Formation, Speciation, and Chemical Processing of Atmospheric Particulate Matter

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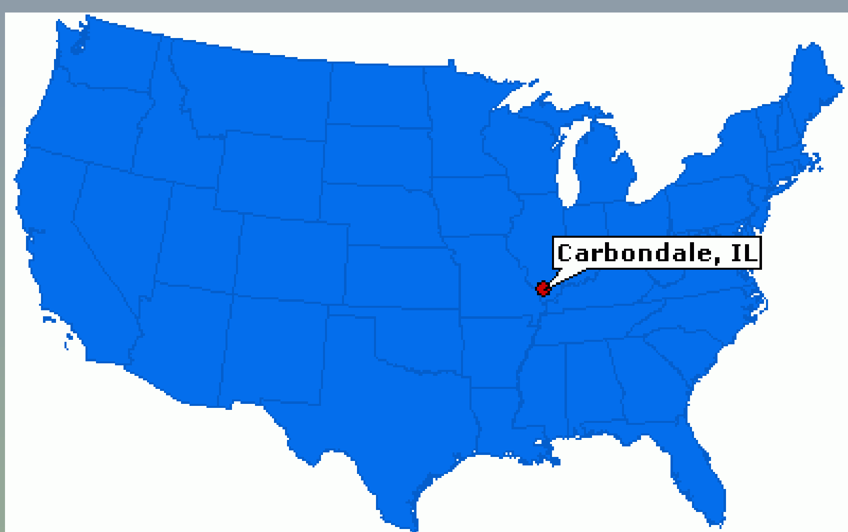
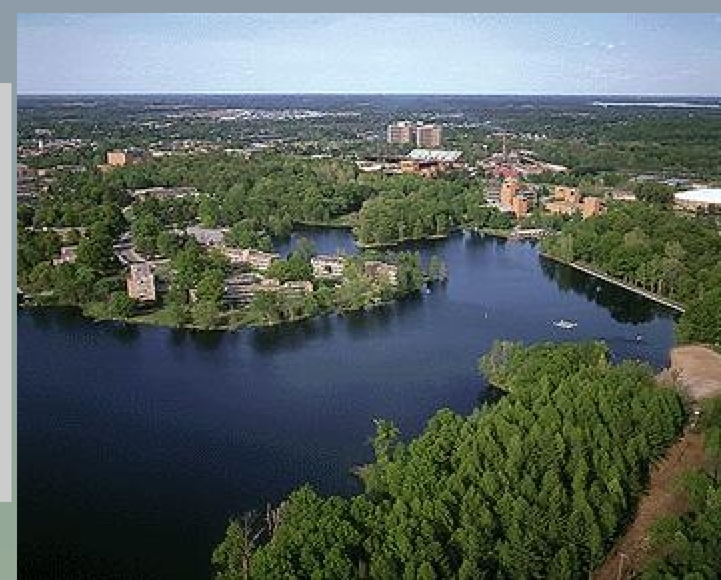




Academic and Research Background

- B.S. in chemistry and environmental studies, Iowa State University
  - advised by Cheng Lee (protein sensors and capillary electrophoresis)
  - advised by Thomas Steinheimer at National Soil Tilth Laboratory (analyzed watershed samples for herbicides by HPLC and ELISA)

- Ph.D. in analytical chemistry, Purdue University
  - advised by Dale Margerum
  - thesis title "Kinetics and Mechanisms of Non-metal Redox Reactions of Oxyhalogen Anions"
  - topics included water disinfection disinfection byproducts, kinetics and mechanisms elucidation, stopped-flow and UV-vis spectroscopy, ion chromatography

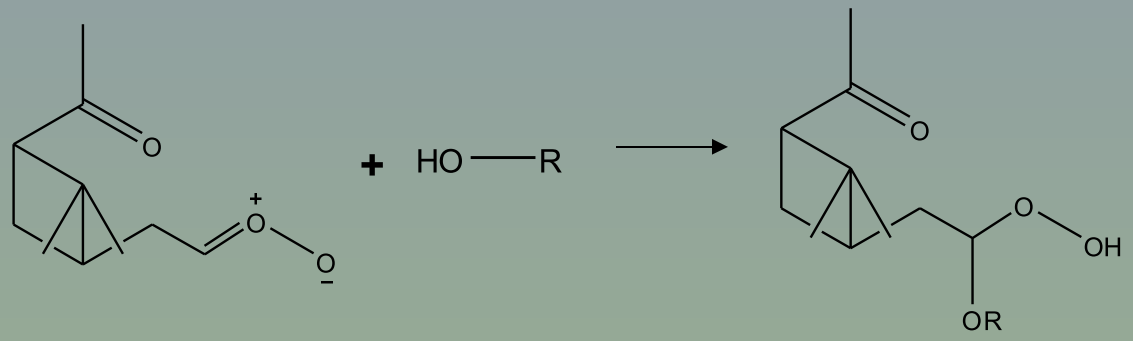
- Post-doctoral research, Carnegie Mellon University
  - advised by Neil Donahue, Spyros Pandis, and Allen Robinson
  - research topics included thermodynamics, kinetics, and chemistry of secondary organic aerosol formation and partitioning and CCN activation of organic aerosols

