



EPRI

ELECTRIC POWER
RESEARCH INSTITUTE

Roadmap for Development of CMAQ-MADRID

Eladio M. Knipping

**4th Annual CMAS Models-3 User's
Conference**

Chapel Hill, NC

September 26, 2005

CMAQ-MADRID Development Group

- **Atmospheric and Environmental Research: Principal Developers**
 - Christian Seigneur, Prakash Karamchandani, Kristen Lohman, Betty Pun, Krish Vijayaraghavan
- **Principal Academic Research Groups**
 - John Seinfeld, California Institute of Technology
 - James Pankow, Oregon Health & Science Institute
 - Robert Griffin, University of New Hampshire
 - Yang Zhang, North Carolina State University
- **Principal Collaborators**
 - Titan Corporation: Ian Sykes, Biswanath Chowdhury
- **EPRI Research Managers**
 - Alan Hansen, Naresh Kumar, Leonard Levin
- **Additional Support**
 - California Air Resources Board, U.S. Department of Defense, U.S. Environmental Protection Agency...

... And Our Newest Member



Major Components of CMAQ-MADRID (1/2)

- **MADRID_{1/2}: Model of Aerosol Dynamics, Reaction, Ionization and Dissolution**
 - State-of-the-art PM module developed by AER and Caltech in collaboration with other academic research groups
 - Sectional aerosol treatment (2 or more bins)
 - Incorporates latest developments in organic/inorganic aerosol research
 - MADRID₁ option utilizes Pankow-Odum-Griffin partitioning model for secondary organic aerosol formation
 - MADRID₂ option utilizes Caltech Atmospheric Chemistry Mechanism (CACM) and Multiple Phase Model for Partitioning of Organics (MPMPO)

Major Components of CMAQ-MADRID (2/2)

- **APT_{G/PM}: Advanced Plume Treatment**

- Plume-in-grid module for accurate treatment of elevated point sources
- Based on the Second Order Closure Integrated Puff Model with Chemistry (SCICHEM)
- Gas-phase chemistry or gas/particle chemistry options
- PM module consistent with both EPA PM and MADRID PM modules

- **Hg^{TEAM}: Mercury chemistry**

- Detailed model of gas-phase and aqueous-phase mercury chemistry
- Based on the Trace Elements Analysis Model (TEAM)
- Currently available for use with CMAQ-MADRID grid model
- Incorporation of Hg chemistry into additional configurations, including both APT PM configurations

Main Configurations of “CMAQ-MADRID”

Configuration Name	PM Module	APT	Hg ^{TEAM}
CMAQ (Host)			
CMAQ-APT _G	x	✓ (gas only)	x
CMAQ-Hg ^{TEAM}	EPA	x	✓
CMAQ-APT _{PM}	EPA	✓	x
CMAQ-APT _{PM} -Hg ^{TEAM}	EPA	✓	✓
CMAQ-MADRID	MADRID ₁	x	x
CMAQ-MADRID-APT _{PM}	MADRID ₁	✓	x
CMAQ-MADRID-Hg ^{TEAM}	MADRID ₁	x	✓
CMAQ-MADRID-APT _{PM} -Hg ^{TEAM}	MADRID ₁	✓	✓

Current Development of MADRID Modules

1. Active Development of MADRID Module
 - Abridged SOA Module
 - New SOA Species
 - RH Effect on SOA Formation
 - Computational Considerations
2. Acid Catalyzed SOA and “Oligomer” Formation
 - Experimental Studies
 - Theoretical Studies
 - Ambient Studies
3. Research & Development of MADRID Module
 - Thermodynamics
 - Extended UNIFAC/UNIQUAC
 - Future Challenges

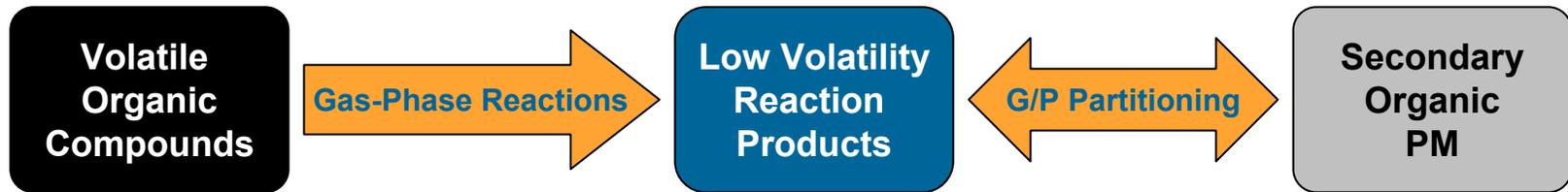


EPRI

ELECTRIC POWER
RESEARCH INSTITUTE

Active Development of MADRID Module

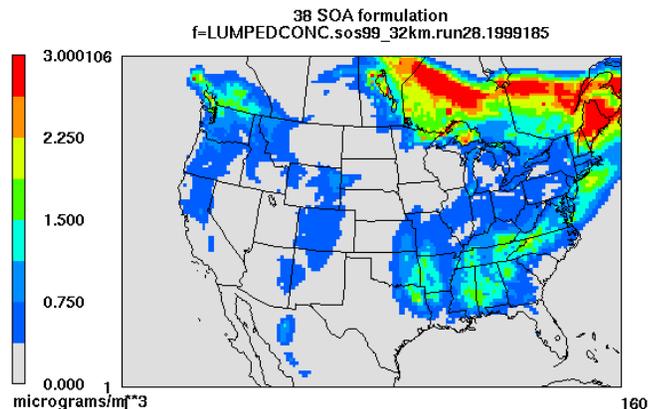
Standard Oxidative Route to SOA formation



