New Particle Formation and Growth From the Reaction of Methanesulfonic Acid with Amines and the Ozonolysis of Terpernes

Véronique Perraud,[1] Matthew L. Dawson,[1] Carla Waring-Kidd,[1] Michael J. Ezell,[1] Mychel E. Varner,[1] R. Benny Gerber,[1] Andrew S. Martinez,[2] Donald Dabdub[2] and Barbara J. Finlayson-Pitts[1]

[1]Department of Chemistry, University of California, Irvine, CA, United States; [2]Department of Mechanical and Aerospace Engineering, University of California, Irvine, CA, United States

Introduction / Previous Work on MSA + Amines + H_2O

- Atmospheric aerosols negatively impact human health, reduce visibility and affect the climate by scattering and absorbing solar radiation and changing cloud properties.[1-4]
- Models typically consider sulfuric acid (H_2SO_4) nucleation as the major source of new particles in the atmosphere. However, these methods consistently underpredict particle formation, indicating that other sources and/or co-nucleating species may play a role.[2,3,5]
- Ammonia and amines have recently been identified as important co-nucleating species in particle formation from sulfuric acid.[6-12] Also, recent research at AirUCI using a flow tube reactor (Fig.1) has identified methanesulfonic acid (MSA, CH_3SO_3H) and amines as a potentially important source of particles.[13]

Figure 1: Flow tube utilized for particle formation experiments

- Particle formation in these multicomponent systems shows a complex dependence on precursor concentration (Fig. 2), making them difficult to model using parameterizations based on nucleation theory. Two kinetics-based nucleation mechanisms, one for sulfuric acid, amines and water, and one for MSA, amines and water (Fig. 3), have been proposed as accurate, computationally-inexpensive methods for predicting particle formation from these systems.[12,13]

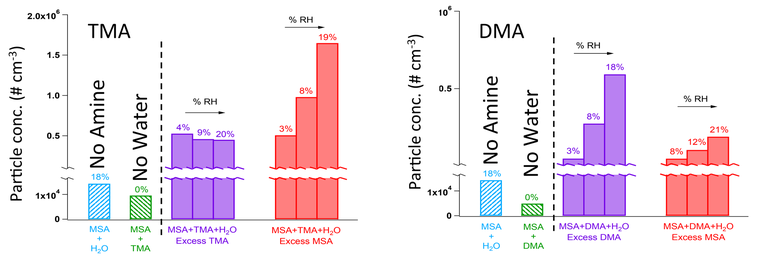


Figure 2: Complex dependence of particle formation on precursor concentration in the MSA-amine-water system, for trimethylamine (TMA) and dimethylamine (DMA).[13]

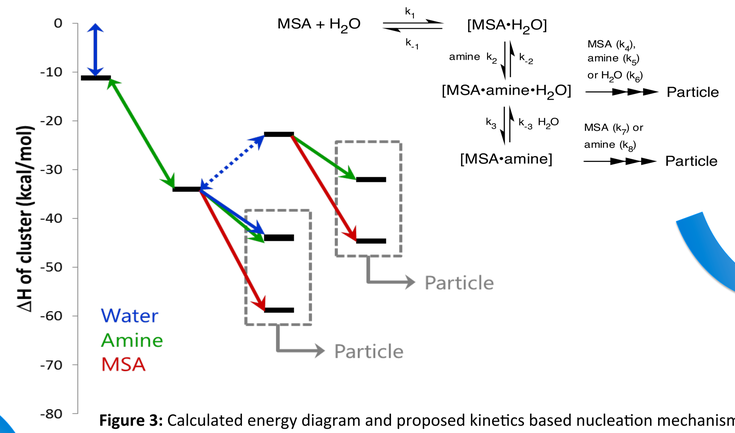


Figure 3: Calculated energy diagram and proposed kinetics based nucleation mechanism[13]

References:

