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THE STATE UNIVERSITY
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Secondary and Regional Contributions to Organic PM

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With Contributions from:
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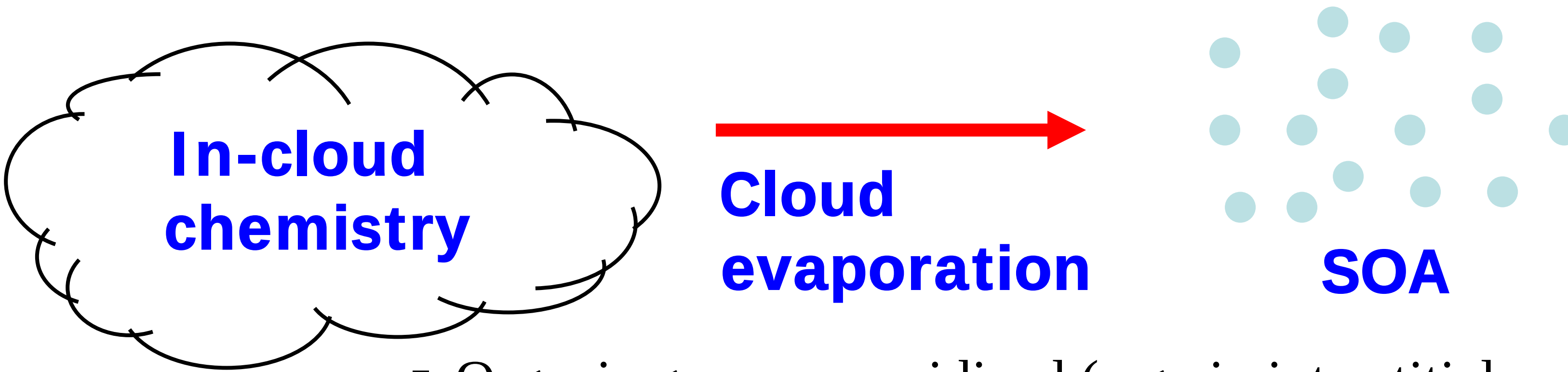
Objective

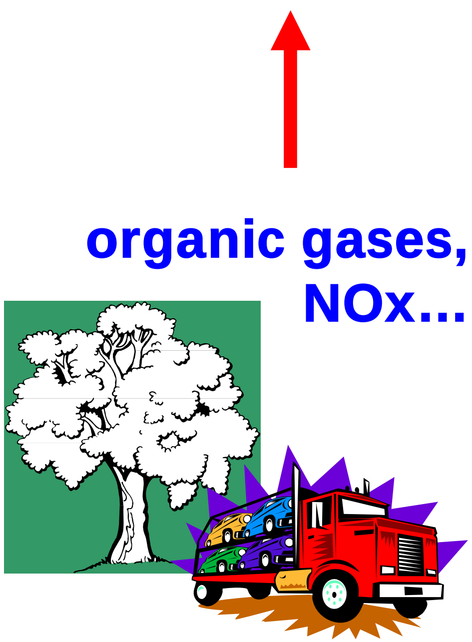
Conduct controlled laboratory experiments investigating secondary organic aerosol (SOA) formation through cloud processing

In the Process

- Consider whether experiments suggest “source tracers” or “process indicators” to aid field investigations of SOA
- Examine Pittsburgh Supersite data for evidence of SOA formation through cloud processing
- Provide kinetic/mechanistic data needed to refine SOA models

In-Cloud SOA Formation





- Organic gases are oxidized (e.g., in interstitial spaces of clouds) to water-soluble compounds.
- Water-soluble gases partition into cloud droplets and oxidize further (e.g., by ·OH formed photochemically).
- Low volatility products remain in the particle phase upon cloud evaporation, contributing secondary organic aerosol (SOA), especially in FT

(Blando and Turpin, 2000; Gelencser and Varga, 2005)

Evidence for In-Cloud SOA

Organic PM Concentrations Aloft

- Heald et al., 2005 (ICART): Organic PM concentrations in FT exceed current model predictions (i.e., without in-cloud SOA).
- **Polidori et al., 2006 (Pittsburgh);** Lim and Turpin, 2002 (Atlanta): Elevated ground level SOA with down-mixing of air from aloft.

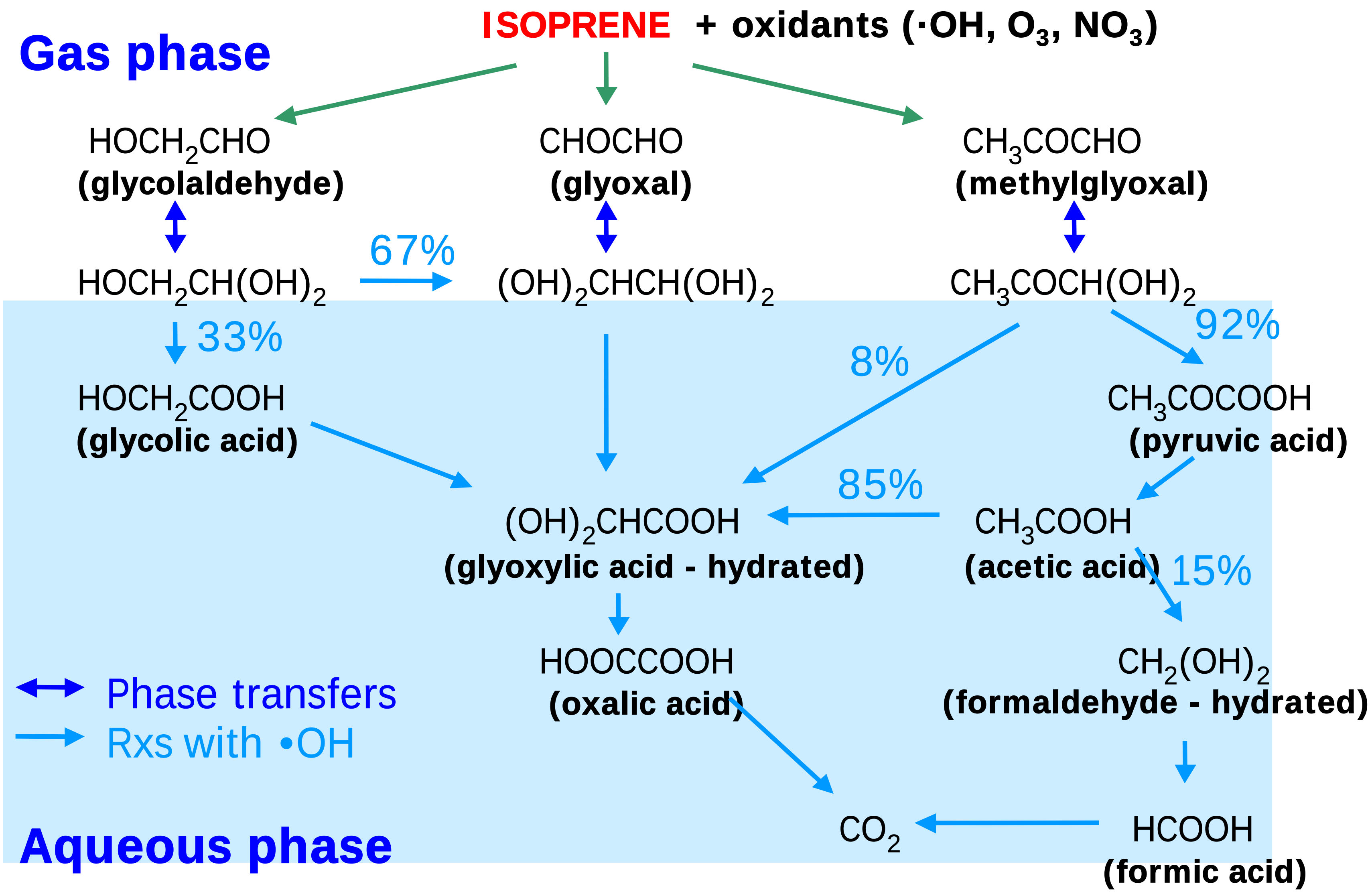
Oxalic Acid Concentration Dynamics

- Heald et al., 2006; Chebbi and Carlier, 1996; Yu et al., 2005; Kawamura et al., 1993: Concentration dynamics link oxalic acid with potential aqueous precursor aldehydes or with sulfate (formed through cloud processing).
- Sorooshian et al. 2006 (ICART); 2007(MACE); Crahan et al., 2004: In-cloud organic acid measurements/simulations suggest oxalic acid is formed through cloud processing.

Cloud Chemistry Modeling

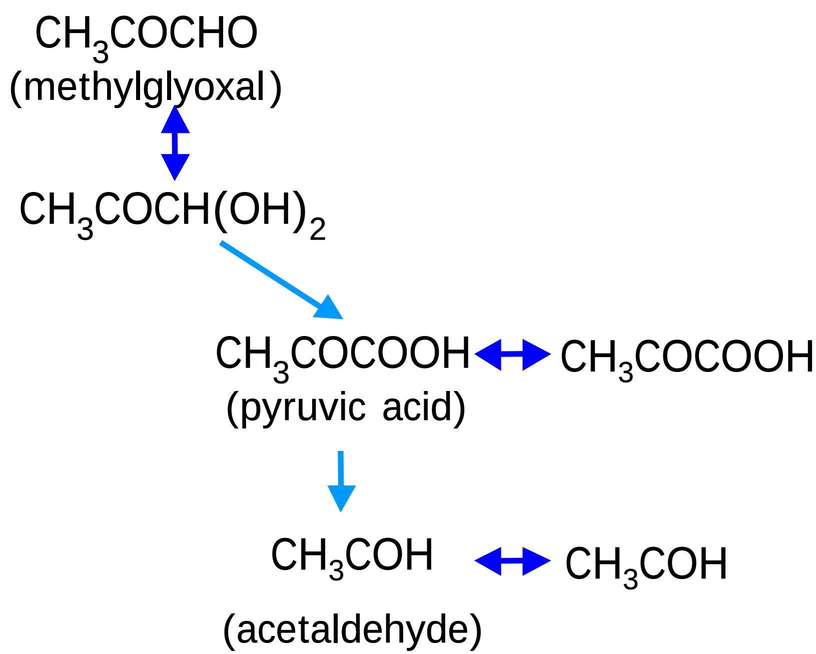
- Warneck, 2003; Ervens et al., 2004; **Lim et al., 2005**: predict in-cloud organic acids and SOA from emissions

Lim Cloud Chemistry Model (to guide experiments):



