Aerosol Formation from Atmospheric Organics

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California Institute of Technology

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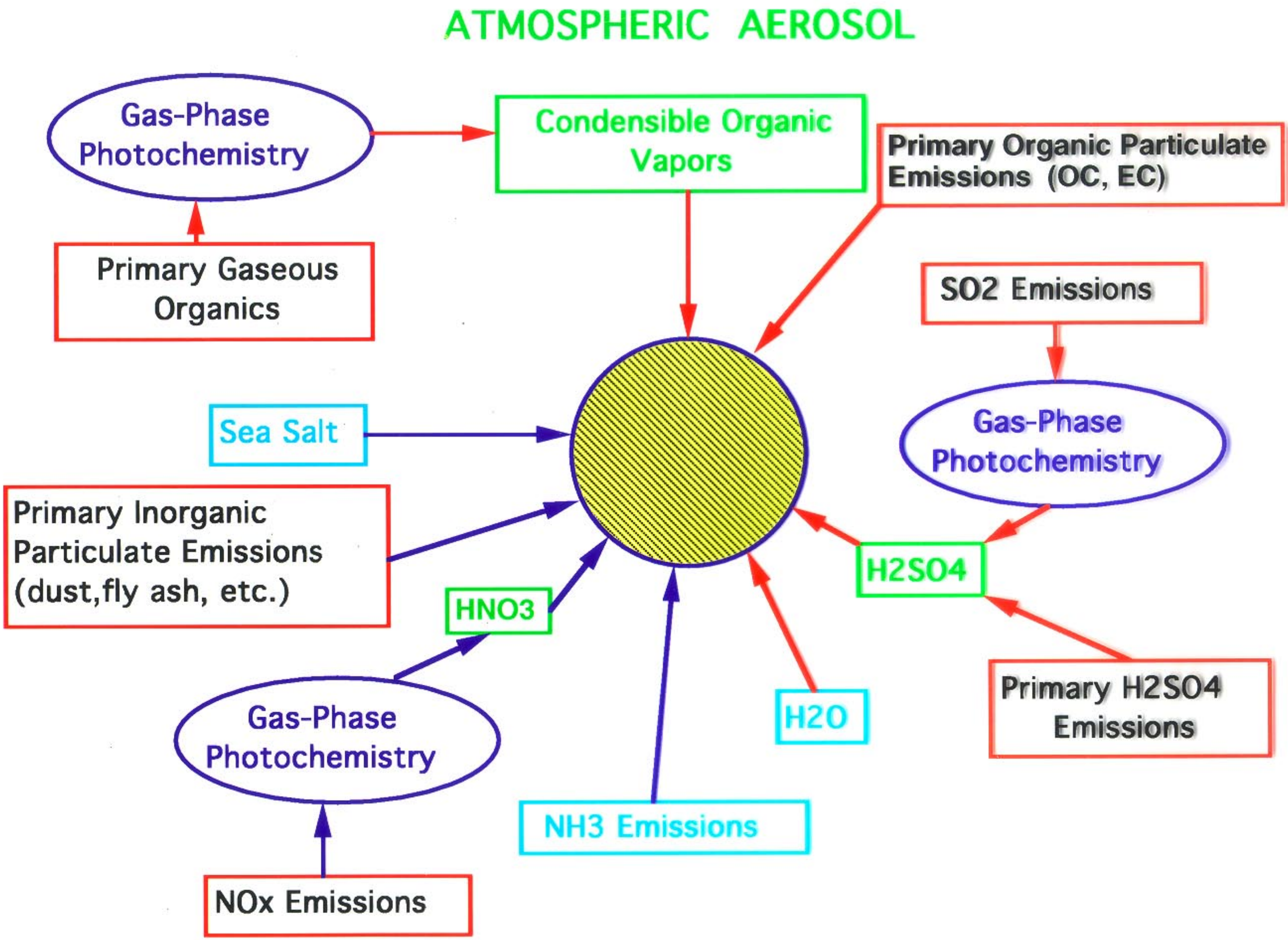
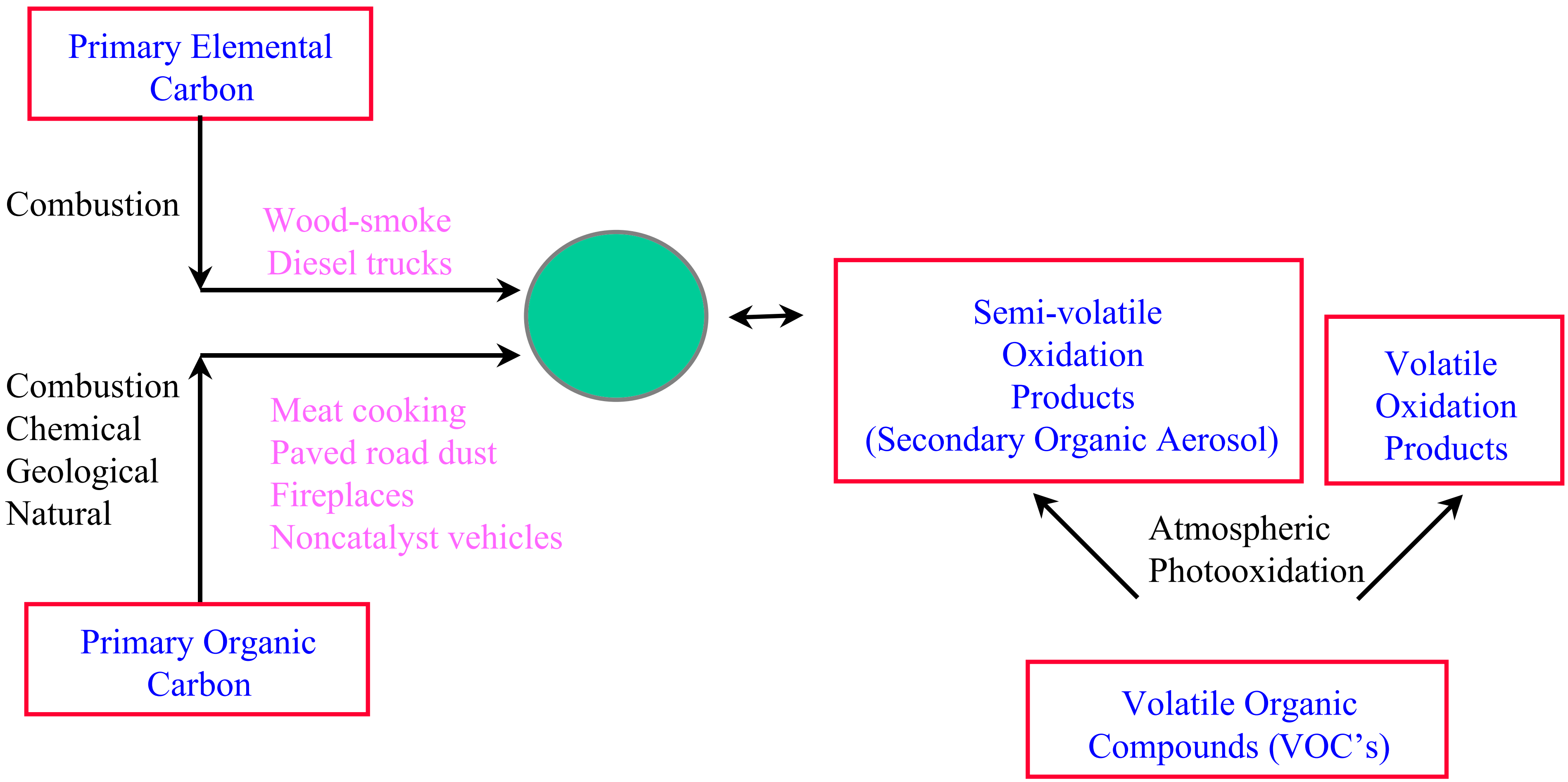
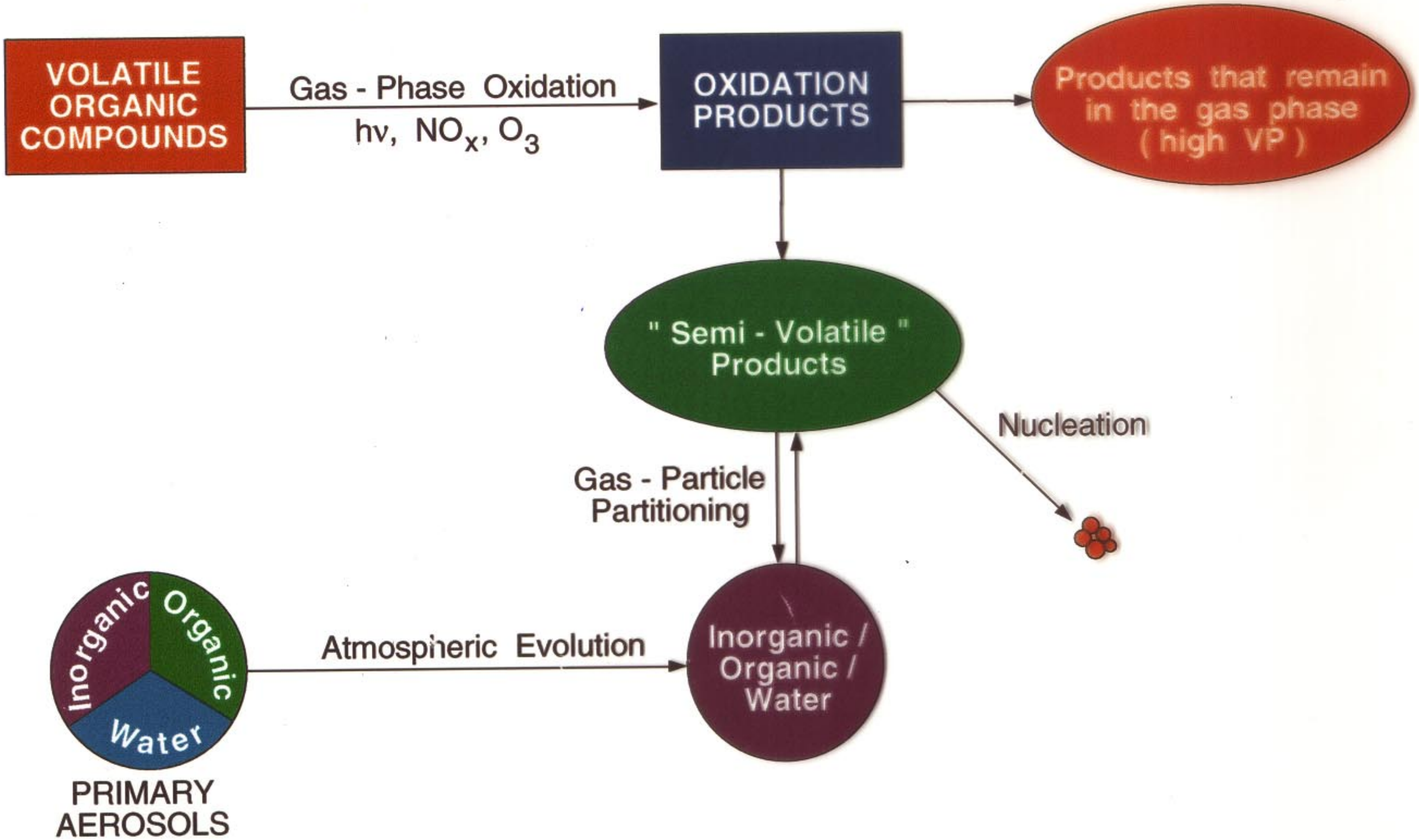