- Current position: Assistant Professor of Chemistry and Biochemistry
  Analytical Division
  Southern Illinois University Carbondale

Research Interests

- Fundamental chemical reaction mechanisms of SOA formation and processing
- SOA speciation and analysis
- Indoor air quality

  - What chemical reactions are important for atmospheric PM formation?
  - Are the products of BSOA using a complex precursor mixture different from a single precursor experiment?



Experimental Facility

5.5 m³ Teflon smog chamber

PM mass measurements
(TSI SMPS equipped with 3081 LDMA and 3010 CPC)

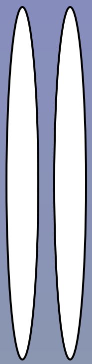
PM samples

Gas samples (via SPME)

filter extraction

Off-line analysis via GC/MS

Organic Aerosol Speciation



Solvent Extraction[a]
Derivitization

Filter Samples

Gas chromatography/mass spectroscopy
(structural identification
and analytical determination)

Three modes of MS detection and structural elucidation:

1.) Electron Impact
2.) Chemical ionization
3.) MS/MS

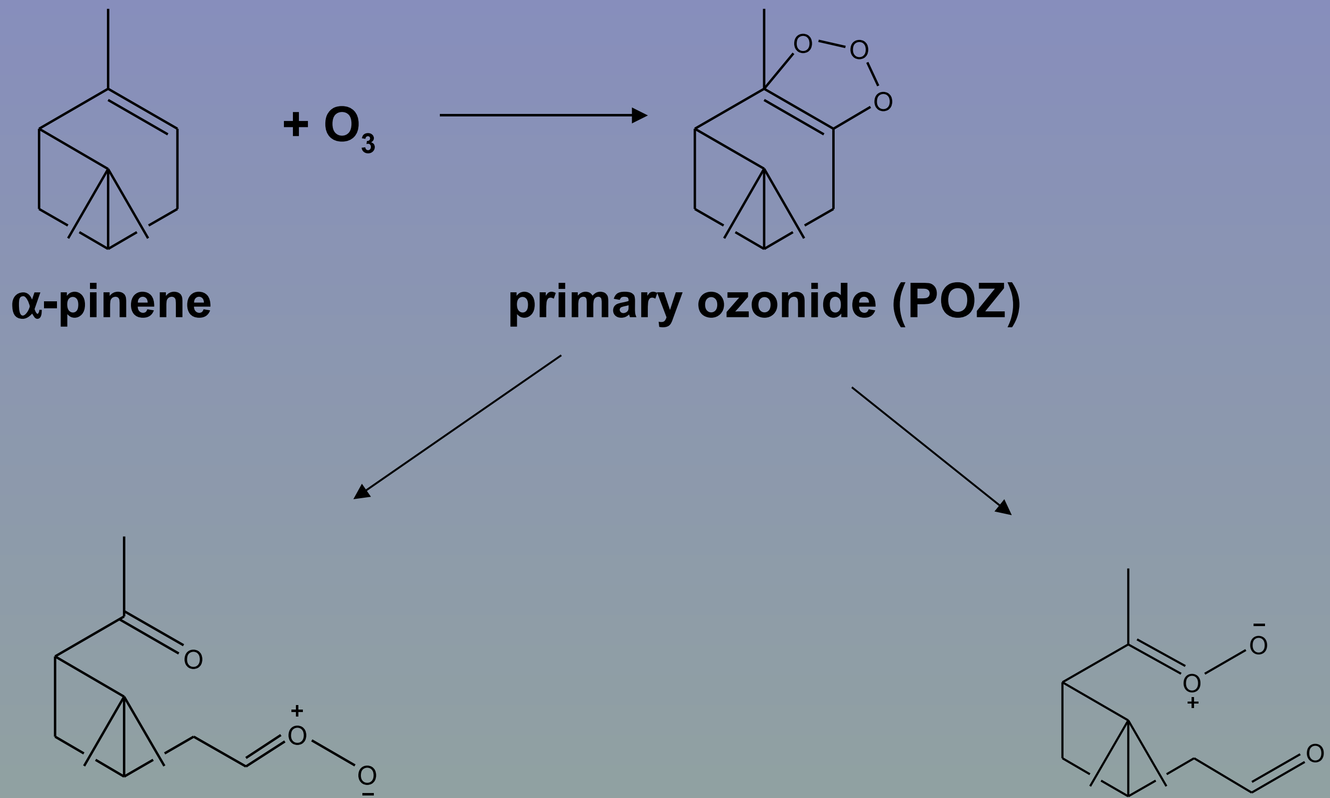
[a]Nolte, et al., 2002.