1. Forester et al., *IPPC Report* (2007); 2. Finlayson-Pitts & Pitts (2000); 3. Seinfeld & Pandis (2006); 4. Pope & Dockery, W. *J. Air Waste Manage. Assoc,.* 56, 709–742 (2006); 5. Sipila et al., *Science,* 327, 1243–1246 (2010); 6. Angelino et al., *Environ. Sci. Technol.*, 35, 3130–3138 (2001); 7. Berndt et al., *Atmos. Chem. Phys.*, 10, 7101–7116 (2010); 8. Kirkby et al., *Nature,* 476, 429–U77 (2011); 9. Smith et al., *PNAS,* 107, 6634–6639 (2010); 10. Yu et al., *Geophys. Res. Lett.*, 39, (2012); 11. Zollner et al., *Atmos. Chem. Phys.*, 12, 4399–4411 (2012); 12. Chen et al., *PNAS,* 109, 18713-18718 (2012); 13. Dawson et al., *PNAS*, 109, 18719-18724 (2012).

Modeling

Goal:

Use a regional air quality model (UCI-CIT) to asses the impact of kinetics-based nucleation mechanisms in the South Coast Air Basin of California

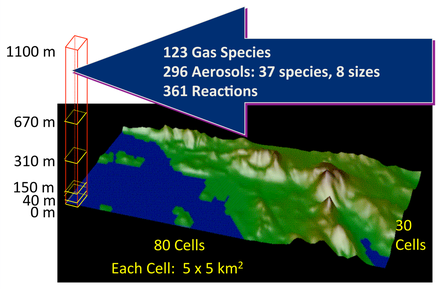


Figure 4: UCI-CIT Specifications

- UCI-CIT solves the Diffusion-Advection-Reaction equation in three dimensions in a 30x80x5 grid encompassing the South Coast Air Basin of California (SoCAB).
- Emissions of species besides MSA and amines follows 2005 emissions inventories.
- Amines and reduced sulfur species (precursors for sulfuric acid and MSA) were not previously included in the UCI-CIT model. However, SO_2 (an important source of sulfuric acid) and ammonia are included and show areas of overlapping concentration (Fig. 5).

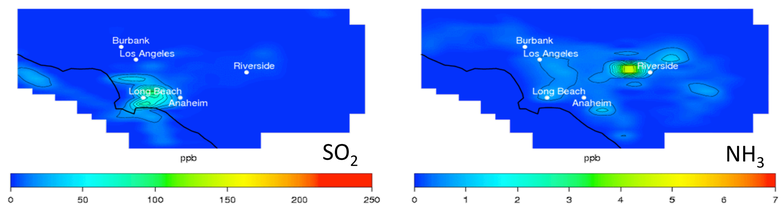


Figure 5: Co-location of amine particle precursor species in SoCAB

Methodology

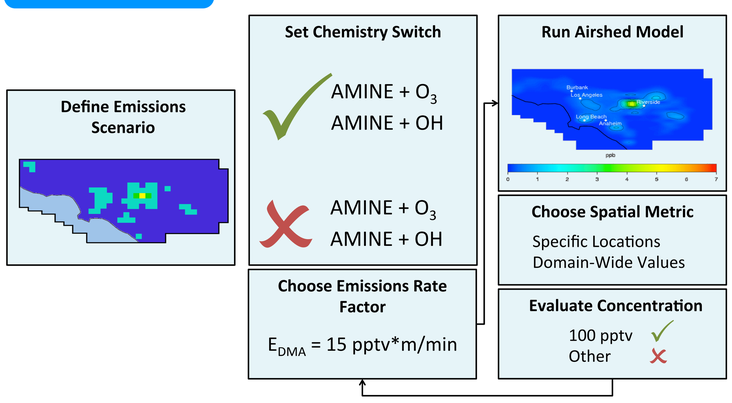


Figure 6: Iterative model execution and analysis process

- Amine emissions were set to track those of ammonia.
- The magnitude of the amine emissions was iteratively adjusted until average concentrations were 100 pptv[14,15] between 6 and 9 am.
- Model results with and without oxidation chemistry were performed to assess the impact of oxidation reactions on amine concentration.