Lim et al., 2005

Ervens Model: aqueous methylglyoxal and pyruvic acid photo-oxidation does not form low volatility organic acids



Predicted In-Cloud SOA Concentrations:

(Ervens et al., 2004; Lim et al., 2005)

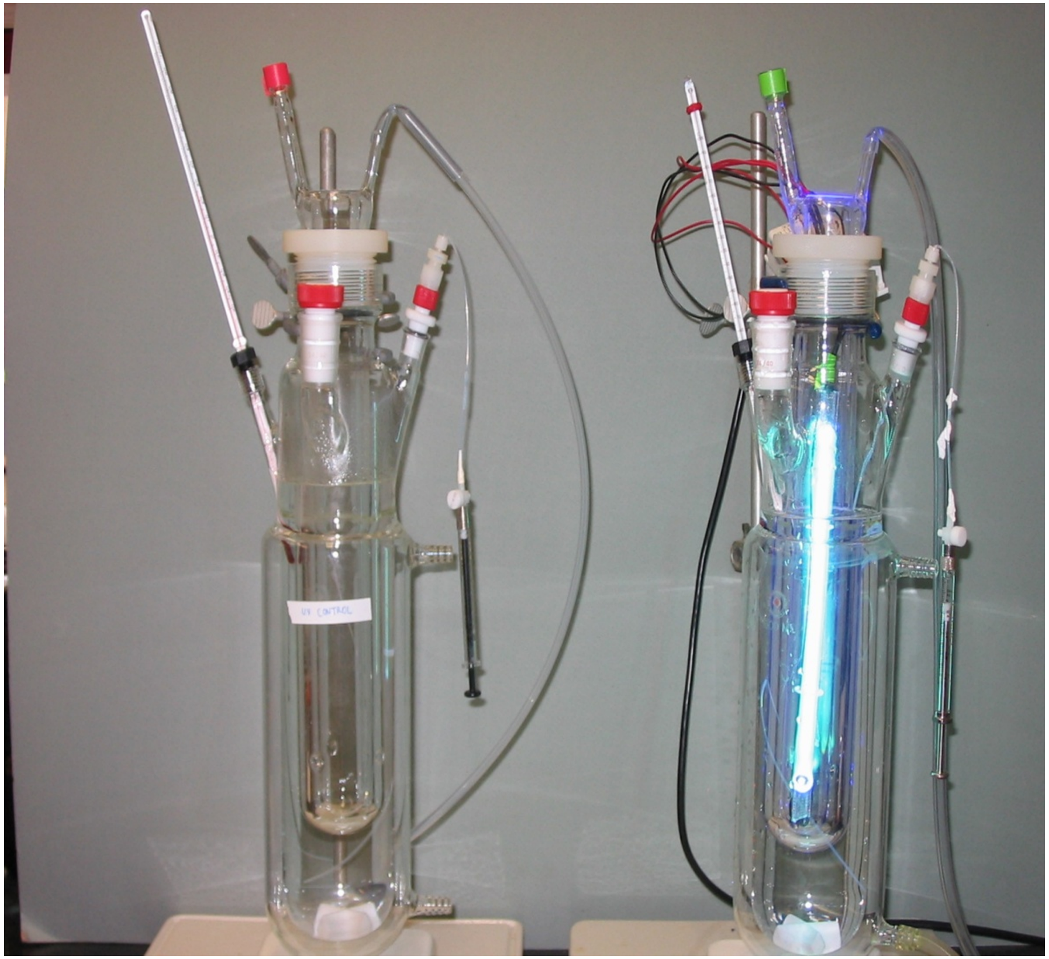
- 10 – 25% of measured oxalic acid formed from aqueous reactions with methylglyoxal, glyoxal and glycolaldehyde (clean – polluted continental)
- Oxalic acid remains mostly in the particle phase upon droplet evaporation, forming SOA.
- Additional precursors
- Additional low volatility organics
- Aqueous photooxidation pathways/products largely assumed
- Predicted products had not been verified experimentally

Objective:

Validate and refine aqueous-phase reaction pathways and improve kinetics

Approach:

Conduct aqueous-phase photooxidation experiments, measure products, model product formation



Organic + H_2O_2 + UV (plus controls)

To provide supply of ·OH

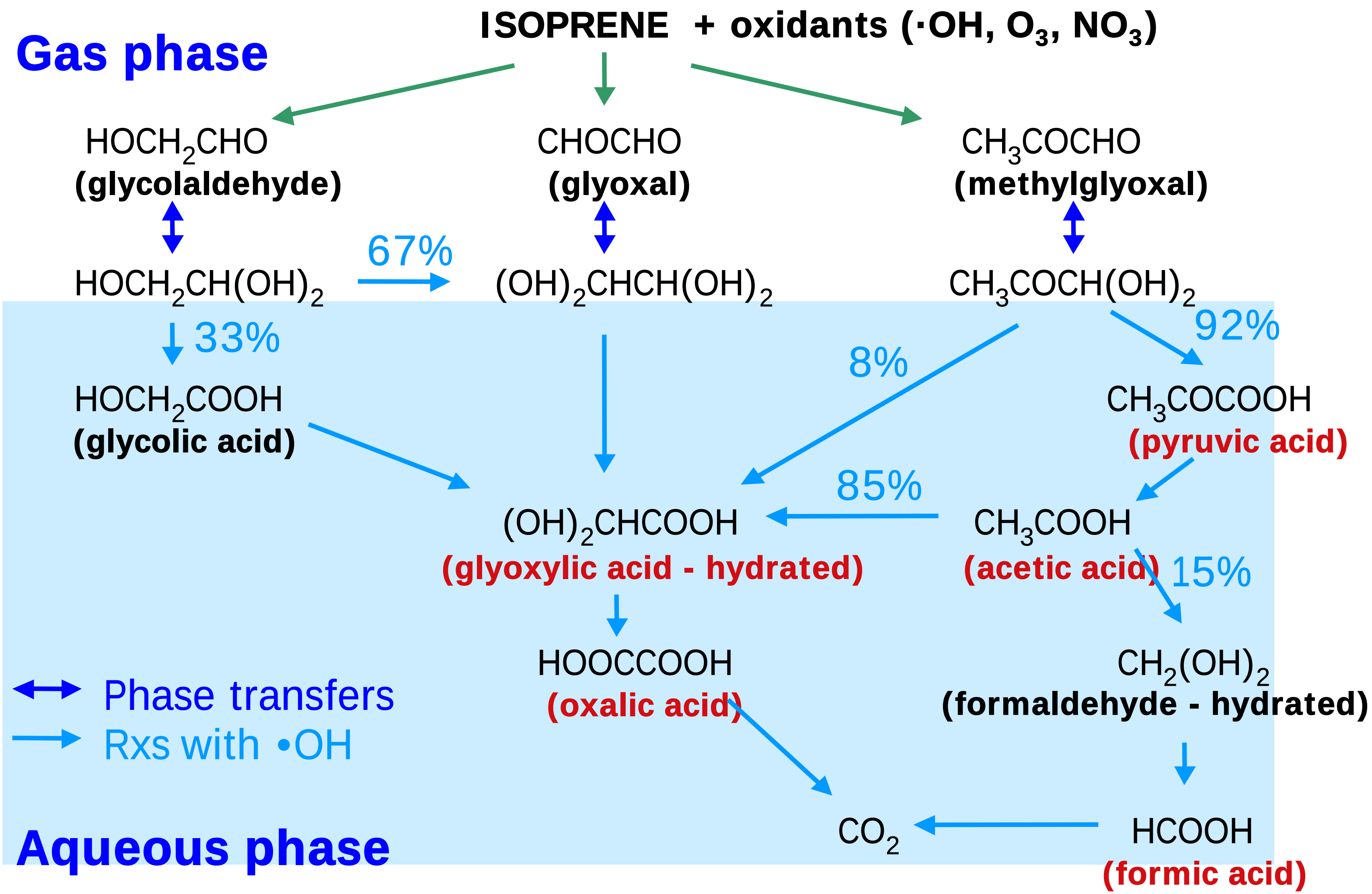
Results: Oxalic acid is formed from GLY, MG, PA

Organic	Glyoxal	Methylglyoxal	Pyruvic Acid
Conc.	2 mM	2 mM	10 mM
(N)	(3)	(3)	(3)
H_2O_2	10 mM	10 mM	20 mM
pH*	4.1 - 4.8	4.2 – 4.5	2.7
Experiment		$ORG+UV+H_2O_2$	
UV Control		$ORG+H_2O_2$	
H_2O_2 Control		ORG+UV	
Organic Control		$UV+H_2O_2$	