Future work

-Looking for field samples and modeling for re-direction and confirmation (Collaboration)

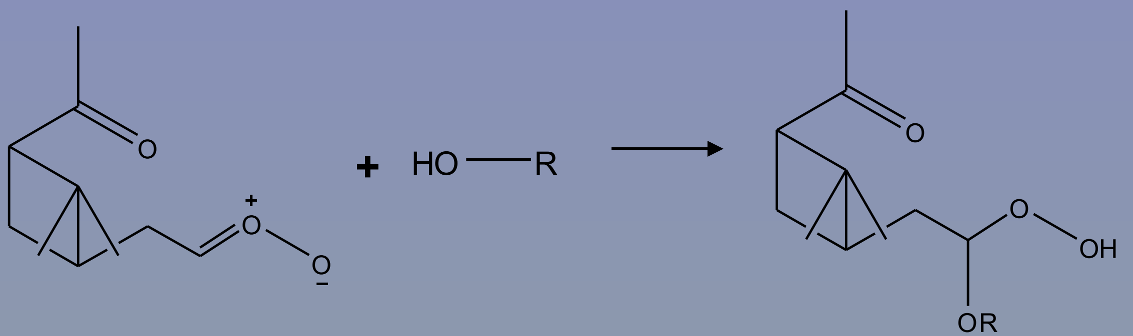
-Interested in affects of BSOA on vegetation

Ozonolysis of a Carbon-Carbon Double Bond

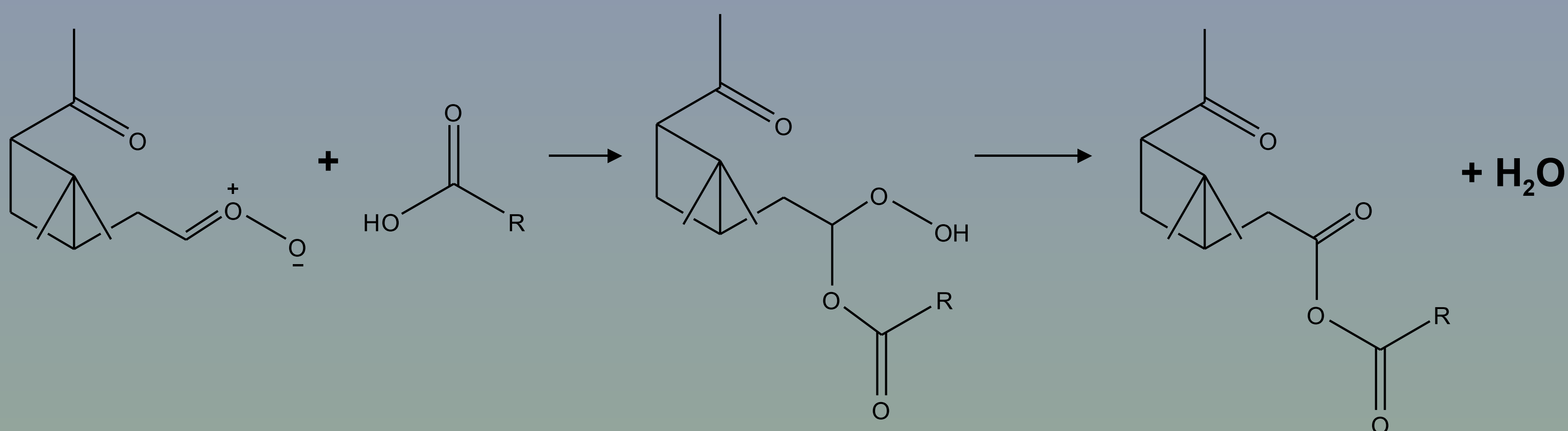


Crigee Intermediates

Do Cross Reactions Decrease SOA Volatility?