Table 1: Oxidation reaction rates

Amine	Oxidant	Rate Constant (ppm/min)
MMA	OH	3.4E+04
	O_3	1.1E-05
DMA	OH	1.0E+05
	O_3	2.6E-03
TMA	OH	9.3E+04
	O_3	1.2E-03

- The species MSA, methylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA) were included in the UCI-CIT model along with their oxidation reactions with OH and ozone (O_3).

Results

- Modeled amine concentrations are a linear function of emission factors (Fig.7)
- Fast oxidation rates lead to chemistry dominating over advection in determining amine concentrations (Fig. 7)
- Magnitude of required emission factors varies slightly between amine species but by several orders of magnitude by geographical location (as low as 45 in the domain's peak, to 460 in Long Beach, and 1900 in Anaheim, all in units of pptV-m/min)

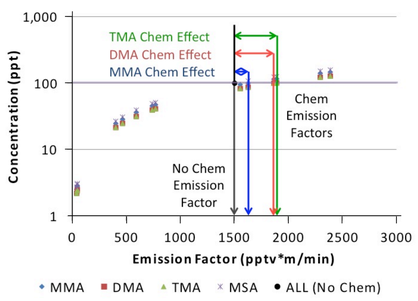


Figure 7: Long Beach concentration-emission trends

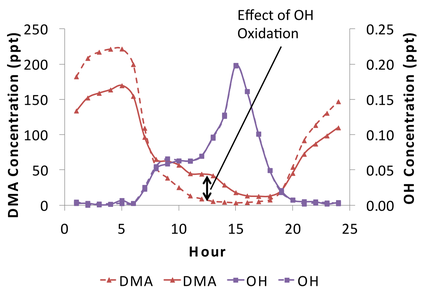


Figure 8: Long Beach hourly variations in OH and DMA. Solid: Oxidation Disabled. Dashed: Oxidation Enabled.

- Low amine concentrations suggest a smaller role for amines in particle formation during the day
- Competition for amine chemistry is driven mostly by oxidation via OH. Amines and OH are observed to have inversely correlated temporal variations (Fig. 8 and Fig. 9).
- Predicted emission factors are in reasonable agreement with global average measurements of NH_3:amine ratios (Fig. 10). Differences are likely due to local variation in NH_3 and amine emission rates.

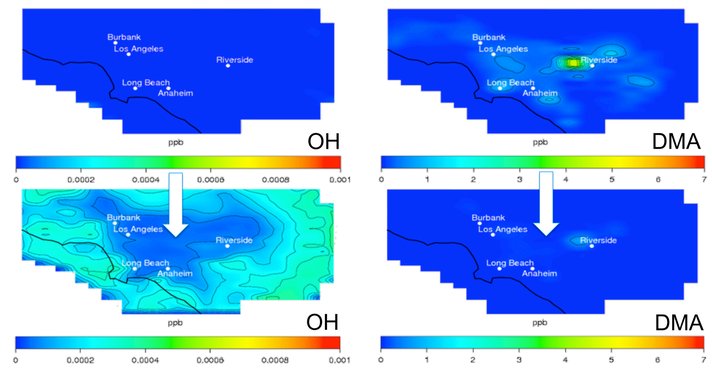


Figure 9: Top: OH and DMA at time of low OH oxidation
Bottom: OH and DMA during time of high OH oxidation

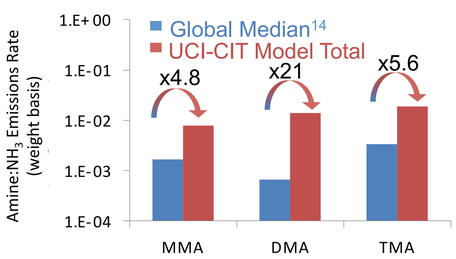


Figure 10: Comparison of model emission rates to literature values

Conclusions

- Under this emissions scenario, there appears to be a potential for particle formation in the morning hours.
- Oxidation of amines by OH presents the greatest competition to particle formation through amine-acid reactions.

