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Heterogeneous uptake of ammonia and dimethylamine into sulfuric and oxalic acid particles

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Supplementary Figures

Figure S1: Experimental setup of simultaneous absorption of dimethylamine and ammonia in sulfuric acid and oxalic acid particles. The experimental procedure includes RH conditioning, Gas generation, Flow cell reaction, Particle analysis with the Ion Chromatograph, and Phase state and morphology observation with a Microscope Raman. Abbreviations: HP N ₂ , high purity nitrogen gas, RH, relative humidity; DMA, dimethylamine.....	2
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Methods

Experimental setup

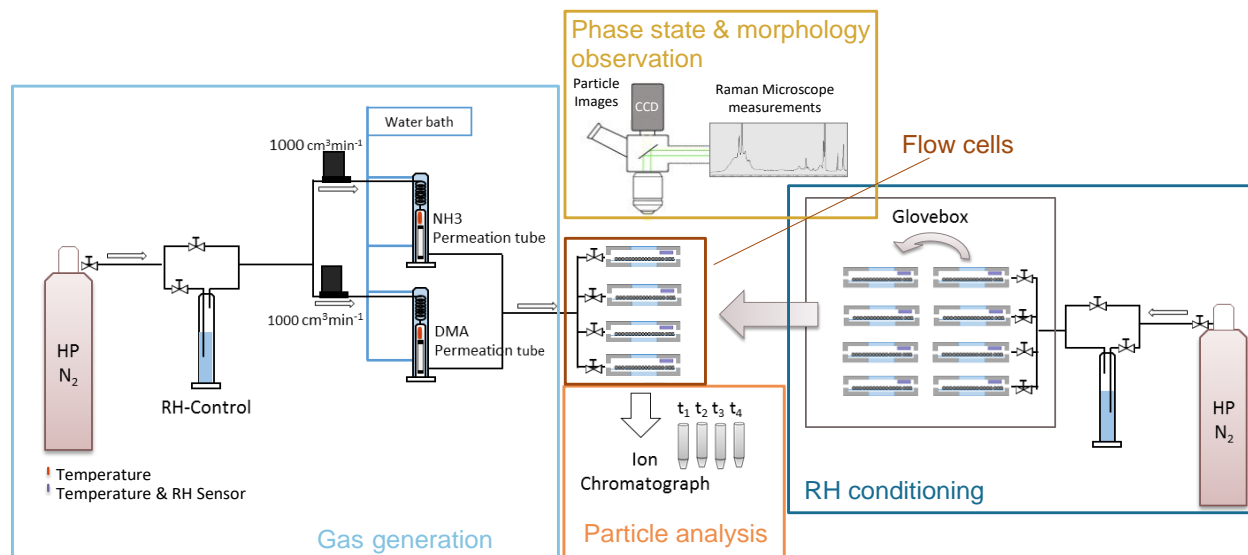


Figure S1: Experimental setup of simultaneous absorption of dimethylamine and ammonia in sulfuric acid and oxalic acid particles. The experimental procedure includes RH conditioning, Gas generation, Flow cell reaction, Particle analysis with the Ion Chromatograph, and Phase state and morphology observation with a Microscope Raman. Abbreviations: HP N₂, high purity nitrogen gas, RH, relative humidity; DMA, dimethylamine.

Gas generation system

The general setup including the gas generation system was tested using an ion-molecule reaction mass spectrometry (IMR-MS, AirSense, V&F Analyse-und Messtechnik GmbH).

Temperature sensitivity

Temperature sensitivity of the gas generation system was tested with permeation tubes for NH₃ (permeation rates: ~2700 ng/min at 293 K) and for the DMA (permeation rates: ~4400 ng/min at 293 K). Temperatures inside permeation tube holders were increased in small steps between 19.0 and 21.0 K. The temperature raise yielded a stronger increase in NH₃ than in DMA concentrations, causing a systematic decrease in DMA/NH₃ ratio of 4%/K. DMA concentrations generated from smaller permeation tubes (permeation rates ~550 ng/min at 293 K, flowrate: 2000cm³/min) were near the detection limit of the IMR-MS. Permeation rate changes with temperature were estimated based on

$$\text{Log } P_1 = \text{log } P_0 + \alpha (T_1 - T_0)$$

where P_0 = Rate at temp T_0 (°C), P_1 = New rate at temp T_1 (°C), and α = the temperature coefficient (0.034), and would yield an approximate change in DMA concentrations by 3%/K. In the final experiment temperature could be controlled to ± 0.2 K, hence DMA/NH₃ ratio changes due to temperature fluctuations were <1%.

These uncertainties in the DMA/NH₃ gas phase ratios due to temperature fluctuations were significantly smaller than uncertainties related to gravimetric measurements. The overall uncertainty of DMA/NH₃ gas phase ratios was estimated to be 5-8 % as listed in Table 1 of the manuscript.

Equilibration time

As NH₃ and DMA are both very “sticky” gases (Robacker and Bartelt 1996, Hansen et al. 2013, Dawson et al. 2014), they are prone to adsorb to instrumental surfaces. Yet, the stickiness varies among different amines and ammonia (Namieśnik et al. 2003, Dawson et al. 2014). Test measurements using IMR-MS connected to the gas generation system showed that the reestablishment of stable gas concentrations at the inlet of the flow cell after the system underwent a cleaning process took up to 4 hours for NH₃ and up to 8 hours for DMA. A much shorter recovery time of <1 hour for both gases, was observed if only the gas supply was temporarily interrupted (e.g. for weighing permeation tubes, and/or changing the N₂ cylinder).

Since a drop in the concentration of one or both gases (e.g. due to wall losses) would result in a change of DMA/NH₃ ratio, we allowed 2 h equilibration time when the gas supply was interrupted and about 12 hours for reconditioning after the setup was cleaned. Since flow cells were likewise conditioned with DMA and NH₃ gas, we equilibrated the sulfuric acid or oxalic acid particles to the respective RH of 10% or 50% in separate clean cells.

Results and discussion

Section 3. Uptake into oxalic acid particles

ox0.5_{70%}

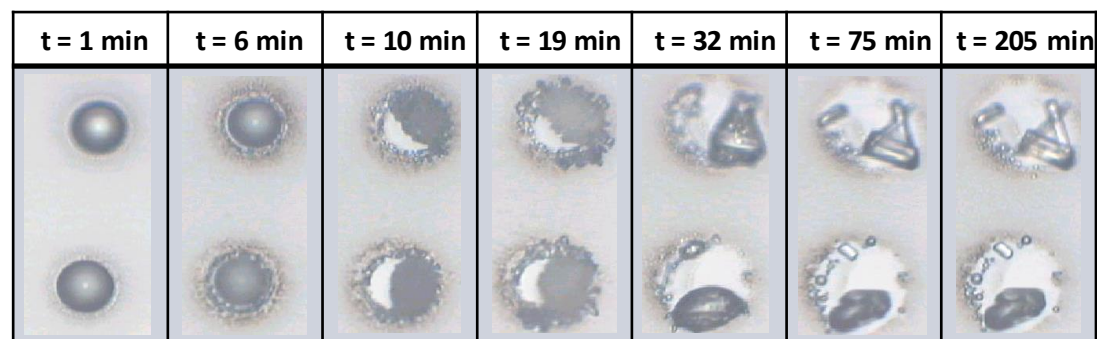


Figure S2: Morphological changes during the uptake of 1.0 ppm DMA and 1.9 ppm NH₃ into oxalic acid particles at 70% RH.

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