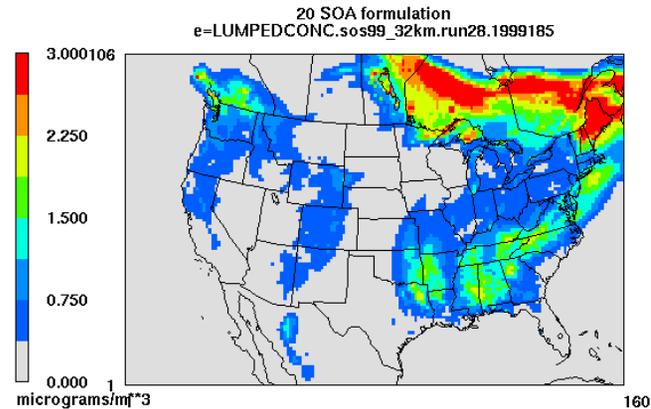
Predicting the formation of secondary organic particulate matter in the atmosphere requires **an understanding of all relevant reaction products and pathways**

Updating & Streamlining CMAQ-MADRID

24-hour average:TOTAL_SOAf



24-hour average:TOTAL_SO Ae



- **Streamlining SOA Mechanism in CMAQ-MADRID**

- Original SOA formulation:

- 2 anthropogenic SOA precursors, 12 biogenic SOA precursors
 - $38 \times n$ condensable surrogate products ($n = \text{number of sections}$)

- Abridged SOA formulation:

- 2 anthropogenic SOA precursors, 6 biogenic SOA precursors
 - $20 \times n$ condensable surrogate products

- Improvement in simulation time and storage requirements

Effects of RH on SOA Formation

- MADRID (or any PM model) does not consider RH effects on organic PM formation (20 hypothetical products in the abbreviated MADRID have no assigned chemical structures);
- Roadmap for incorporating RH effects:
 1. For each product, assign a probable carbon number and chemical functionality based on:
 - a) VOC precursor;
 - b) reaction; and
 - c) presumed volatility from the K_p value of the (α, K_p) pair.
 2. Develop an expression for the activity coefficient ζ for each organic compound that is a function of PM composition, including water content.
 3. Repeat (2) for water.
 4. Conduct RH-dependent model runs for total PM formed (organics + H_2O).

Preparation of Emission Inputs for Aerosol Precursors: Long-Chain Alkanes and PAHs

- (α, K_p) pairs have been developed for long-chain alkanes and PAHs
- Use SMOKE to process emissions
- Create new GSPRO file with PAH and long-chain alkanes as model classes
 - PAH class includes biphenyl, naphthalene, fluoranthene, phenanthrene, anthracene, etc.
 - Long-chain alkane class includes straight chained or branched alkanes with 12 or more carbons
- Optional step for reactivity scaling: scale all alkane species based on RADM emissions

Computational Aspects

- Updating to EPA CMAQ-4.5
- Parallelization of all code configurations to provide computationally efficient platform
- Updated User's Guide and Sample Applications
- Model Evaluation in Peer-Reviewed Literature



EPRI

ELECTRIC POWER
RESEARCH INSTITUTE

Acid Catalyzed Formation of Secondary Organic Aerosol

Heterogeneous Atmospheric Aerosol Production by Acid-Catalyzed Particle-Phase Reactions

REPORTS

Heterogeneous Atmospheric Aerosol Production by Acid-Catalyzed Particle-Phase Reactions

Myoung Jang,¹ Nadine M. Czoschke, Sangdon Lee, Richard M. Kamens

According to evidence from our laboratory, acidic surfaces on atmospheric aerosols lead to potentially multiplied increases in secondary organic aerosol (SOA) mass. Experimental observations using a multichannel flow reactor, Teflon (polytetrafluoroethylene) film bag batch reactors, and outdoor Teflon-film smog chambers strongly confirm that inorganic acids, such as sulfuric acid, catalyze particle-phase heterogeneous reactions of atmospheric organic carbonyl species. The net result is a large increase in SOA mass and stabilized organic layers as particles age. If acid-catalyzed heterogeneous reactions of SOA products are included in current models, the predicted SOA formation will be much greater and could have a much larger impact on climate forcing effects than we now predict.