References:

14. Ge et al., *Atmos. Environ.,* 45, 524-546 (2011)
15. Facchinni et al., *Environ. Sci. Technol.,* 42, 9116-9121 (2008)

New Mini Flow tube Experiments

Goal:

Study the formation and growth mechanism/kinetics of SOA from MSA + Amines +H_2O at shorter reaction time.

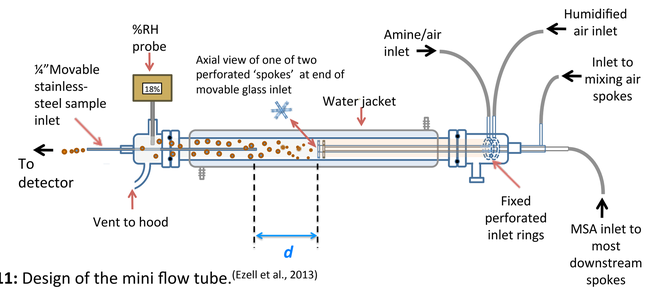


Figure 11: Design of the mini flow tube.(Ezell et al., 2013)

Step 1: Residence time measurements

- Laminar flow/residence time tested with the measurement of NO_2 in air by UV-vis spectroscopy).
- First experiments with MSA + amines + H_2O are underway (see B.J. Finlayson-Pitts' talk on Tuesday/NPF breakout session)

Table 2: Residence time in the flow tube

	Total Flow (Lpm)		
	6	11	17
Distance *d* (cm)	t_r(s)	t_r(s)	t_r(s)
3.5	1.2	0.8	0.5
0.9	2.5	1.5	0.9
12	4.2	2.6	1.6
22	7.7	4.9	3.0
32	11.2	7.1	4.3
42	14.7	9.3	5.7
52	18.2	11.5	7.1

New Particle Formation and Growth from Ozonolysis of Terpenes

- Recent studies show that aerosols are *semi-solid or glassy,*[16-27] which will affect the way SVOCs partition into SOA.
- The uptake of SVOCs may be better represented by a condensation mechanism.[28-30]

Goal: Investigate SOA phase and uptake of VOCs

1 - ATR-FTIR Experiments

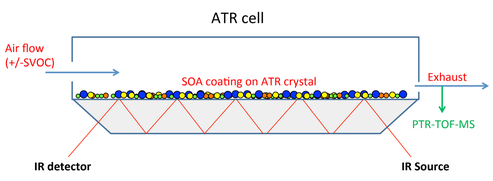


Figure 12: Experimental design

SOA evaporation
- IR spectrum of SOA coating
- IR signal monitored as a function of time
- Evaporation rate and IR spectrum of evaporated material obtained

$RONO_2$ uptake
- $RONO_2$ uptake rate
- $RONO_2$ loss rate

Results

- Very little evaporation, less than 20% loss in 20 hrs
- Good agreement with results from Vaden et al., (2011) for lab generated and ambient SOA particles
- Evaporation behavior is *not* consistent with that predicted based on instantaneous equilibrium partitioning of known ozonolysis products

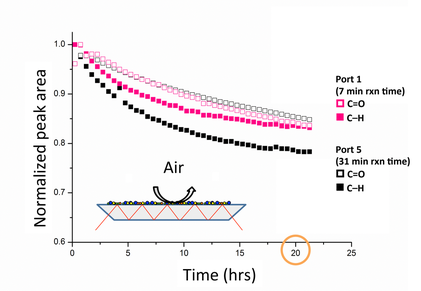


Figure 13: α-Pinene/O_3 SOA Evaporation experiments

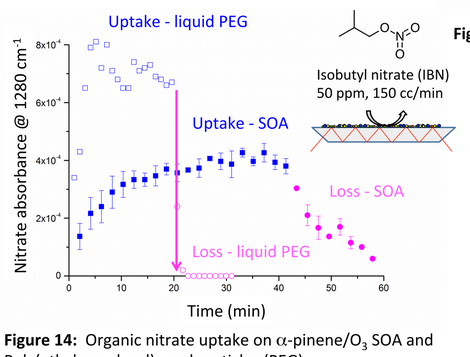


Figure 14: Organic nitrate uptake on α-pinene/O_3 SOA and Poly(ethylene glycol) seed particles (PEG)