ATMOSPHERIC AEROSOL
Gas-Phase Photochemistry
Condensible Organic Vapors
Primary Organic Particulate Emissions (OC, EC)
Primary Gaseous Organics
SO2 Emissions
Sea Salt
Gas-Phase Photochemistry
Primary Inorganic Particulate Emissions (dust,fly ash, etc.)
HNO3
H2SO4
Primary H2SO4 Emissions
H2O
Gas-Phase Photochemistry
NH3 Emissions
NOx Emissions

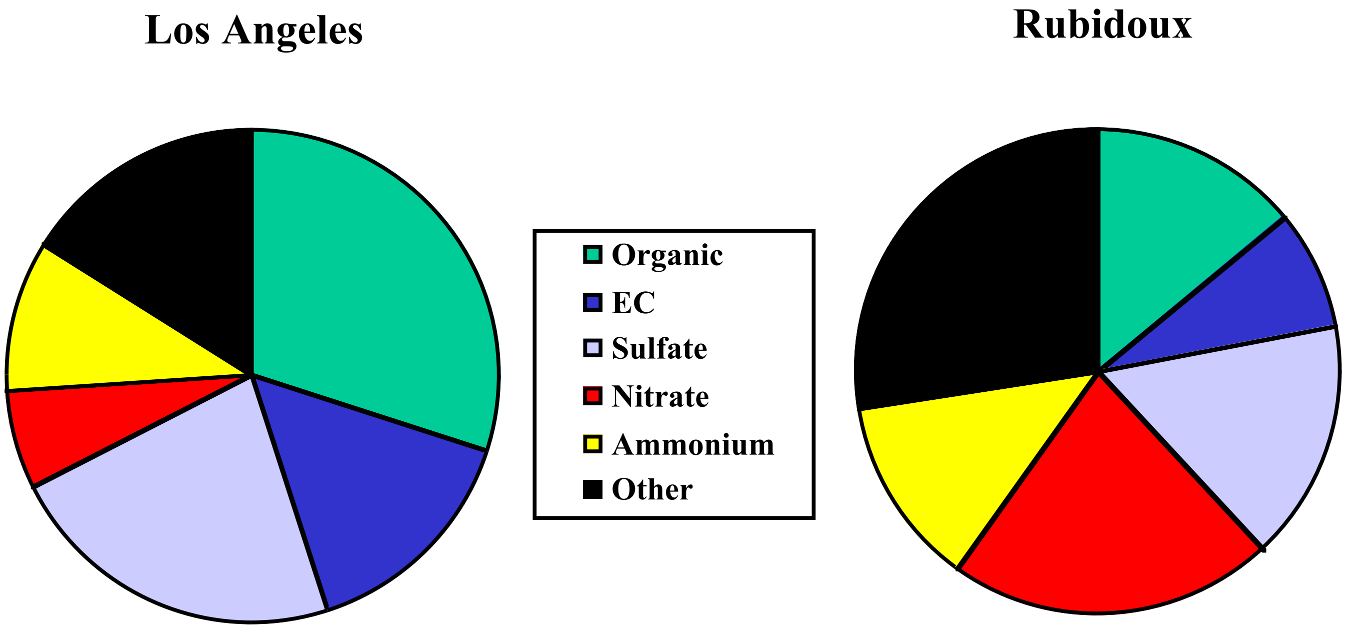
Sources of Carbonaceous Aerosol



FORMATION OF SECONDARY ORGANIC AEROSOLS



Importance of Secondary Organic Aerosol

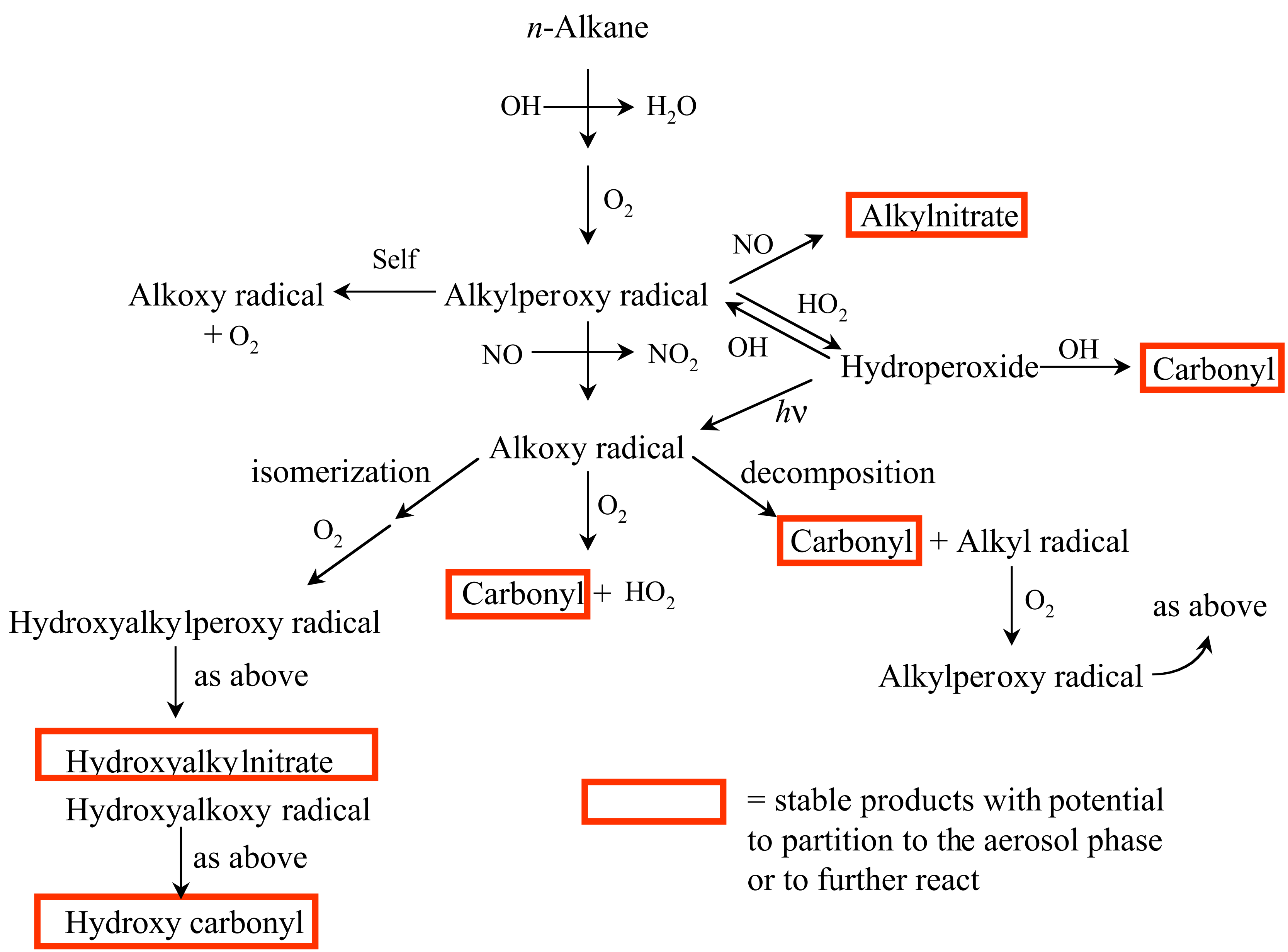