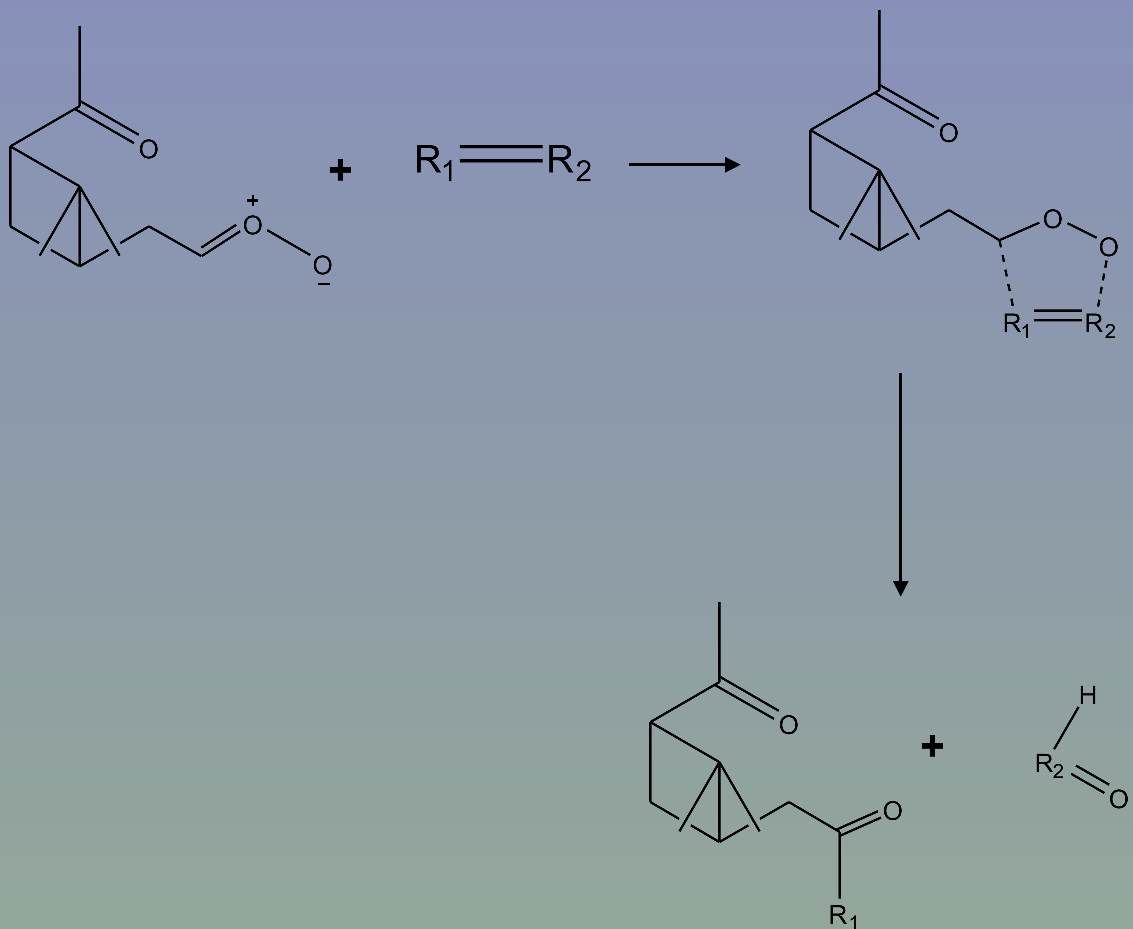


cholesterol, Dreyfus, et al. 2005



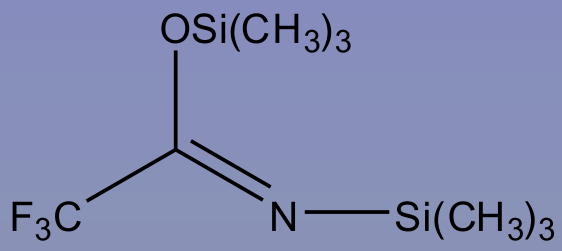
oleic acid, Zehardis, et al. 2004

Possible Cross Reactions that Decrease SOA Volatility?



oleic acid, Katrib, et al. 2004

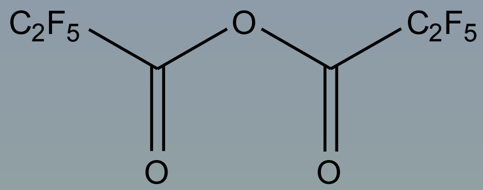
Derivatization Reactions



+ $CH_3(CH_2)_nCOOH$ → **$CH_3(CH_2)_nC(O)OSi(CH_3)_3$**

BSTFA
N,O-bis(Trimethylsilyl)trifluoroacetamide

Nolte, et al., 2002.