Gas-phase reactions of volatile organic compounds (VOCs) associated with photochemical oxidant cycles have been of great interest in predicting ozone (O_3) concentrations and, more recently, SOA formation. SOA has received much attention for a variety of reasons, many of which are associated with the establishment of a national ambient air quality standard for atmospheric fine particles (1). From a public health perspective, SOAs, which are a major contributor to fine particulate matter, have potentially negative health effects. In particular, it is now believed that the potency of a mixture of environmental chemicals, such as an organic and inorganic multicomponent SOA, may be greater than its constitutive parts (2). At the regional scale, SOA formation can contribute to the formation of visibility-reducing haze (2). SOAs affect the Earth's radiative balance (3, 4) directly by altering the scattering properties of the atmosphere and indirectly by changing cloud properties. These climate forcing effects are thought to lead to a net cooling effect at the tropospheric level (3). Furthermore, the composition of SOAs influences the extent of these effects. For example, the water content of cloud aerosols, and thus a cloud's lifetime, is mainly influenced by particle acidity and sulfate content.

Our understanding of the role SOAs play in climate change and their connection to health effects is limited by numerous uncertainties, particularly the total SOA particle concentration and mass, the contribution of tropospheric SOAs to the total particle load, the composition and physical structure of atmospheric aerosols, and the heterogeneous chemistry that influences these parameters. What is known is that biogenic terpenes from terrestrial vegetation (5) and aromatics from anthropogenic sources (6) are SOA precursors. Also, the gas-phase photooxidation reaction of these VOCs generates large amounts of multifunctional organic carbonyls (7–10), which are major SOA components. In addition, these components may react heterogeneously to form an additional generation of products in the particle phase. A major class of these heterogeneous reactions is the acid-catalyzed reactions of atmospheric carbonyls (10, 11). Principal candidates for atmospheric acid catalysts are sulfuric acid (H_2SO_4) and nitric acid (HNO_3), which are produced through oxidation processing of SO_2 and NO_2 emitted from fossil fuel combustion (12–15). These are inorganic acids; thus, the effects of acid-catalyzed heterogeneous reactions are essentially inter-

- **Non-acid seeds** are generated from ammonium sulfate $[(NH_4)_2SO_4]$ solutions
- **Acid seeds** are generated from solutions of sulfuric acid (H_2SO_4) and $(NH_4)_2SO_4$
- **Oxidized and non-oxidized organics** are added to the Teflon bags
- **Analysis of the product functional groups** is performed using FTIR spectroscopy

9. T. Barlow, R. Schurr, H. J. Gorthon, *Phys. Rev. Lett.* **84**, 4930 (2000).
 10. Q. Yang, A. S. DePreto, *J. Catal.* **190**, 223 (1994).
 11. F. Bellito, R. Ferrando, A. Fontana, F. Mentel, *J. Chem. Phys.* **116**, 2056 (2002).
 12. Because the only degree of freedom of the metal atoms is their Cartesian vibrations, the steric contribution to the free energy is small and differs very little with cluster size. This Eq. 1 is also often applied to describe the size dependence of internal energy as well as the energy. Generally, it is assumed to be independent of particle radius at the value for bulk metal [3, 4, 13–15].
 13. X. Lu, D. W. Goodwin, *J. Mol. Catal. A* **162**, 23 (2000).
 14. M. J. Jai, *J. Surf. Sci.* **474**, 23 (2001).
 15. M. J. Jai, C. Kompa, A. v. Kossowatz, J. Verhoeven, W. Frank, *Surf. Sci.* **487**, 259 (2002).
 16. D. E. Starr, D. J. Baki, J. E. Hagen, J. T. Ramsey, C. T. Campbell, *J. Chem. Phys.* **114**, 2752 (2001).
 17. The assumption of a constant number density of seeds is probably slightly incorrect in that their number generally increases slowly with coverage in the range for such systems [13, 4]. Considering that the model came from measured decreases in stability with radius to be even more dramatic, that shows.
 18. W. R. Tyson, W. A. Miller, *Surf. Sci.* **62**, 257 (1977).
 19. Using every non value of γ for 19 (46) (1997) gives even poorer agreement with experiment. Using Eq. 1 here neglects the energy of the flat face of the droplet, which is significant in testing the Kelvin adsorption energy at the face equal to the Pd-Pd adsorption energy. If the Pd-Pd adsorption energy were zero, the factor of 2 in Eq. 1 would increase to 3. Finally, the seeded condition is much smaller (16).
 20. J. Calzavara, N. Papadimitrakou, F. H. Dedering, *Surf. Sci.* **511**, 1 (2002).
 21. R. C. Tolman, *J. Chem. Phys.* **17**, 323 (1949).
 22. H. Z. Zhang, R. L. Finn, E. J. Hearn, J. F. Burfield, *J. Phys. Chem. B* **102**, 4522 (1998).
 23. D. L. Lide, Ed., CRC Handbook of Chemistry and Physics (CRC Press, Boston, MA, ed. 77, 1996).
 24. M. Haddad, D. Hering, M. Schurr, *Appl. Phys. A* **35**, 442 (1992).
 25. DePreto estimated that relative empirically by extrapolating between measured energies of the gas-phase dimer ($CH_2 = O_2$) [11] and trimer ($CH_2 = O_3$) and the bulk ($CH_2 = O_2$) [11]. Furthermore, we used DePreto's relation to estimate the errors in the MA model of Fig. 1 and found that the errors due to the decrease in bond energy with CH_2 nearly compensate for the errors associated with extrapolating between only the most stable cluster, further justifying this use.
 26. G. B. McVicker, R. L. Gorio, R. T. Slator, *J. Catal.* **54**, 129 (1978).
 27. We simplified the definition of $E_{rel} = \frac{dW}{dV} - \frac{dE_{rel}}{dV} = \frac{dE_{rel}}{dV} + \frac{dE_{rel}}{dV}$ has slightly from that of W-1 in that we neglected any volume activation energy beyond the bulk reaction energy associated with a monomer attaching from a small particle to zero onto the support surface, because the latter relation is not.
 28. There is another large error in Eq. 1 with derivation. W-1 separated the exponential factor such as $e^{-\frac{dE_{rel}}{dV}}$ in Taylor series and neglected all but the first two terms. This is equivalent to assuming that $dE_{rel} = dE_{rel}$ is small compared to dE_{rel} . Inspection of the heat data in Fig. 1 shows that this is clearly not the case below 1000 K for particles with a radius of a few nanometers.
 29. D. E. Starr, C. T. Campbell, *J. Phys. Chem.* **105**, 2776 (2001).
 30. C. E. Szwedko, H. H. Lee, *Chem. Eng. Sci.* **50**, 1237 (1995).
 31. C. H. Bartholomew, Ed., *Synthesis Kinetics of Supported Metals: Preparation from a Generalized Power Law Approach*, vol. 68 of Studies in Surface Science and Catalysis (Elsevier Science, Amsterdam, Netherlands, 1994).
 32. V. Rodos, S. C. Parker, C. T. Campbell, *Catal. Lett.* **3**, 143 (1980).
 33. F. C. Corradi, T. L. Muddy, *Surf. Sci. Lett.* **7**, 2 (2001).
 34. S. C. Parker, A. W. Coats, V. A. Rodos, C. T. Campbell, *Surf. Sci.* **441**, 10 (1999).
 35. H. Giese, S. Giorgio, C. R. Hery, *Philos. Mag. B* **31**, 1169 (2000).