*Typical cloud/fog pH 2-5; Catalase to stop reactions; Samples frozen

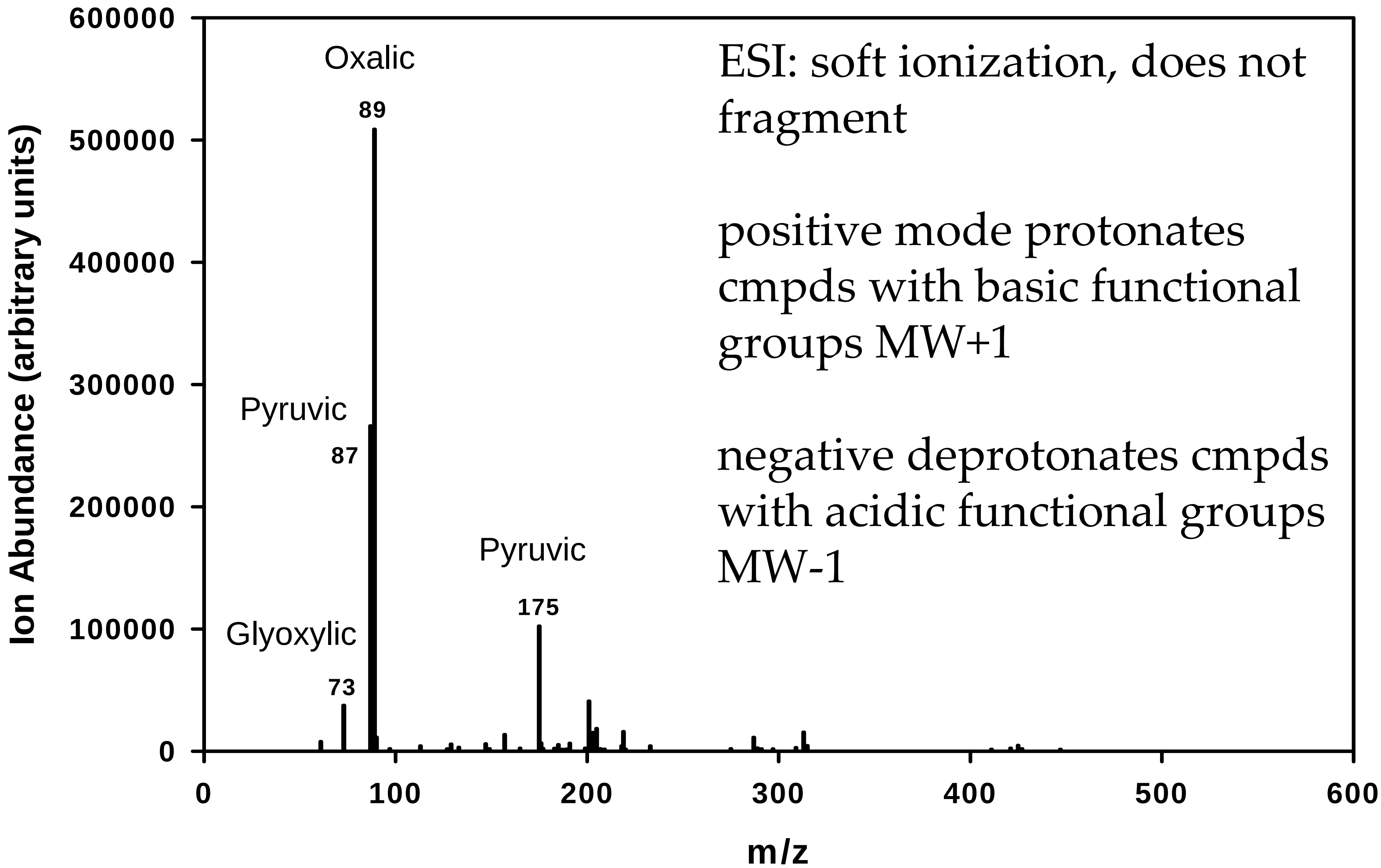
Carlton et al., 2006; Altieri et al., 2006; Carlton et al (2007)

Pyruvic Acid Results:



Carlton et al., 2006

Electrospray Ionization Mass Spectrum (ESI-MS): Mixed Standard of Pyruvic Acid and Predicted Products

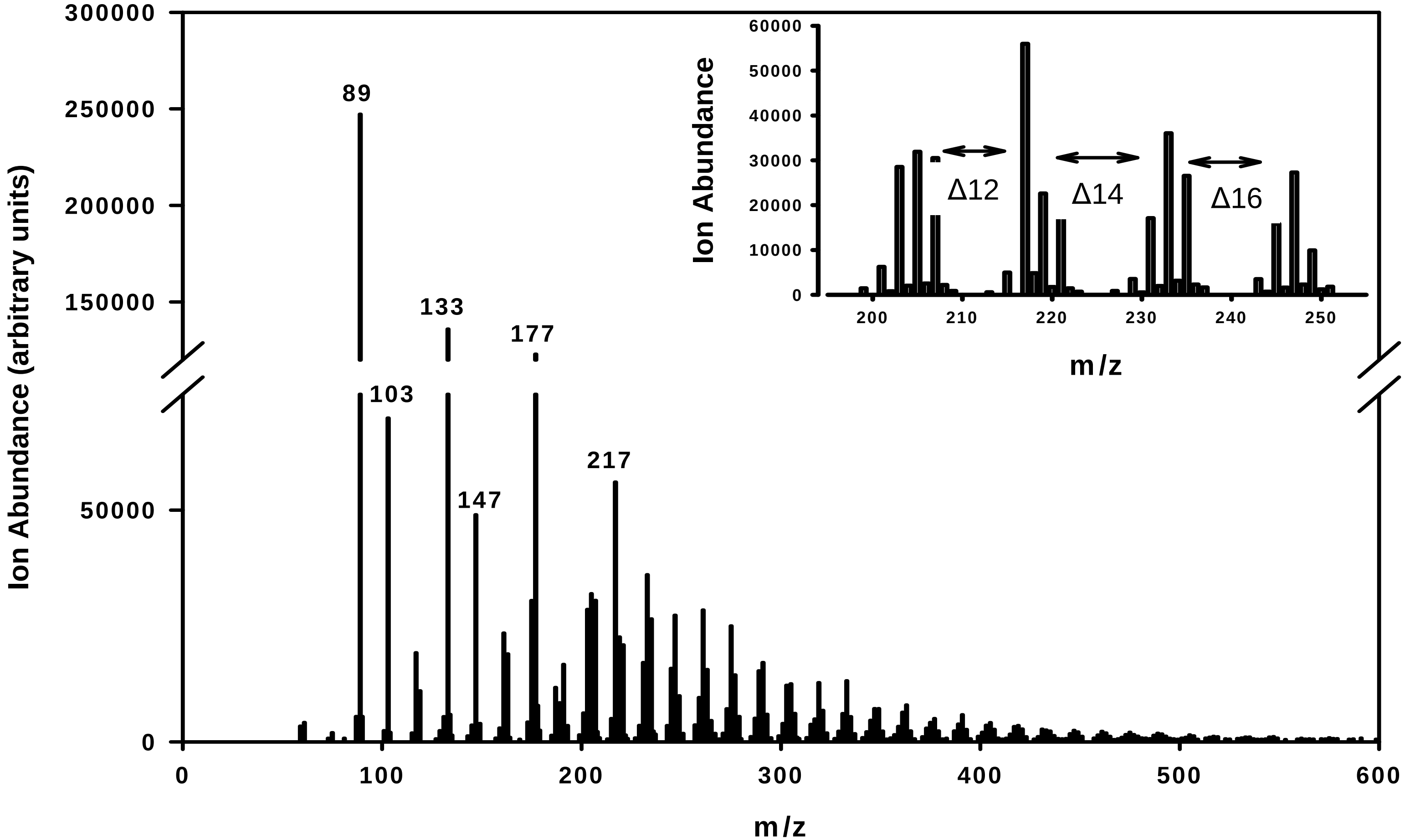


ESI: soft ionization, does not fragment

positive mode protonates cmpds with basic functional groups MW+1

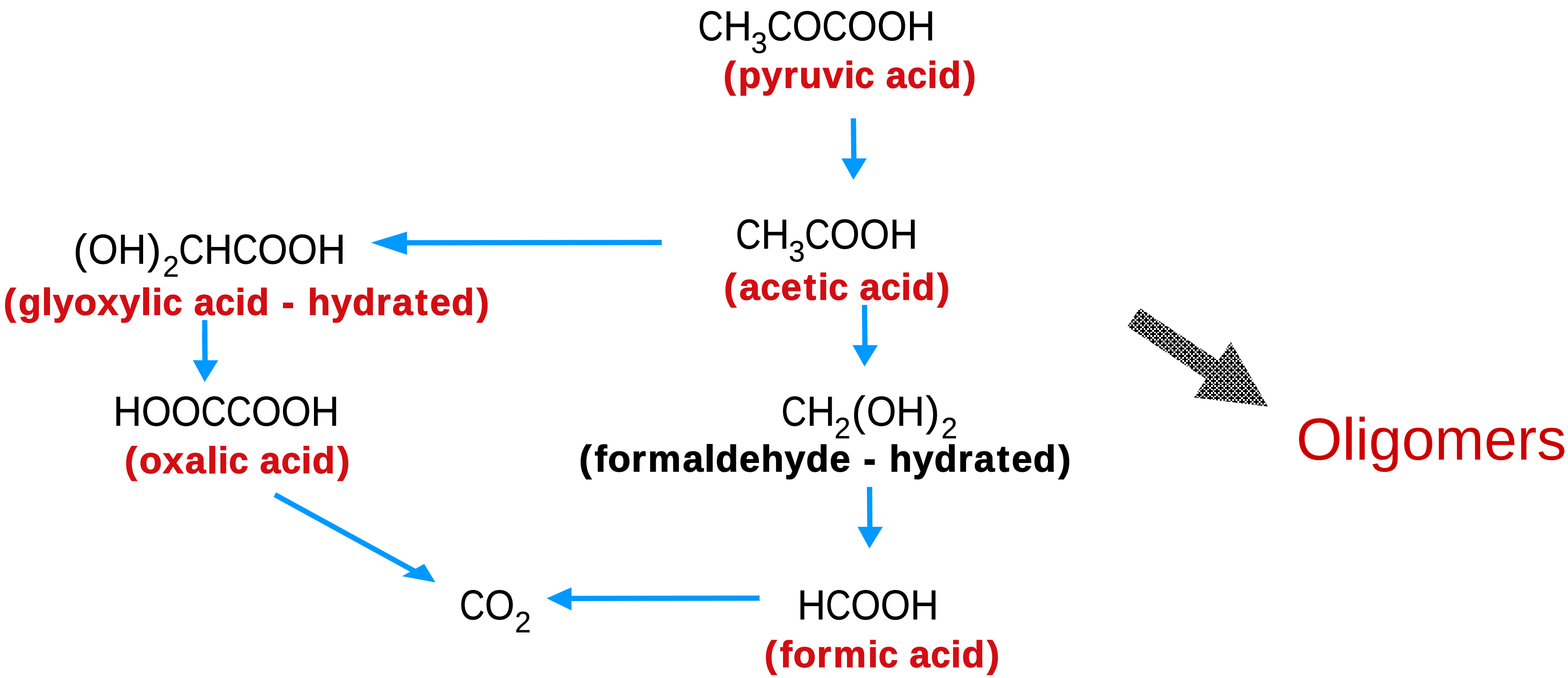
negative deprotonates cmpds with acidic functional groups MW-1

ESI-MS Spectrum of Pyruvic Acid Experiment (t=202 min): Regular Distribution of Oligomer System



Lim mechanism is incomplete; oxalic acid and larger MWt (oligomers) form

Altieri et al., 2006



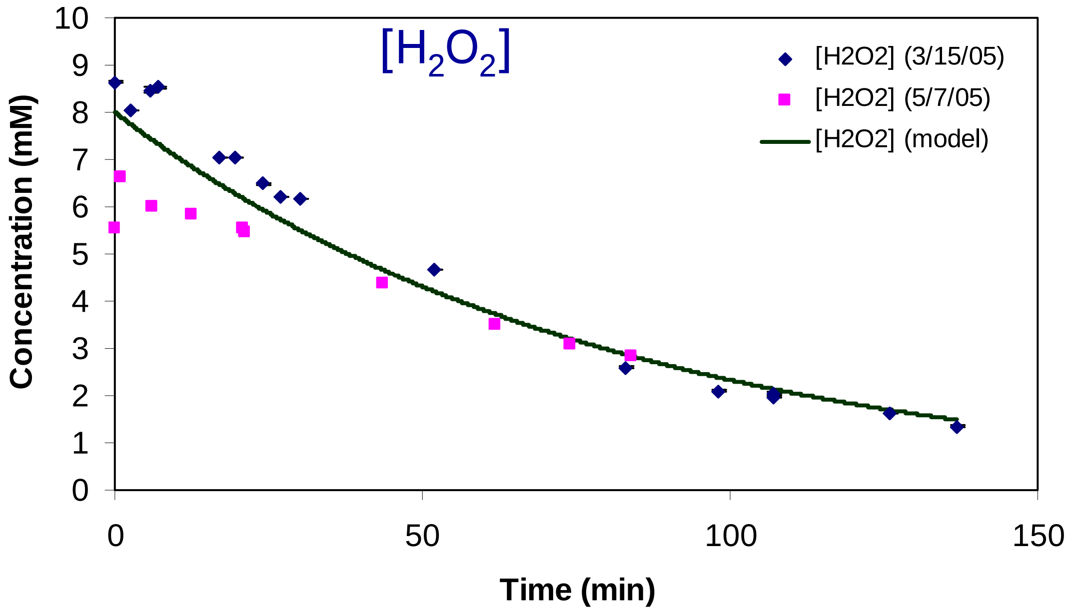
Oxalic acid and oligomers form.
Both are likely to contribute to SOA after droplet evaporation.