- IBN uptake and loss much slower in SOA than liquid PEG model system
- SOA has a higher viscosity than PEG (0.1 pa s)
- Loss of IBN from SOA is very slow considering the high vapor pressure of IBN (10 Torr)
- SOA behaving like a semi-solid and hindering diffusion
- Aim to extend method to other organic nitrates/ SVOCs/model systems

2 - A New Approach for SOA analysis: Atmospheric Solid Analysis Probe Mass Spectrometry (ASAP-MS)[31-32]

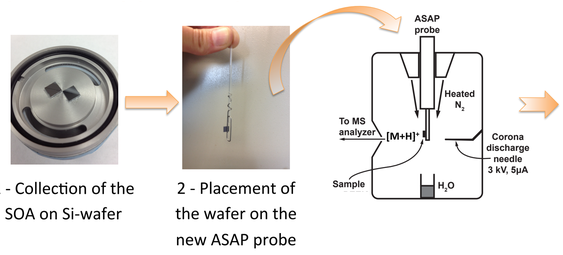
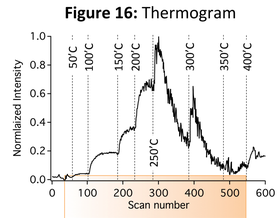


Figure 15: Sampling/Analysis sequence

- Thermal desorption of the SOA products using a temperature ramp from 20°C to 450°C.
- Soft ionization forming $[M+H]^+$ ions.
- Detection using a time-of-flight mass spectrometer allowing accurate mass determination.

Figure 16: Thermogram



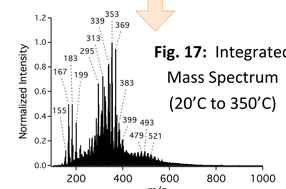


Fig. 17: Integrated Mass Spectrum (20'C to 350'C)

Results

- New sampling/analysis method: no more transfer of the sample!!!
- The new method increases run-to-run reproducibility.
- Able to compare different conditions, such as those presented here for d > 500-nm particle vs. 250-nm < d < 500-nm particles (Sioutas impactor, stage C and D respectively; sampling at 9 Lpm, from Port 5 [31min rxn time])

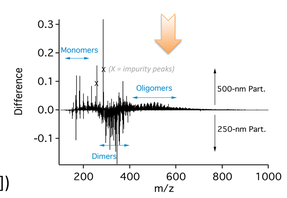


Fig. 18: Comparison Spectrum

References:

16. Zobrist et al., *ACP,* 8, 5221-5244 (2008); 17. Virtanen et al., *Nature,* 467, 824-827 (2010); 18. Virtanen et al., *ACP,* 11, 8759-8766 (2011); 19. Vaden et al., *PNAS,* 107, 6658-6663 (2010); 20. Vaden et al., *PNAS,* 108, 2190-2195 (2011); 21. Cappa and Wilson, *ACP,* 11, 1895-1911 (2011); 22. Koop et al., *PCCP,* 13, 19238-19255 (2011); 23. Tong et al., *ACP,* 11, 4739-4754 (2011); 24. Mikhailov et al., *ACP,* 9, 9491-9522 (2009); 25. Saukko et al., *Atmos. Meas. Tech.,* 5, 259-265 (2012); 26. Zelenyuk et al., *EST,* 46, 12459-12466 (2012); 27. Abramson et al. *PCCP,* 15, 2983-2991 (2013); 28. Perraud et al., *PNAS,* 109, 2836-2841 (2012); 29. Kleinman et al., *ACP,* 9, 4261-4278 (2009); 30. Riipinen et al., *ACP,* 11, 3865-3878 (2011); 31.Bruns et al., *Anal. Chem.*, 82, 5922-5927 (2010); 32. Bruns et al., PCCP, *J. Phys. chem.*, 116, 5900-5909 (2012)