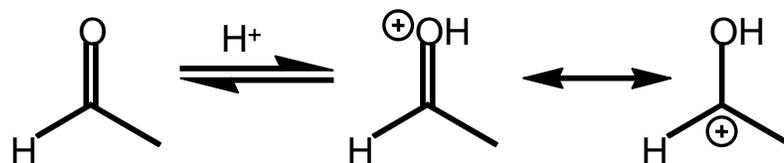
36. C. T. Campbell, D. E. Starr, *J. Am. Chem. Soc.* **124**, 8212 (2002).
 37. The average initial radius of Au clusters grown on TiO₂(110) under similar deposition conditions was estimated by scanning tunneling microscopy (12) and high-resolution scanning electron microscopy (20) to be about 1 nm. We used a slightly smaller average size because those techniques could have missed the smallest particles.
 38. M. Gillet, A. A. Mohammed, K. Maek, E. Gillet, *Thin Solid Films* **274**, 134 (2000).
 39. S. C. Parker, thesis, University of Washington, Seattle, WA (2000).

14 June 2002; accepted 24 September 2002

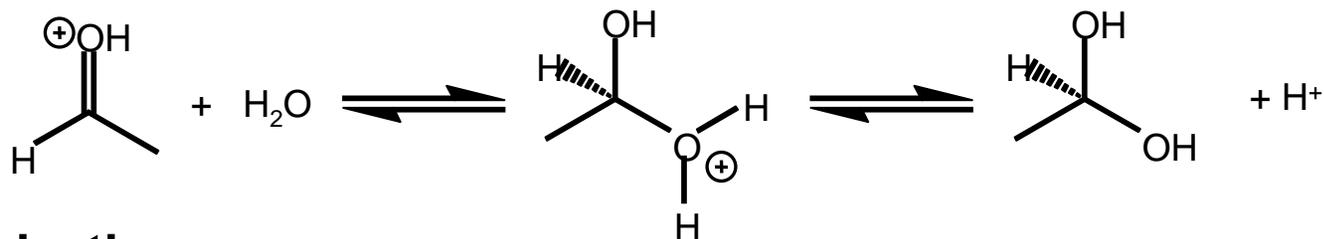
Department of Environmental Science and Engineering, CB 7421, Rosenau Hall, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA.
 *To whom correspondence should be addressed. E-mail: mjjang@ems.unc.edu