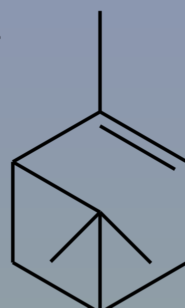
+ $CH_3(CH_2)_nCOOH$ → **$CH_3(CH_2)_nC(O)C_2F_5$**

PFPA
Pentafluoropropionic anhydride

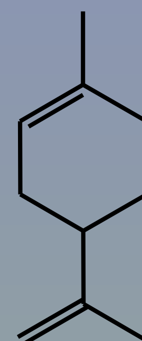
Aubert and Rotini, 2000

Secondary Organic Aerosol (SOA) Precursors

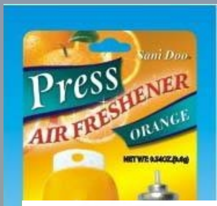
atmospheric



α-pinene



limonene



•The formation of SOA has environmental importance on both globa small (in home and workplace) scales (Wainman, 2000)

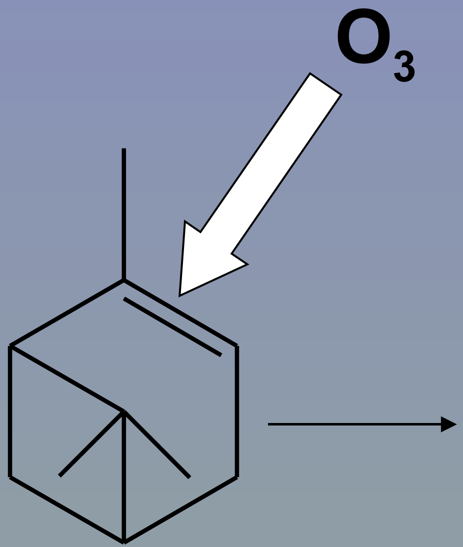
•Little is known about the reaction mechanism.

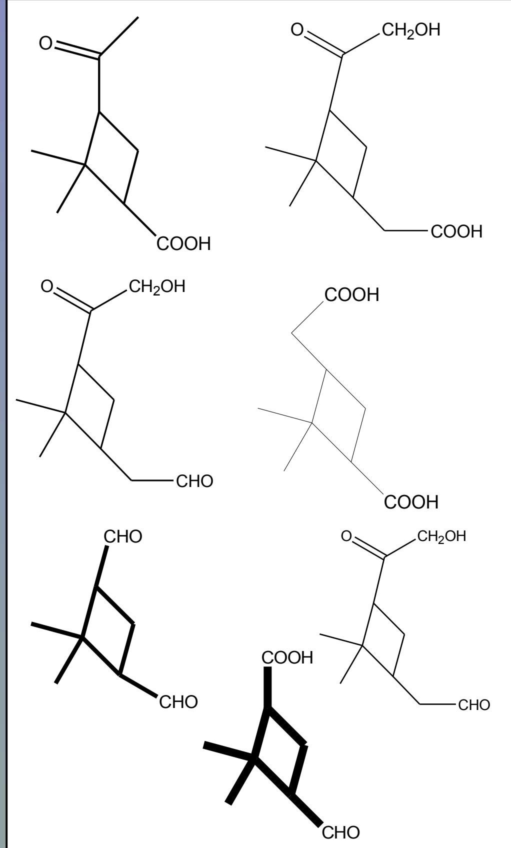
indoor

First-order Questions

- Which home products react with ozone to form secondary organic aerosol?
- What are the products?