In the SoCAB, SOA *generally* contributes 20-80% of the observed total organic aerosol

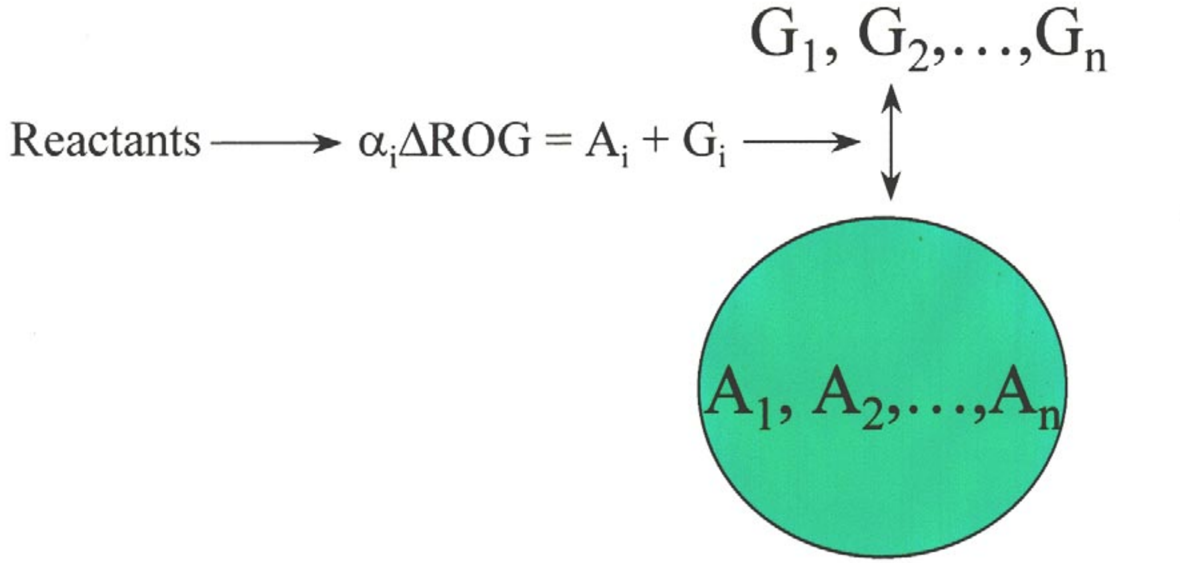
Major Questions of SOA Formation

- What are the gas-phase mechanisms leading to semi-volatile species? What are the molecular identities of these species? Are these first- or higher-generation products of the oxidation of the parent molecule?
- Can we predict from first principles the gas-particle partitioning of semi-volatile organic products to particles that consist of organics, water, and dissolved electrolytes?