Potential Acid Catalyzed Reactions

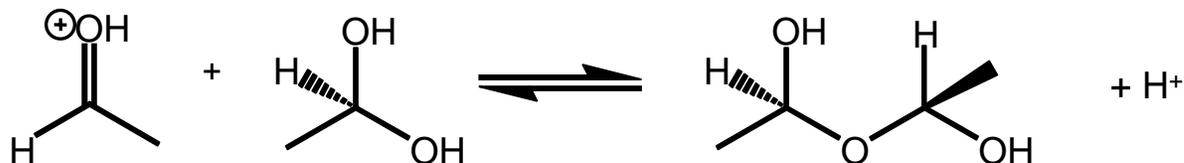
- Acid catalyzing step



- Hydration



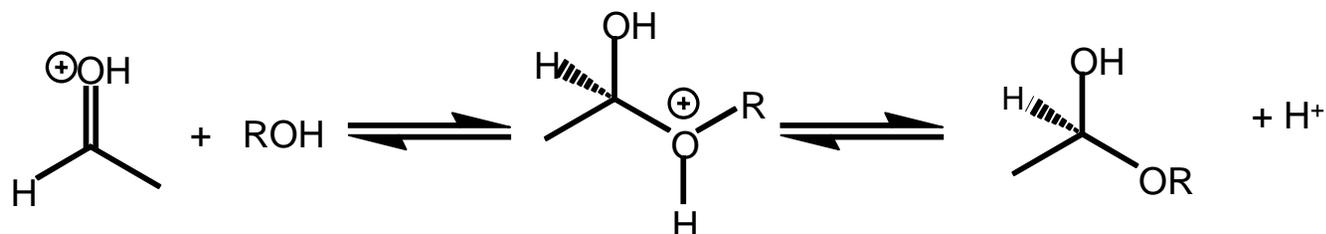
- Polymerization



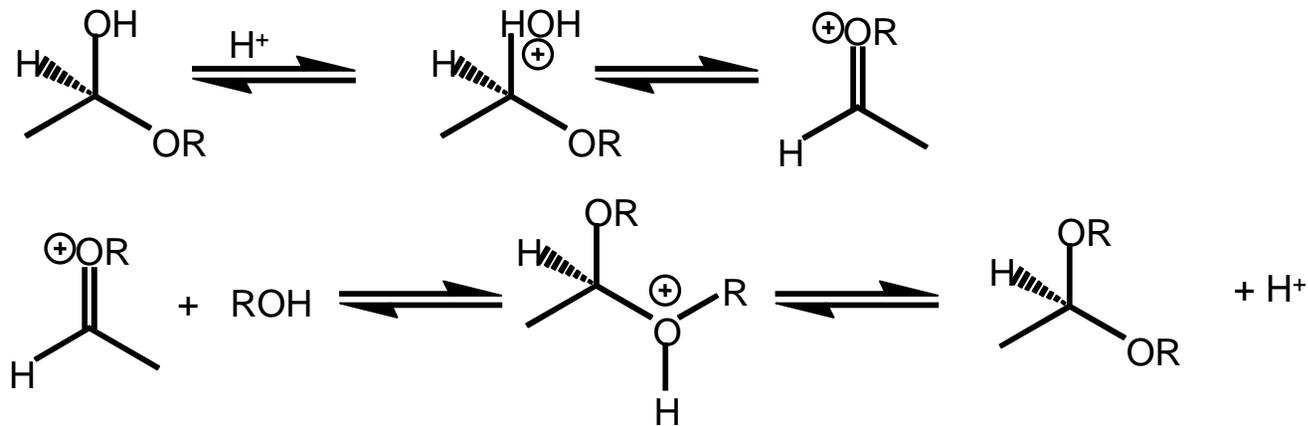
... with potential propagation of the above steps to form higher n-mers

Potential Products in Presence of Alcohols

- **Hemiacetal formation**



- **Acetal formation**



Acid Catalyzed Formation of SOA

A Brief Summary of Some Key Literature to Date

<p>Jang and Kamens, <i>Environmental Science & Technology</i>, 2001 Jang et al., <i>Science</i>, 2002</p>	<p>Acid catalyzed formation of SOA first suggested to cause large increases in production of organic PM; unrealistic concentrations and conditions for various organic gases and acidic particle seeds</p>
<p>Iinuma et al., <i>Atmospheric Environment</i>, 2004</p>	<p>For the alpha-pinene/ozone system, using more atmospherically relevant conditions, an increase of 40% in production with sulfuric acid seed compared to neutral ammonium sulfate seed – a potential upper limit for this system</p>
<p>Gao et al., <i>Environmental Science & Technology</i>, 2004 Gao et al., <i>Journal of Physical Chemistry A</i>, 2004</p>	<p>For the alpha-pinene/ozone system, an increase of 5% in production with moderately acidic ammonium bisulfate seed (more typical of ambient particle conditions) compared to neutral ammonium sulfate seed. Acidity not necessary to form “oligomer” products.</p>

Thermodynamic Analysis of “Oligomers”

Research Question

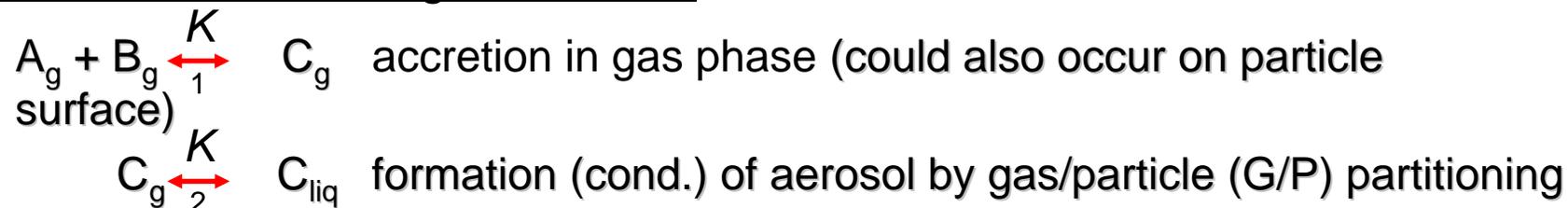
- Organic PM now modeled assuming oxidation of atmospheric VOCs leads to monomeric oxidation products that condense to form SOA
 - VOC + oxidant \rightarrow prod \rightarrow SOA
- Laboratory results suggest that oxidation products may *also*
 - continue to react
 - combine to form dimers & higher oligomers (**acid-catalyzed?**)
 - condense and/or persist in the particle-phase
 - VOC + oxidant \rightarrow prod(gas/particle)
 - prod1 + prod2 \rightarrow dimer \rightarrow (\rightarrow) low volatility SOA
 - ...