Formation of Secondary Organic Aerosol via α-pinene Ozonation





carboxylic acids, aldehydes, and ketones

gas phase

Nucleation and/or condensation onto existing particles

evaporation

carboxylic acids
aldehydes
ketones
oligomers
further processing
multi-phase
heterogeneous

condensed phase

Glade ® Wisp

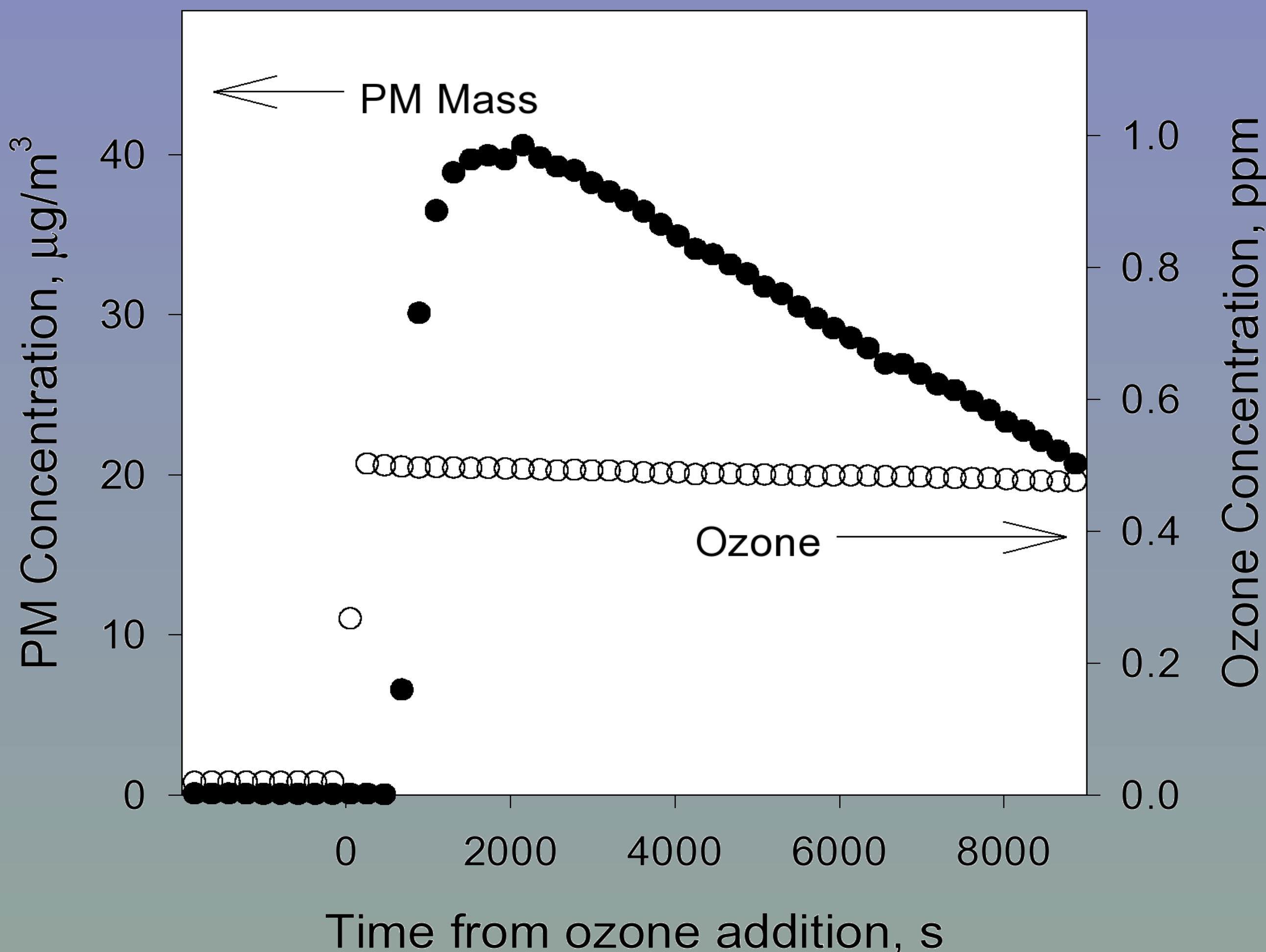
O_3 O_3 O_3 O_3
O_3 O_3 O_3 O_3 O_3 O_3 O_3

→ oxidized products

↓

PM?

PM formation from Ozonolysis of Glade ® Wisp



Aerosol production from the reaction ~500 ppb ozone with Glade Wisp® (mystery garden scent) emissions in the Carnegie Mellon University Air Quality Lab smog chamber.

Indoor Air Quality

- Humans live the majority of their lives indoors (NRC, 1991).
- PM can pollute indoor environments by emissions from primary sources, fine PM intrusion from outdoors, and reactions with invading oxidants.
- Volatile organic compounds emitted from air fresheners can be oxidized by ozone. (Liu et al., Environ. Sci. & Technol., 2004)