Glyoxal:

LIM MODEL: Glyoxal → Glyoxylic Acid → Oxalic Acid

Lim model reproduces H_2O_2 in reaction vessel
but poor prediction of oxalic acid ($r^2 = 0.001$)
meas. glyoxylic acid cannot explain oxalic acid formation

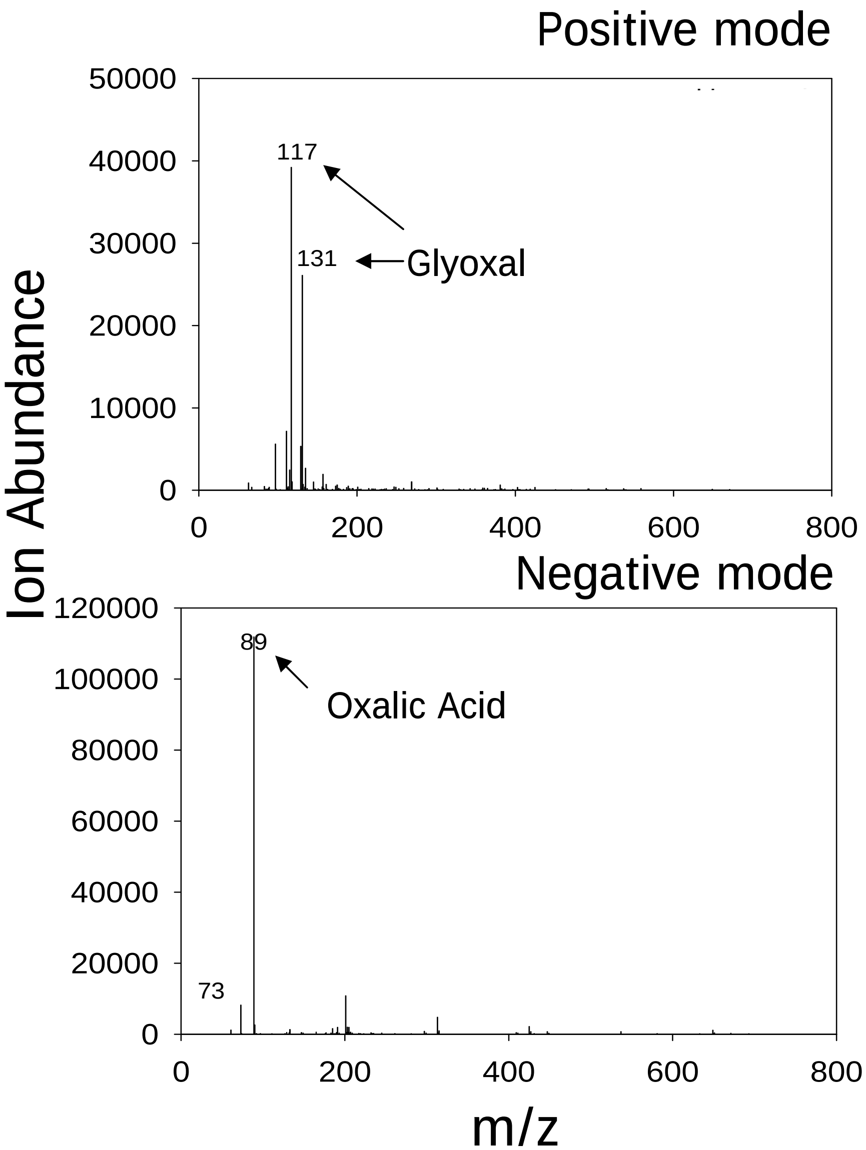
Hydrogen Peroxide → Hydroxyl Radical



Glyoxal Results - ESI-MS:

Mixture standard containing the precursor and products that are predicted by initial model

The spectrum we would expect if the initial mechanism were complete



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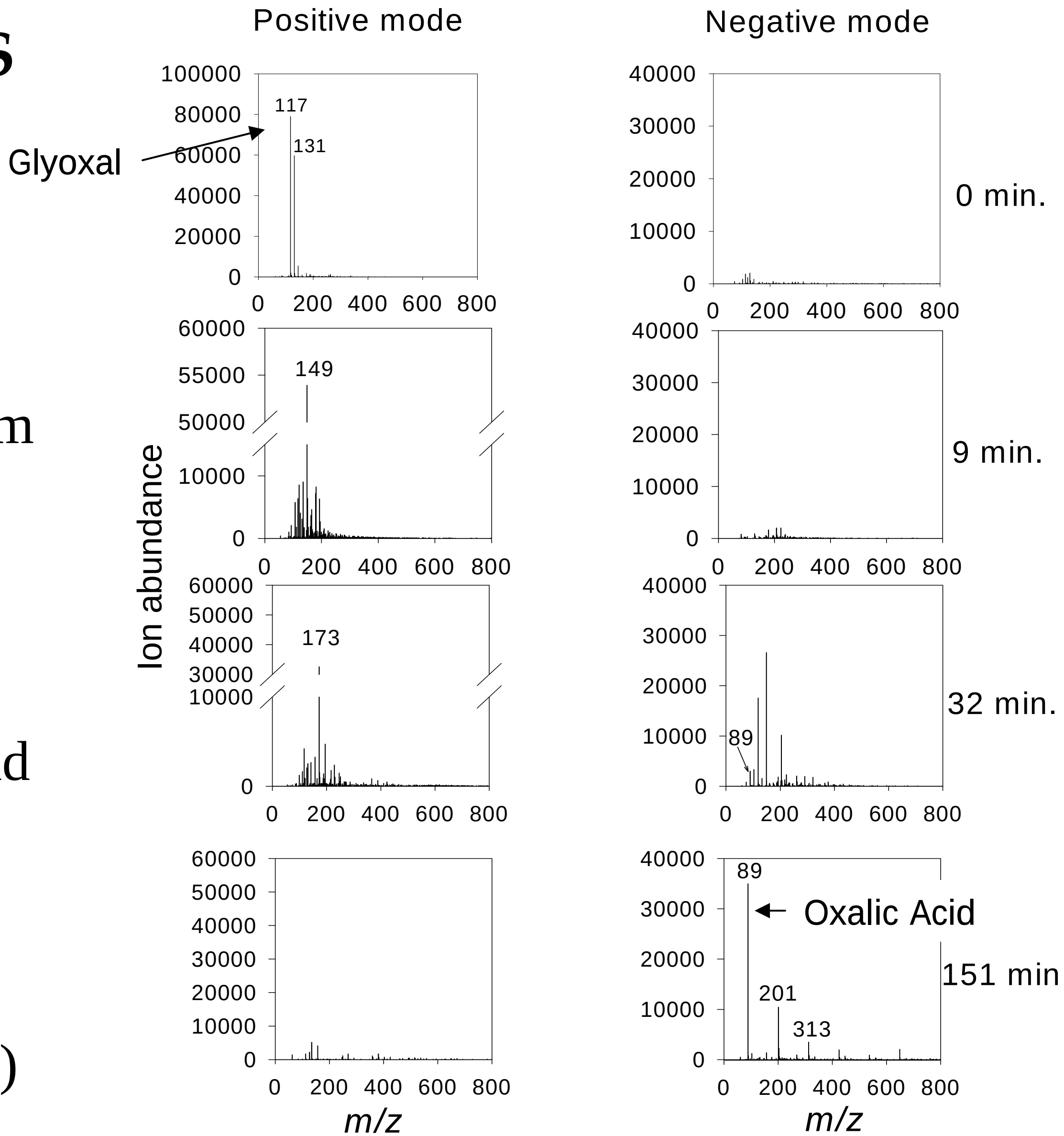
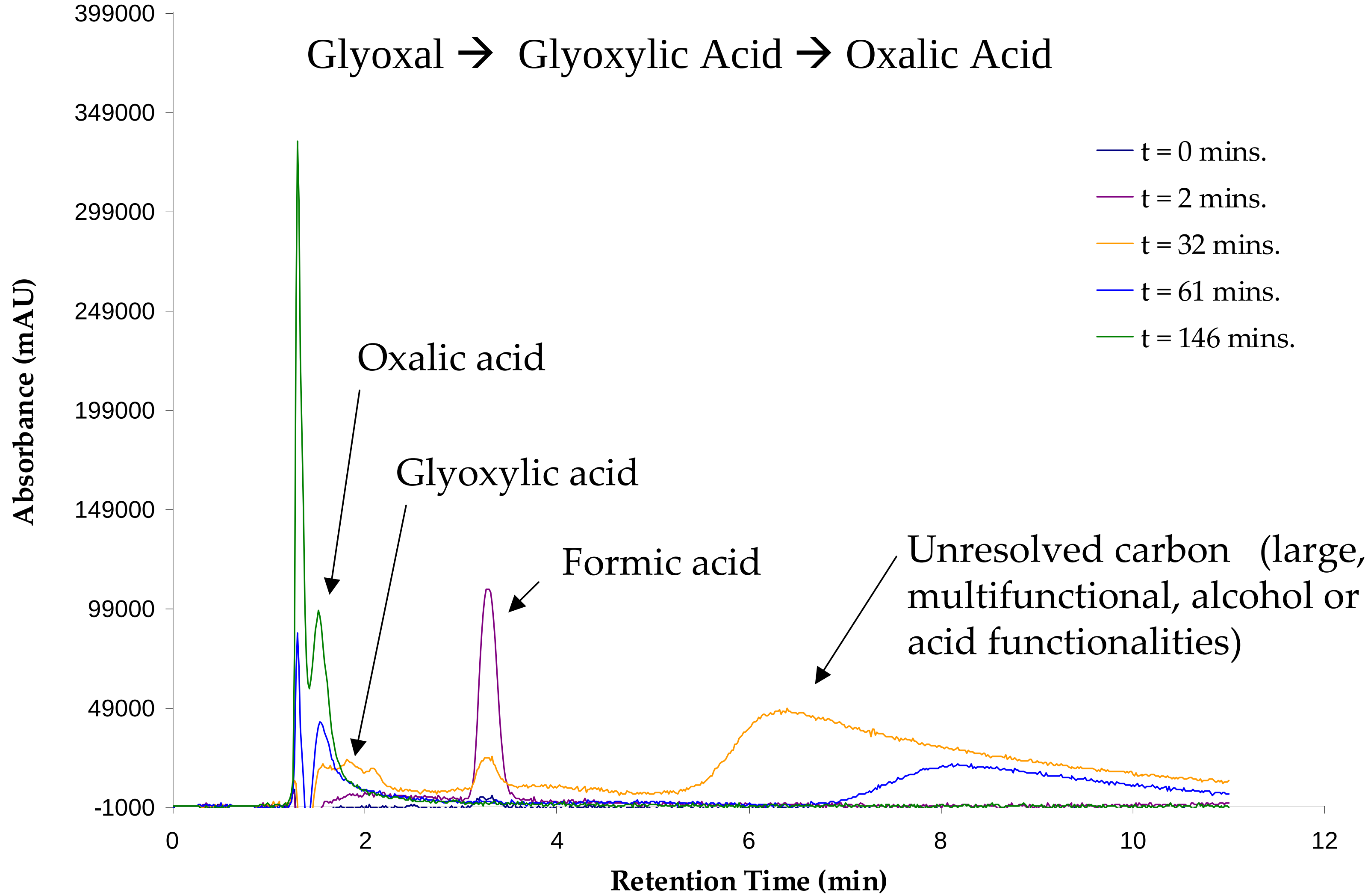
Glyoxal Results: ESI-MS