Although acid-catalyzed reactions may be kinetically controlled, the final product mixture must remain thermodynamically consistent

Accretion Reaction Thermodynamics: Analysis of “Oligomer”[†] Formation

[†]“Oligomer” is term that is currently **overused and misused**.

Accretion reaction; general form:



A, B = oxidation products of VOCs, or other atmospheric constituents (e.g., NH₃)

C = condensable low volatility accretion product

K₁ and K₂ = predictable thermodynamic equilibrium constants

Governing Thermodynamics:

equilibrium for accretion reaction:

$$K_1 = K_{eq} = \frac{p_C}{p_A p_B}$$

p = partial pressures (atm)

equilibrium for G/P partitioning:

$$K_2 = K_p = \frac{C_{liq} / OPM}{C_g}$$

C_{liq} = concentration of constituent in liquid-like OPM phase (ng m⁻³);

C_g = concentration of constituent in gas phase (ng m⁻³);

OPM = atm. level of organic particulate matter into which accretion product constituent can condense (μg m⁻³)

Overview of Reactants of Interest: Accretion Reactions

Reactant	Significant OPM Formation? (No, Yes, or Possible)	Reference
Ketones	No	Barsanti and Pankow, <i>Atmos. Env.</i> (2004)
Diketones	No	Barsanti and Pankow <i>Atmos. Env.</i> (2005)
~C ₅ and lower aldehydes	No	Barsanti and Pankow <i>Atmos. Env.</i> (2004)
~C ₆ and higher aldehydes	Possible by aldol condensation under certain circumstances	Barsanti and Pankow <i>Atmos. Env.</i> (2004)
Glyoxal	Yes by hydration/oligomerization	Barsanti and Pankow <i>Atmos. Env.</i> (2005)
Methylglyoxal	Yes by aldol condensation	Barsanti and Pankow <i>Atmos. Env.</i> (2005)
~C ₅ and lower dialdehydes (except glyoxal)	No	Barsanti and Pankow <i>Atmos. Env.</i> (2005)
~C ₆ and higher dialdehydes	Possible by aldol condensation under certain circumstances	Barsanti and Pankow <i>Atmos. Env.</i> (2005)
Acetic acid	No	Barsanti and Pankow (2006, in preparation)
Dicarboxylic acids	Yes by ester and amide formation	Barsanti and Pankow (2006, in preparation)

“Semiempirical Model for Organic Aerosol Growth by Acid Catalyzed Heterogeneous Reactions of Carbonyls”

- Jang et al., “Semiempirical Model for Organic Aerosol Growth by Acid Catalyzed Heterogeneous Reactions of Carbonyls” *Environ. Sci. Technol.*, 39, 164-174, 2005
- Comment Points: Barsanti et al. (*Environ. Sci. Technol.*, 39, 2005):
 - Absorptive partitioning theory Pankow (1994) was misapplied.
 - “Semiempirical model” characterizes kinetics of their experiments only; cannot be applied to predicting how much organic PM will form under different experimental conditions, or in the atmosphere.
- Response Points: Jang et al. (*Environ. Sci. Technol.*, 39, 2005):
 - Agree that Pankow (1994) model is basis for equilibrium modeling of organic PM formation; and
 - Continue to argue that their results are useful in kinetic considerations of organic PM formation under “acid catalysis” conditions, but do not explain how that could be done.

Ambient Samples from SEARCH Network

- **Analysis of samples to “search” for acid catalysis effects and oligomers**
 - Samples taken at four sites in the Southeastern Aerosol Research and Characterization (SEARCH) Network during Summer 2004 characterized for polar organic components of organic PM.
 - Oligomeric products were not identified in the MW range analyzed.
 - Ambient data showed no evidence of acid catalysis playing any discernable role in SOA production, consistent with laboratory and theoretical studies. (Still possible, but unlikely under ambient conditions.)
 - Ambient data have evidence of biogenic oxidation products and that can be a large regional source of SOA in the Southeast.
 - The most-prevalent **identified** organic compound ($\sim 1/4$ of identified organic PM) contained sulfur and nitrogen in the structure ($C_{10}H_{16}NO_7S$ or other isobaric structures), likely formed by reaction of NO_x and SO_2 with monoterpene oxidation products.

