposing particles from the chamber experiments carried out here to ultrahigh relative humidity can deconvolute the contribution of bulk solute and surface tension depression to the observed hygroscopicity (51). Future work using these methods will help determine whether these mechanisms occur in the atmosphere.

Methods

A schematic of the experimental setup is shown in Fig. 3. A 0.2-M $(\text{NH}_4)_2\text{SO}_4$ solution was prepared using Millipore water and the pH was adjusted to 0 ± 0.1 or 2 ± 0.1 using H_2SO_4 , as the reactions which drive uptake are thought to be promoted by an acidic environment (16). The solution was aerosolized with pure N_2 using a constant output atomizer (TSI). This wet aerosol stream was exposed to either gas-phase MG (250 or 8 ppb) and/or acetaldehyde (250 or 8 ppb) in a continuous-flow 3.5-m³ Teflon aerosol chamber. The organic trace gas and acidified $(\text{NH}_4)_2\text{SO}_4$ particles were added into the chamber together at a total flow rate of 13 L/min for a typical residence time of ~ 5 h. As predicted based on a mass balance on the aerosol chamber ([Supporting Information](#)) and confirmed using chemical ionization mass spectrometry measurements of gas-phase MG concentrations during a typical experiment, the gas-phase organic is not significantly depleted in our experiments. Hence, we do not need to take into account depletion when calculating potential effects as considered by Kulmala et al. (1993) and follow-up studies (52). To characterize the time evolution of these processes, a residence time of 3 h was also tested using the chamber, and a glass flow tube (7.5-cm i.d., 55-cm length) was used for a 3-min exposure time. Relative humidity inside the reactors was maintained between 62% and 67% as measured with a relative humidity meter (Vaisala) by passing the N_2 dilution flow although a bubbler filled with Millipore water. At the outlet of each reactor, the particles were passed through a diffusion dryer, a scanning mobility particle sizer (SMPS, TSI), and a CFSTGC (Droplet Measurement Technologies) to monitor particle concentration and CCN activity, respectively, using scanning mobility CCN analysis (SMCA) (53). Total aerosol number concentrations in the chamber were $9.7 \pm 0.3 \times 10^5 \text{ cm}^{-3}$ (in the aerosol flow tube experiments, $1.5 \pm 0.3 \times 10^5 \text{ cm}^{-3}$). The size distribution had a mean volume-weighted particle radius of $231 \pm 1.3 \text{ nm}$ with a geometric SD of 1.4 (mean surface-weighted particle radius was $203 \pm 1.7 \text{ nm}$ with a geometric SD of 1.6).

The pure $(\text{NH}_4)_2\text{SO}_4$ (nonacidified) solution was aerosolized, passed through a diffusion dryer, and analyzed using SMCA to obtain the salt control. A control experiment with only the inorganic seed aerosol being introduced into the chamber was also conducted and analyzed, and the results were consistent with the pure $(\text{NH}_4)_2\text{SO}_4$ solution data. Bulk aqueous solutions containing 0.5 M of the organic (MG and/or acetaldehyde) in

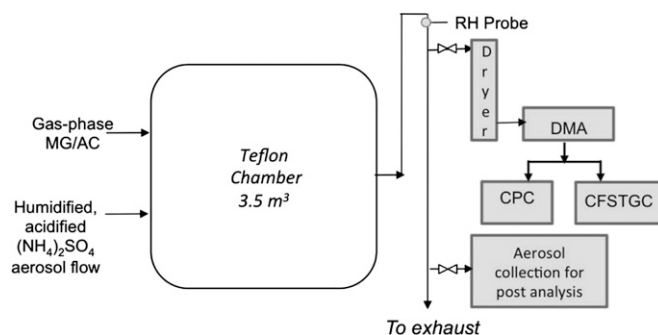


Fig. 3. Schematic of the experimental setup. Gas-phase MG and/or acetaldehyde and ammonium sulfate seed aerosols are introduced into the chamber maintained at 62–67% RH. At the outlet, particles are analyzed using an SMPS and a CFSTGC.

solution form with and without 3.1 M $(\text{NH}_4)_2\text{SO}_4$ were allowed to react for 24 h, and were then atomized and analyzed in a similar manner. For select experiments, the $(\text{NH}_4)_2\text{SO}_4/\text{MG}$ particles were passed through a heated stainless steel tube at 100 °C upstream of the SMPS/CFSTGC. No appreciable difference in the CCN activity spectra was observed with and without heating, suggesting that CCN activity in this system is not affected by volatilization biases (54).

At the end of each chamber experiment, particles from the chamber were collected on Zeflour filters (Pall, 47 mm, 2.0 μm) for ~ 14 h at a pumping rate of 14 LPM, where 7 LPM was the chamber effluent and the rest of the flow consisted of dry N_2 to avoid deliquescence of the filter-sample aerosol. The water-soluble fraction of the collected particles was analyzed following the procedures of Asa-Awuku et al. (2010) (33): The filters were extracted in 8 mL pure water (18 M Ω) during a 1.25-h sonication process in a water bath heated to ~ 60 °C. The filter extracts were then analyzed for WSOC concentration with a Sievers total organic carbon (TOC) turbo analyzer, for soluble anion and cation composition with an ion chromatography system (Dionex DX-500); the CCN activity of the samples was measured by atomizing 3–5 mL of the extracted sample in a collision-type atomizer, drying the aerosol stream with two diffusion dryers, and analyzing using SMCA as described for the chamber experiments. The hygroscopicity of each filter

extract was then determined with respect to a pure water blank. Gas-phase MG was prepared as described previously by Kroll et al. (2005) (3), except that it was collected in a cold finger at -70 °C. While at this temperature, a 5- or 0.5-standard cubic centimeter per min (sccm) N_2 stream was passed through the cold finger for a final concentration of 250 or 8 ppb in the aerosol reaction chamber. Acetaldehyde was prepared by adding 99.9 wt % liquid acetaldehyde (Sigma-Aldrich) to a cold finger under an oxygen-free environment and then passing a 1.4 sccm N_2 stream over it while the cold finger was kept at -78 °C for a final concentration of 250 ppb or passing a 0.3-sccm N_2 stream over it while the cold finger was kept at -92 °C for a final concentration of 8 ppb.

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