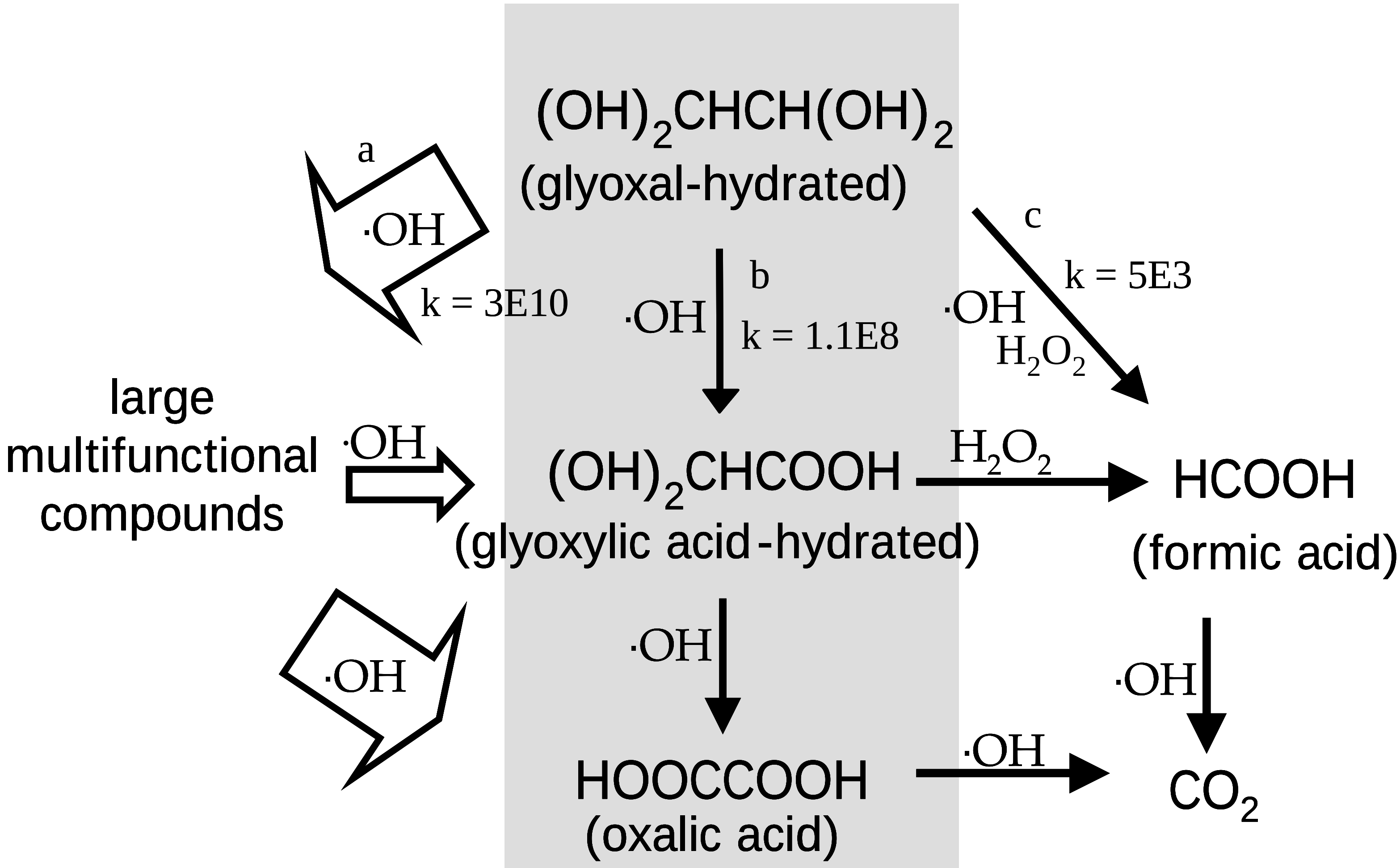
- Glyoxal rapidly destroyed
- Spectral "complexity" develops that cannot be explained by initial mechanism
- (large compounds with alcohol/aldehyde (pos) and acid (neg) functionalities)
- "Complexity" in positive and negative modes dissipates ~ 30-40 min
- oxalic acid formed (dominates 150 min spectrum)



Glyoxal Results: ESI-MS



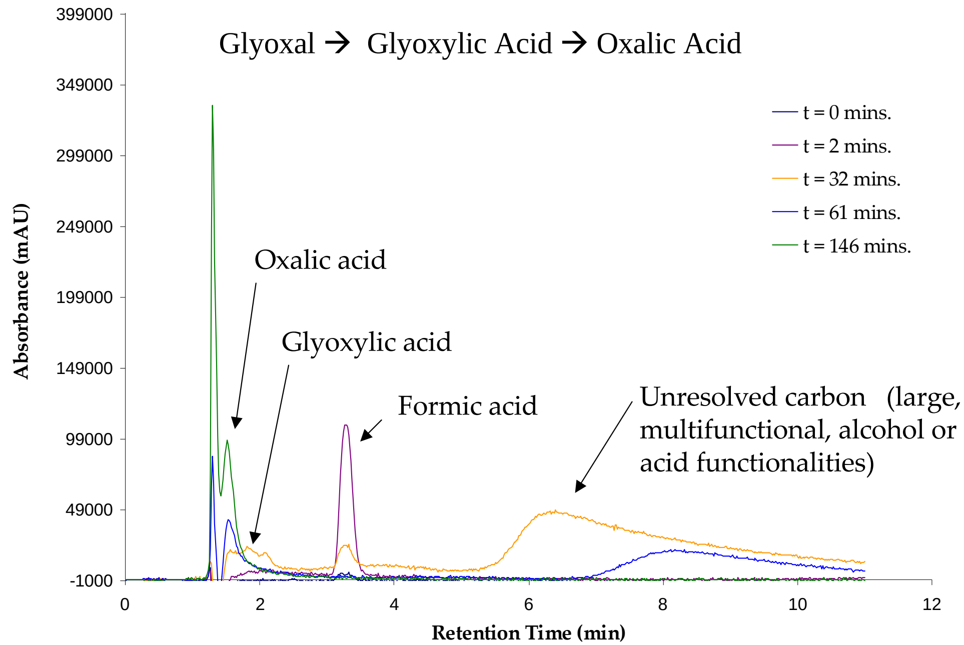
Expanded Glyoxal Photooxidation Mechanism

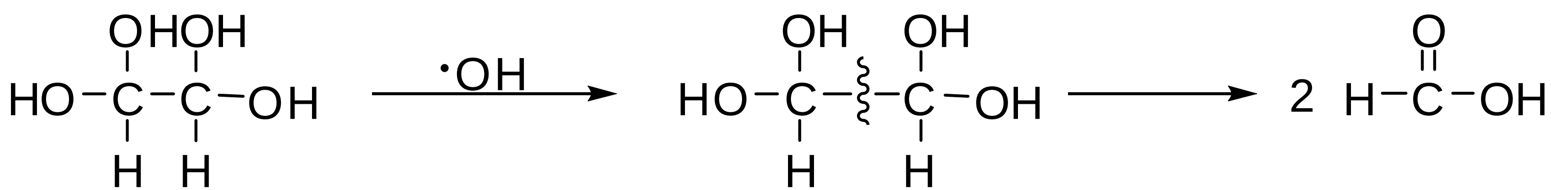


Glyoxal → Formic Acid

- Not identified as an aqueous-phase glyoxal oxidation product in the atmospheric chemistry literature

- Food/Dye Lit: Close proximity of the two carbonyl double bonds enhances reactivity toward nucleophilic attack (Rao and Rao *J.Anal.Chem.*, 2005)