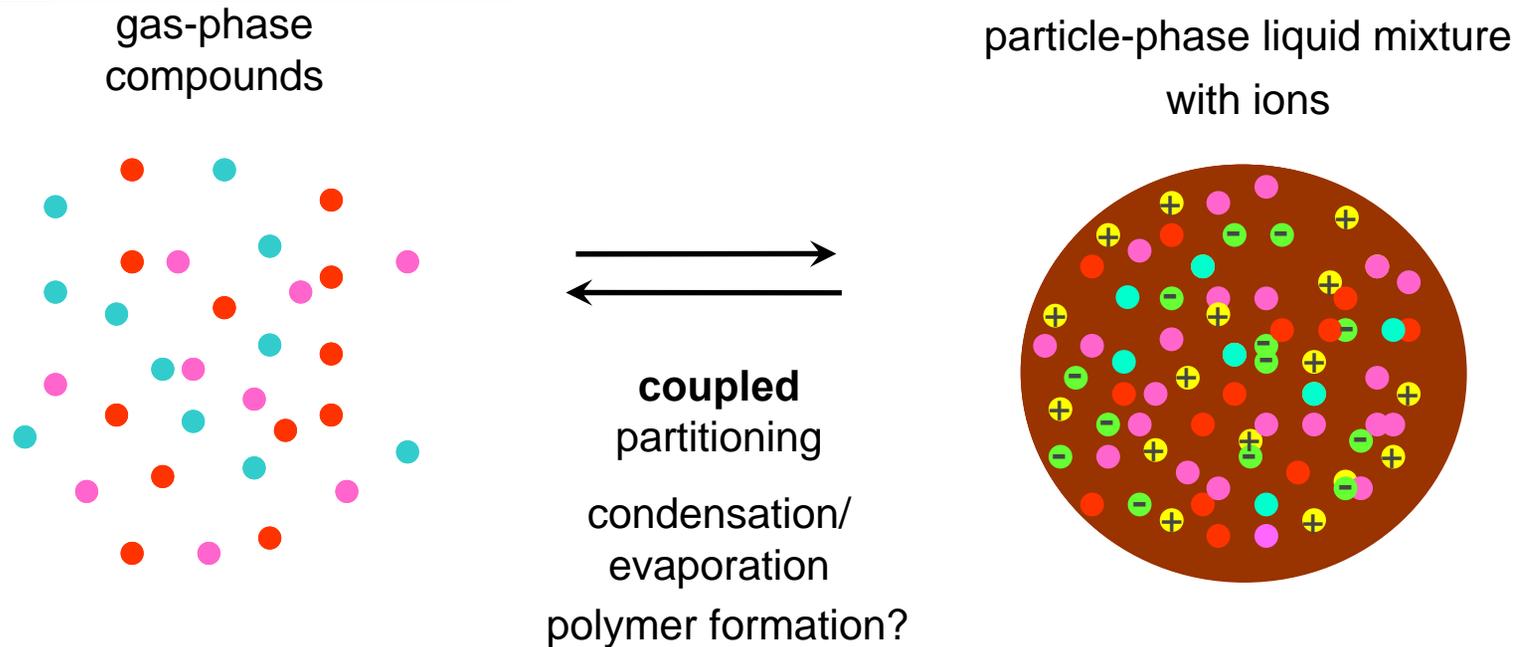


EPRI

ELECTRIC POWER
RESEARCH INSTITUTE

Research & Development

Thermodynamic Modeling of Secondary Organic Aerosol Formation



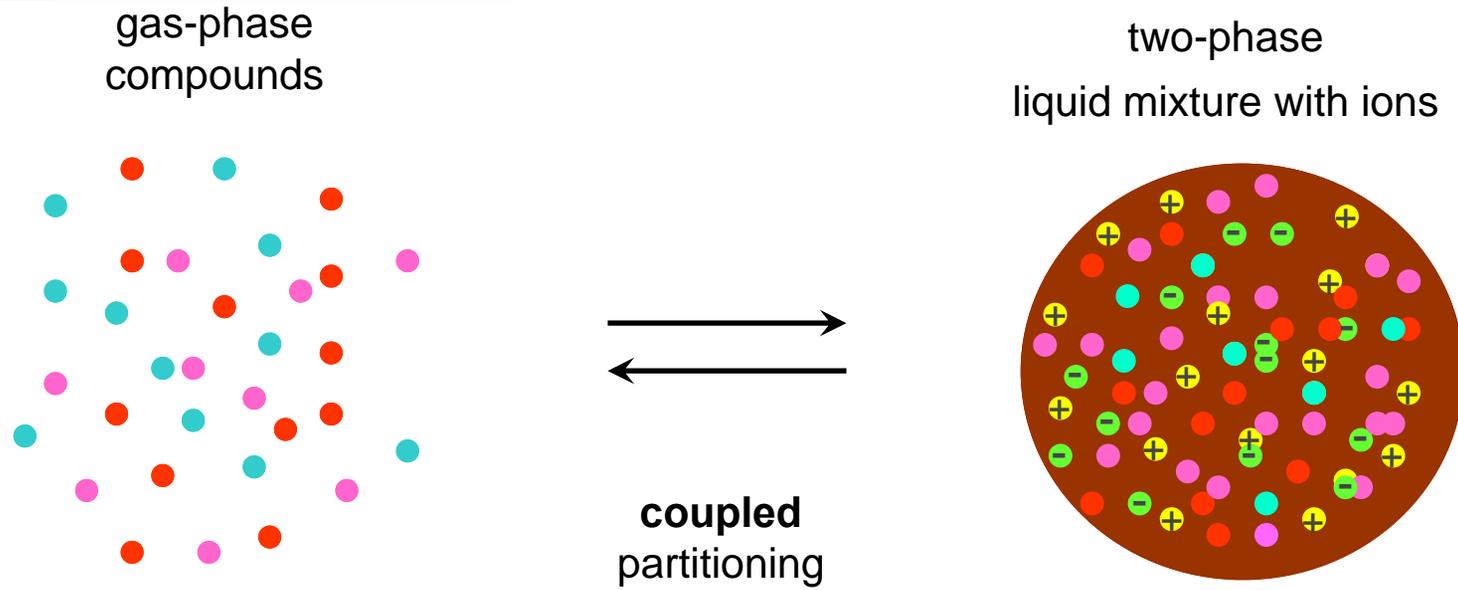
$$K_{p,i} = \frac{(\text{ng}/\mu\text{g})_{\text{particle phase}}}{(\text{ng}/\text{m}^3)_{\text{gas phase}}} = \frac{F_i / \text{TPM}}{A_i} = \frac{760 RT f_{\text{cm}}}{10^6 MW_{\text{cm}} \zeta_i \rho_{L,i}^0}$$

activity coefficient

vapor pressure

Pankow, J.F. 1994 *Atmos. Environ.*, 28, 185-188 and 189-193.

Multiple Liquid (and Solid) Phases



$$F_i = \frac{\sum_k K_{p,i}^k \text{TPM}^k}{1 + \sum_k K_{p,i}^k \text{TPM}^k} T_i$$

Pankow, J.F. 2003. *Atmos. Environ.*, 37, 3323-3333.

Activity Coefficient Methods

Purely Inorganic Mixtures
(water + salts)

Bromley, Kusik-Meissner, Pitzer
as implemented in
SCAPE.2, ISORROPIA

Purely Organic Mixtures
(organics + water)

UNIFAC

Activity Coefficient Methods

Primarily Inorganic Mixtures (water + salts + organics)

Clegg, S. *et al.* **2001**. *J. Aerosol Sci.*, 32,
713-738.

Clegg, S., Seinfeld, J.H. **2004**. *J. Phys.
Chem. A*, 108, 1008-1017

(Extended ZSR method)

Primarily Organic Mixtures (organics + water + salts)

Erdakos, G.B. *et al.* **2004**.

Erdakos, G.B., Pankow, J.F. **2004**.

Extended-UNIFAC method

Extended-UNIFAC

Results from simulations of PM formation in presence/absence of salts suggest that failure to consider salts may cause large errors in PM values.

Future Methods: Extended-UNIFAC/UNIQUAC

- Yan, *et al.* **1999**. *Fluid Phase Equilibria*, 162, 97-113.

$$\ln \zeta = \ln \zeta^{\text{LR}} + \ln \zeta^{\text{MR}} + \ln \zeta^{\text{SR}}$$

- LR = Long-Range electrostatic interactions;

$\ln \zeta^{\text{LR}}$: modified Debye-Hückel equation

- MR = Middle-Range indirect charge interactions (i.e., charge-dipole interactions and charge-induced dipole interactions);

$\ln \zeta^{\text{MR}}$: second virial coefficient-type equation

- SR = Short-Range interactions (i.e., dipole-dipole interactions);

$\ln \zeta^{\text{SR}}$: UNIFAC equation

Extended-UNIFAC: optimization of Yan, *et al.* equation parameters through a fitting of experimental data sets containing atmospherically relevant functional groups (CH₃, CH₂-CO, COOH, OH, H₂O, Na⁺, NH₄⁺, Cl⁻, SO₄²⁻, NO₃⁻, etc.)

Thermodynamics Model for PM

$$K_{p,i} = \frac{(\text{ng}/\mu\text{g})_{\text{particle phase}}}{(\text{ng}/\text{m}^3)_{\text{gas phase}}} = \frac{F_i / \text{TPM}}{A_i} = \frac{760 RT f_{\text{cm}}}{10^6 \text{MW}_{\text{cm}} \zeta_i \rho_{L,i}^0}$$

Unified Gas/Particle Partitioning Theory

Partitioning of all mixture components between k particle phases and the gas phase may be calculated with knowledge of the total concentration (T_i) of all species and all particle-phase component activity coefficients, ζ_i .

All ζ_i can be calculated with **Extended-UNIFAC** and, ultimately... **Extended-UNIQUAC**.

$$F_i = \frac{\sum_k K_{p,i}^k \text{TPM}^k}{1 + \sum_k K_{p,i}^k \text{TPM}^k} T_i$$

Pankow, J.F. 2003. *Atmos. Environ.*, 3323-3333.

(Some) Future Challenges

- Update of aqueous-phase chemistry modules
 - Overall and particularly with respect to aqueous-phase reactions of dissolved organic compounds
- Characterization of primary organic PM within aerosol modules
- Heterogeneous and in-particle processing of organic PM
- Influence of NO_x and SO₂ on organic PM formation
- Identification and formation of organic-nitrogen compounds in particulate matter
- Effects of condensable organic compounds on stabilization of molecular clusters and growth beyond Kelvin barrier
- ...