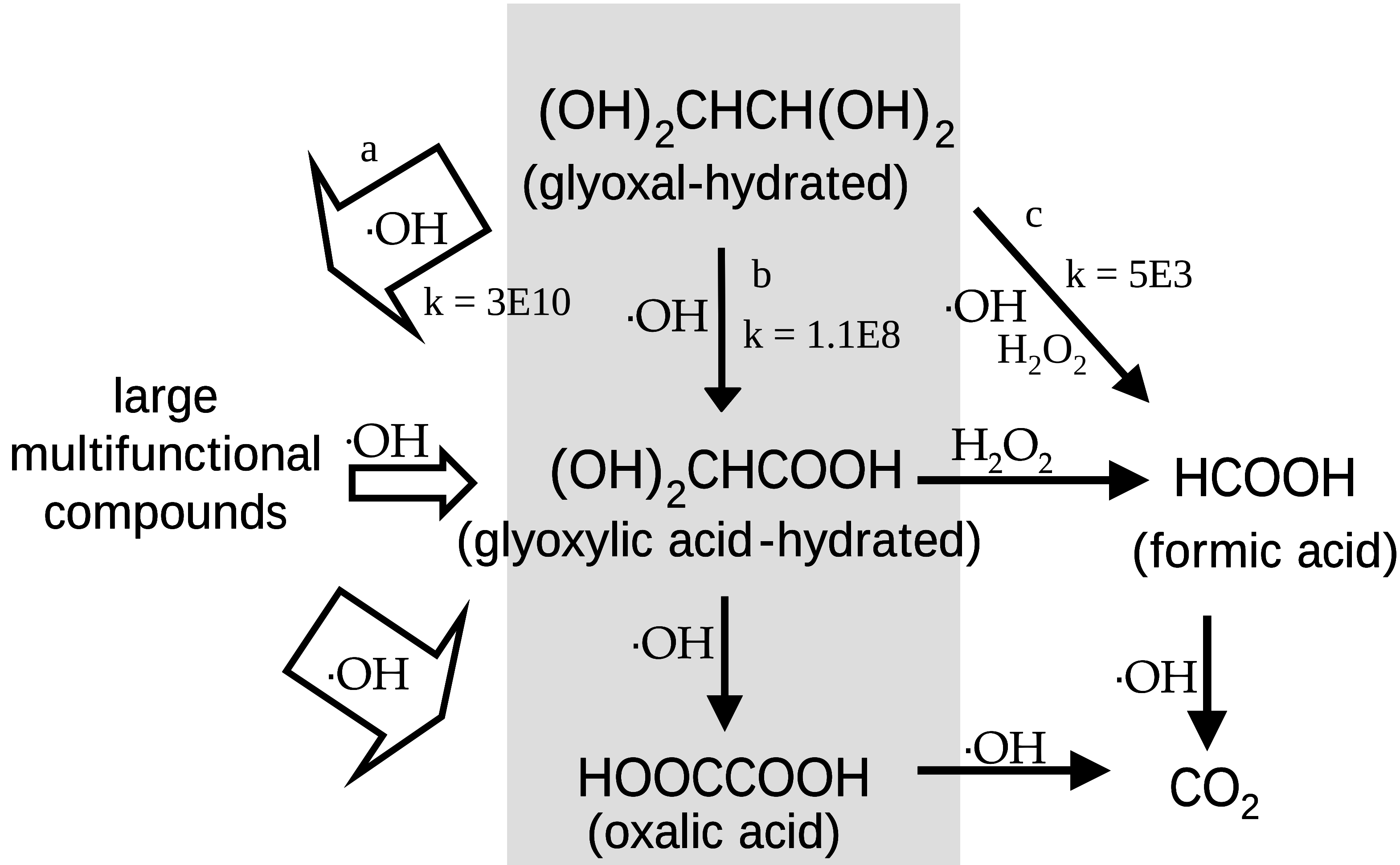




glyoxal hydrated

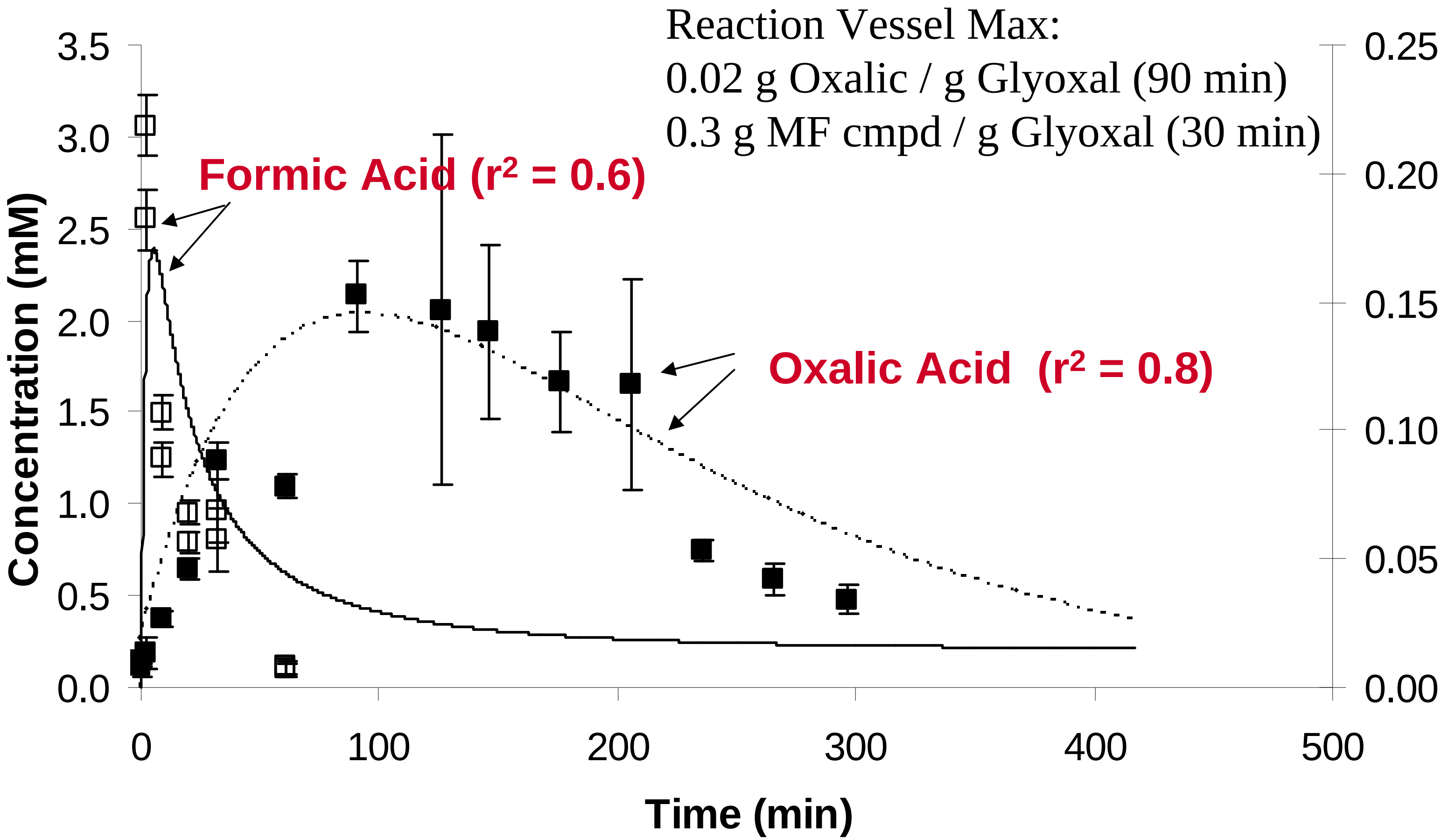
formic acid

Expanded Glyoxal Photooxidation Mechanism



Measurements and Predictions Using Expanded Mechanism

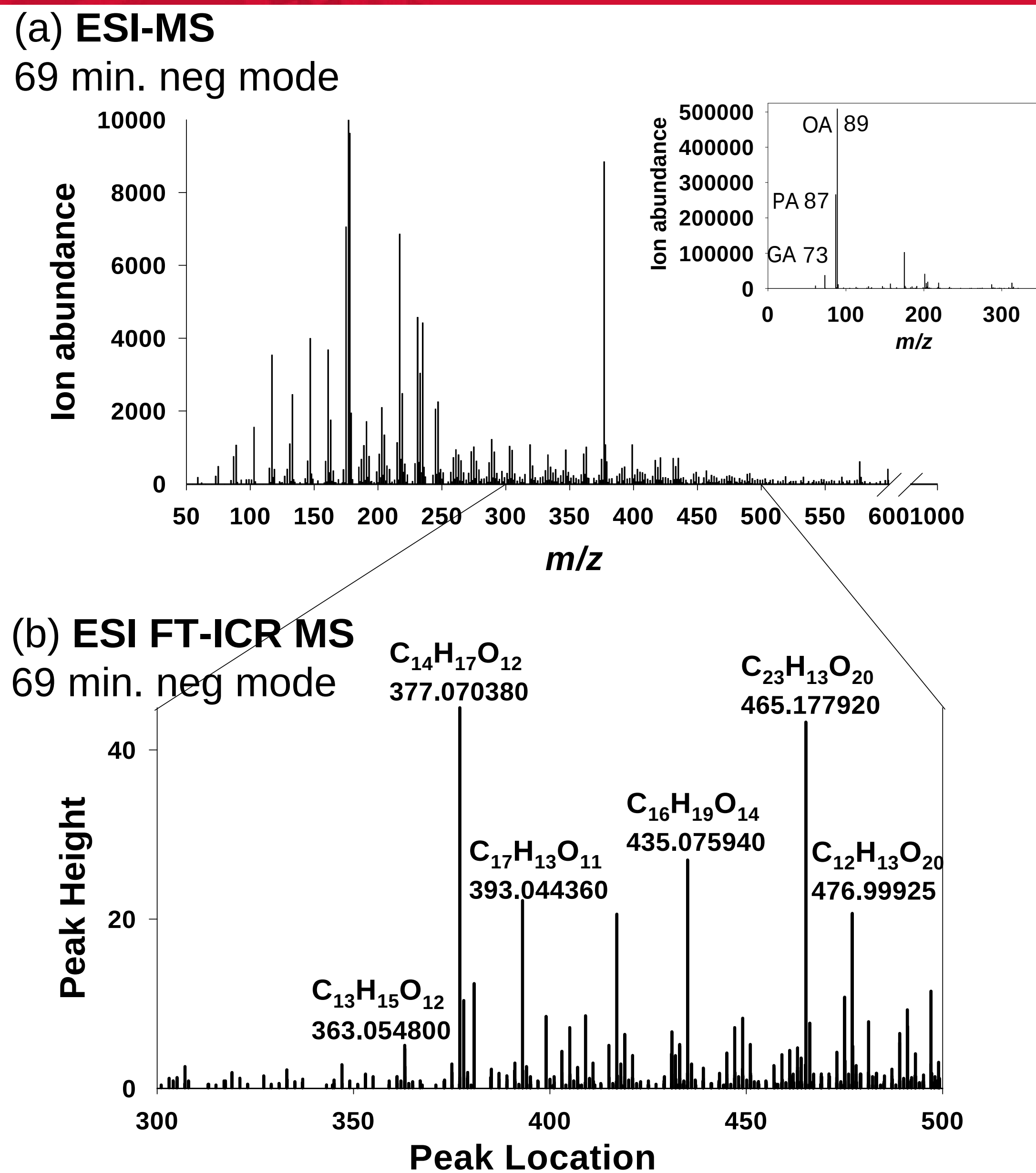
Meas/Modeled glyoxylic acid <MDL. Only 1% of oxalic acid from glyoxal → glyoxylic acid → oxalic acid pathway. Large multifunctional products important to oxalic acid formation and contribute to SOA themselves.



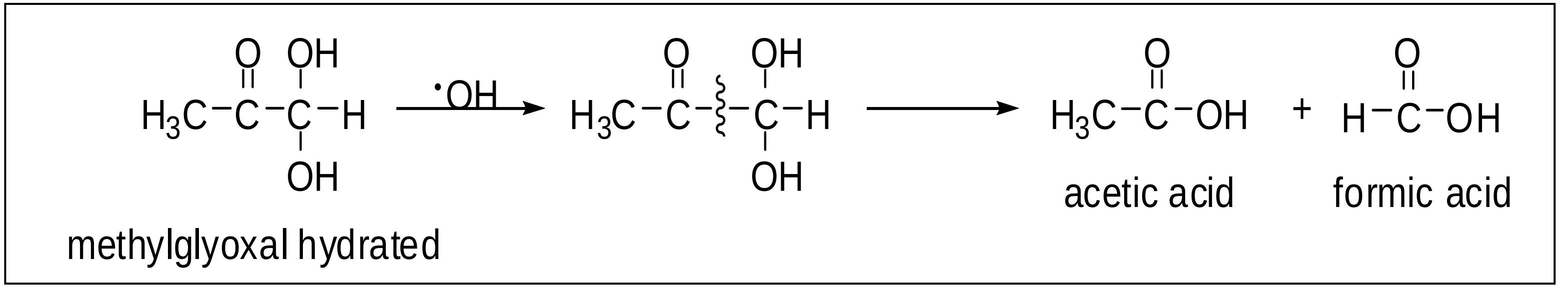
Carlton et al., 2007

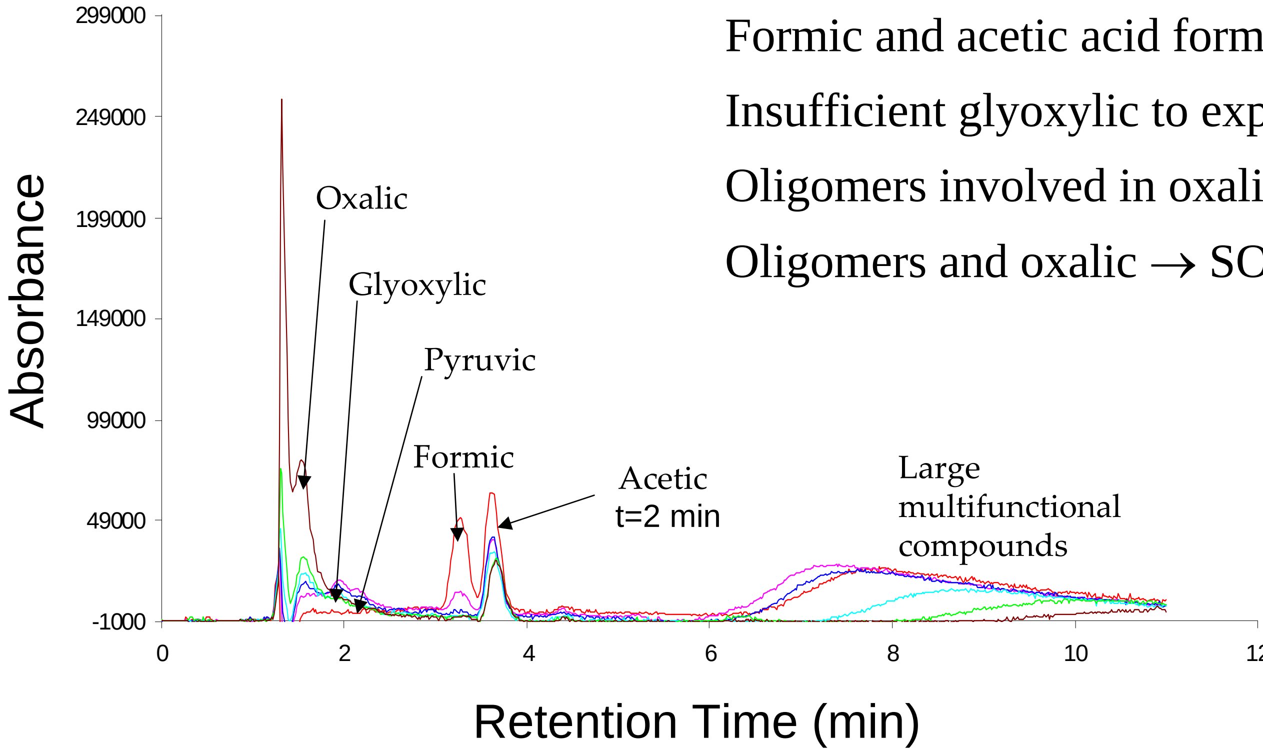
Methylglyoxal Results:

- "haystacks" with regular pattern of mass differences; oligomer system
- Like pyruvic acid experiments (MG itself not involved)
- Structure not seen in mixed stds (not artifact)
- No oligomers in controls (·OH involved)



Methylglyoxal:





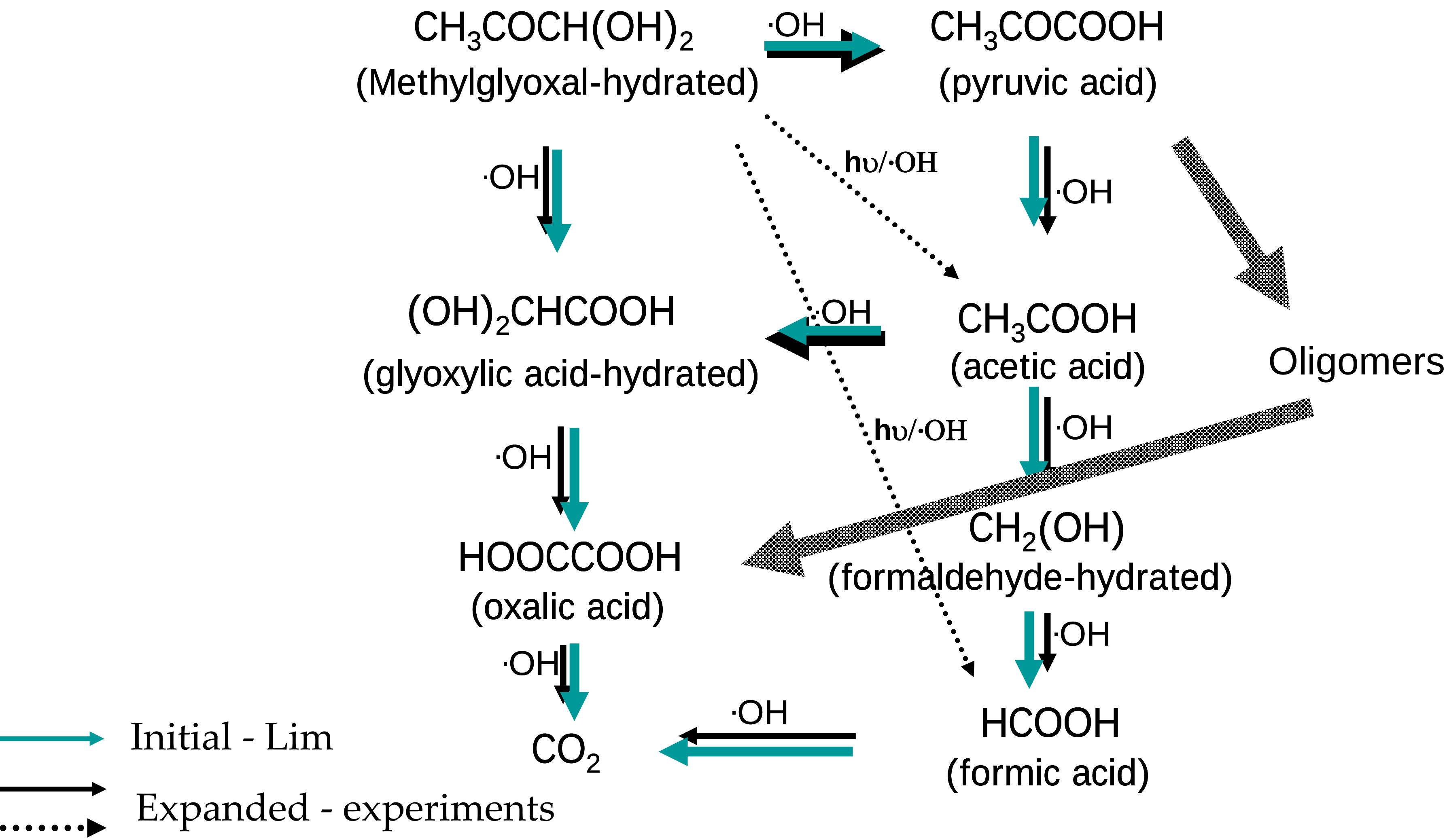
Formic and acetic acid form directly

Insufficient glyoxylic to explain oxalic

Oligomers involved in oxalic

Oligomers and oxalic → SOA

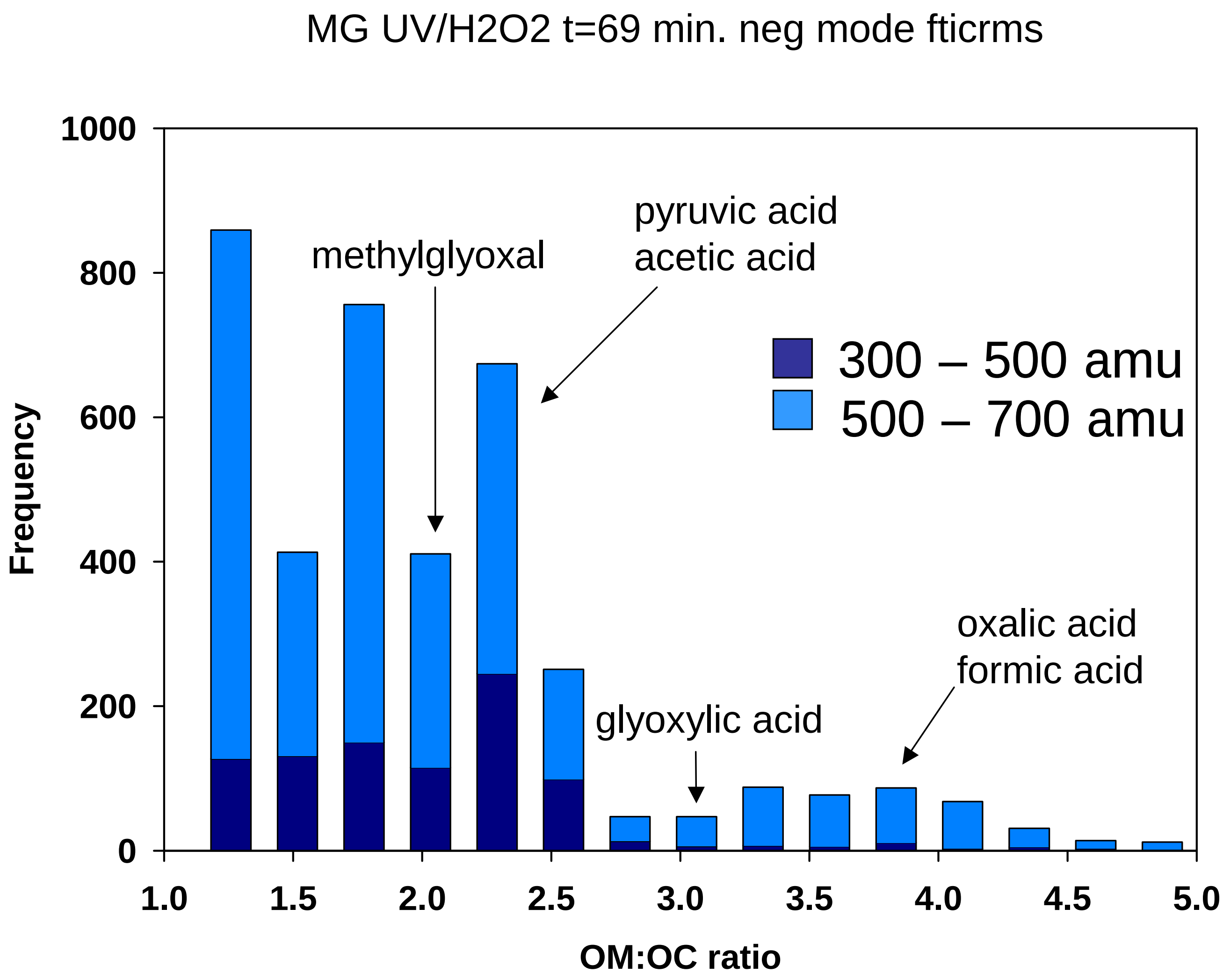
Expanded Methylglyoxal Mechanism



Methylglyoxal Results: OM/OC = 1.0-2.5 (avg 1.9) for m/z>300

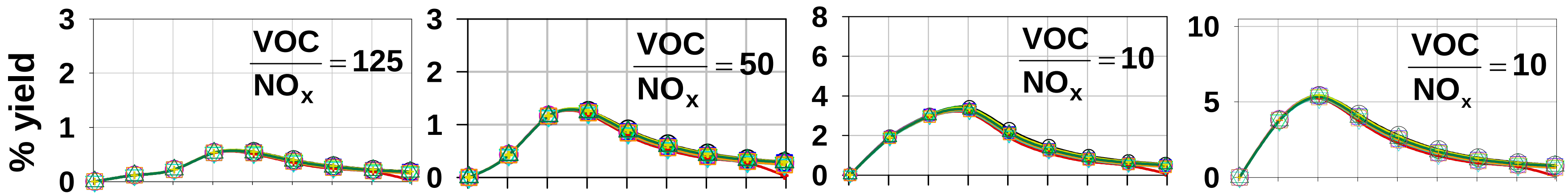
FT-ICR provides exact elemental comp. >300 m/z

OM/OC comparable to cloud water, regional aerosol. Lower than organic acids

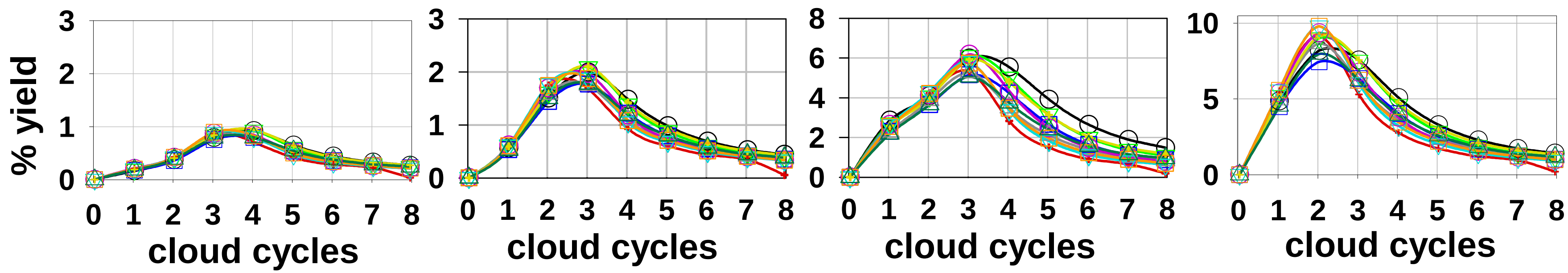


Cloud parcel model: Isoprene with/without cloud chemistry. Barbara Ervens Collaboration (see poster)

Gas phase chemistry + uptake only

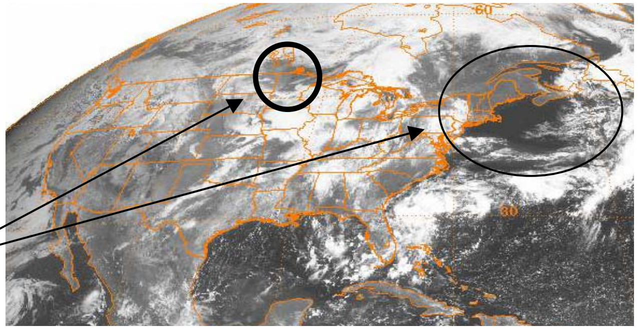


With cloud chemistry

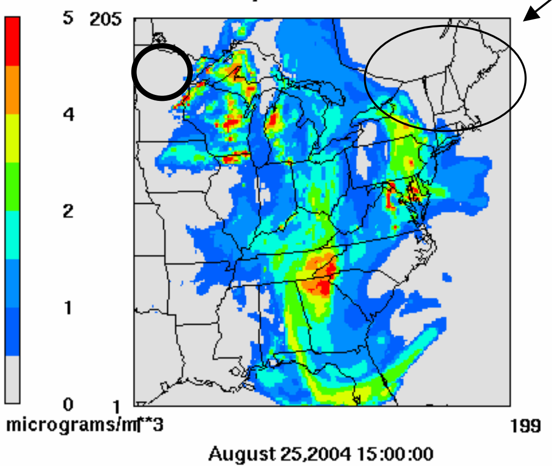


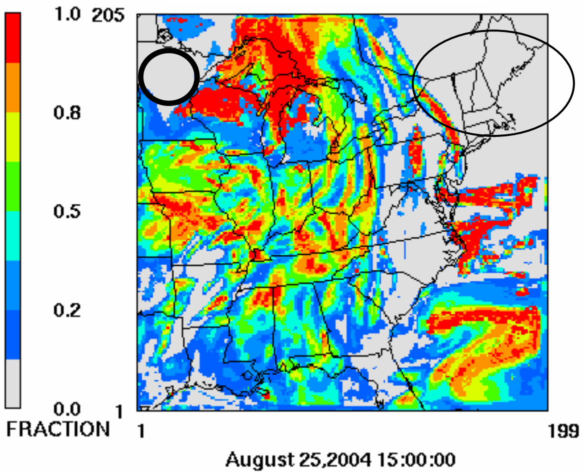
- Cloud chemistry yields ~ 0.5 - 5%
- Approximately doubles SOA

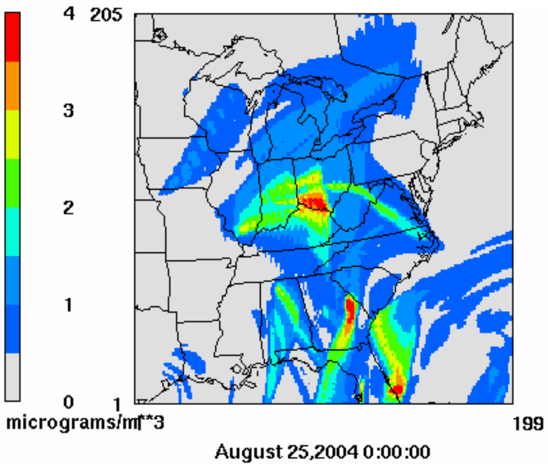
CMAQ runs: Annmarie Carlton Collaboration (see poster) With and without in-cloud SOA formation (using Yields of 4 to 30%)



Cloud-free areas







SOA from cloud processing – Eastern United States

Experimental Findings:

Oxalic acid forms from glyoxal/methylglyoxal in aqueous-phase

Oligomers and other large multifunctional compounds also form

Thus, SOA will form through cloud processing

Large multifunctional compounds (including oligomers) appear to play a role in oxalic acid formation

Experiments used to validate and refine reaction pathways/kinetics

This work demonstrates a linkage between marine, biogenic and anthropogenic precursors of glyoxal, methylglyoxal and pyruvic acid (including isoprene) and in-cloud SOA formation

Future Directions

Use mass spectroscopic tools to better understand:

- The structure and properties of oligomers
- Oligomer formation and degradation

Pursue continued methylglyoxal model improvements:

- Through improved understanding of oligomers
- Through experiments with intermediates

Incorporate this process into atmospheric models:

- Chemical and Cloud parcel models: kinetics to atmospheric yields and parameterizations
- Air quality and climate models: Magnitude and implications

Acknowledgements

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Adam Reff

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John Reinfelder

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U.S. EPA – STAR
NSF

Related Modeling Studies

CMAQ poster - Carlton
Cloud parcel poster - Ervens