Example Mechanism



Equilibrium Partitioning of Semi-Volatile Compounds

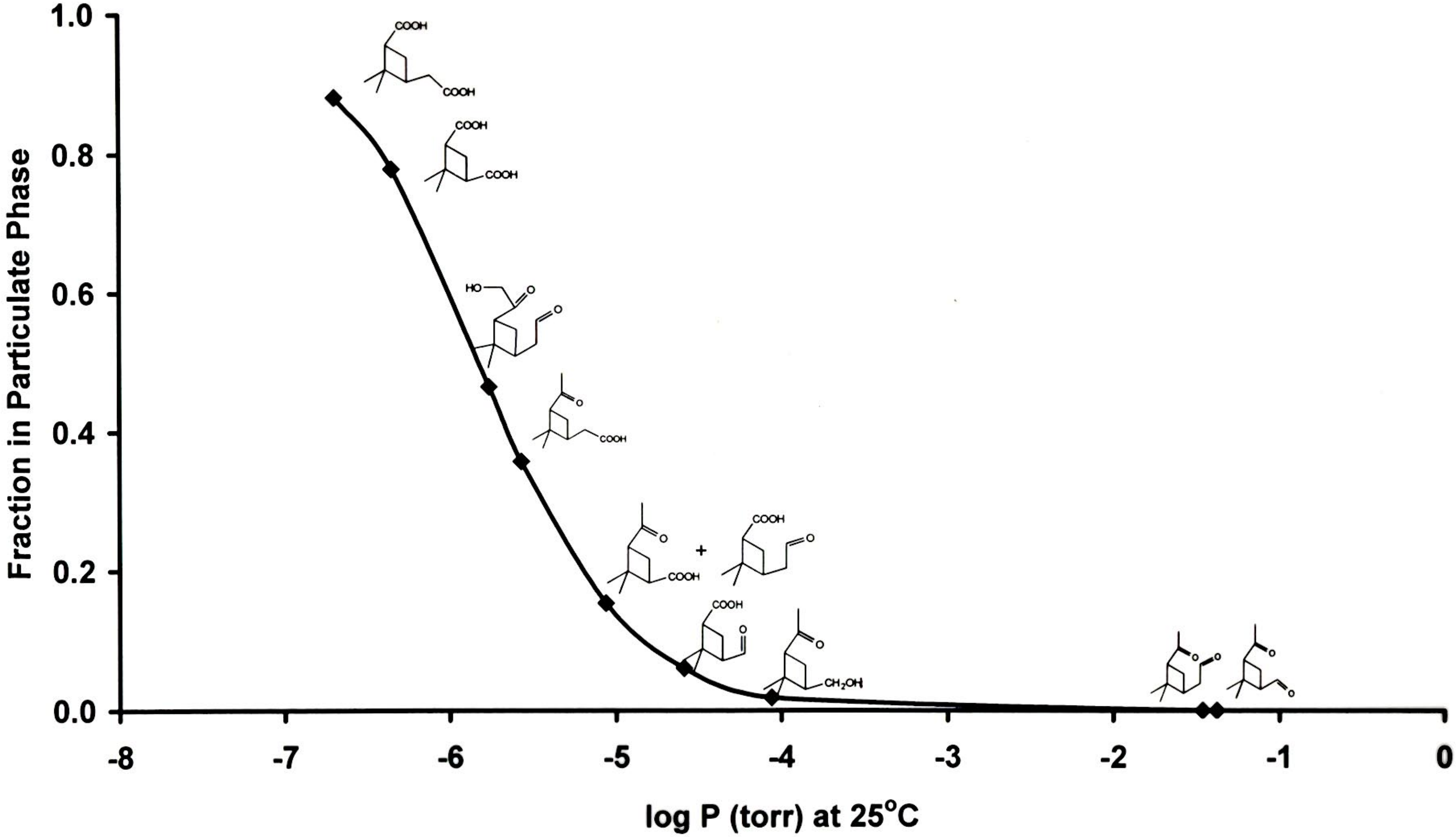


$$K_{om,i} = \frac{A_i/\Delta M_o}{G_i} = \frac{RT}{MW_{om}\gamma_i p^o_{L,i}}$$

$$\gamma_i = \gamma_i(x_1, x_2, \ldots, x_n)$$

$$p^o_{L,i} = p^o_{L,i}\,(T)$$

Partitioning of Products from the O3 Oxidation of a-Pinene between the Particulate and Gas Phase (Assuming a Total Organic Aerosol Mass of 50 µg/m³)



June 15, 2001

Environmental Science & Technology

http://pubs.acs.org/est

A State-of-the-Art Chamber for Investigating Aerosol Chemistry

Endocrine Disrupters in Pulp Mill Effluent

Coastal Marsh Impacts on Water Quality

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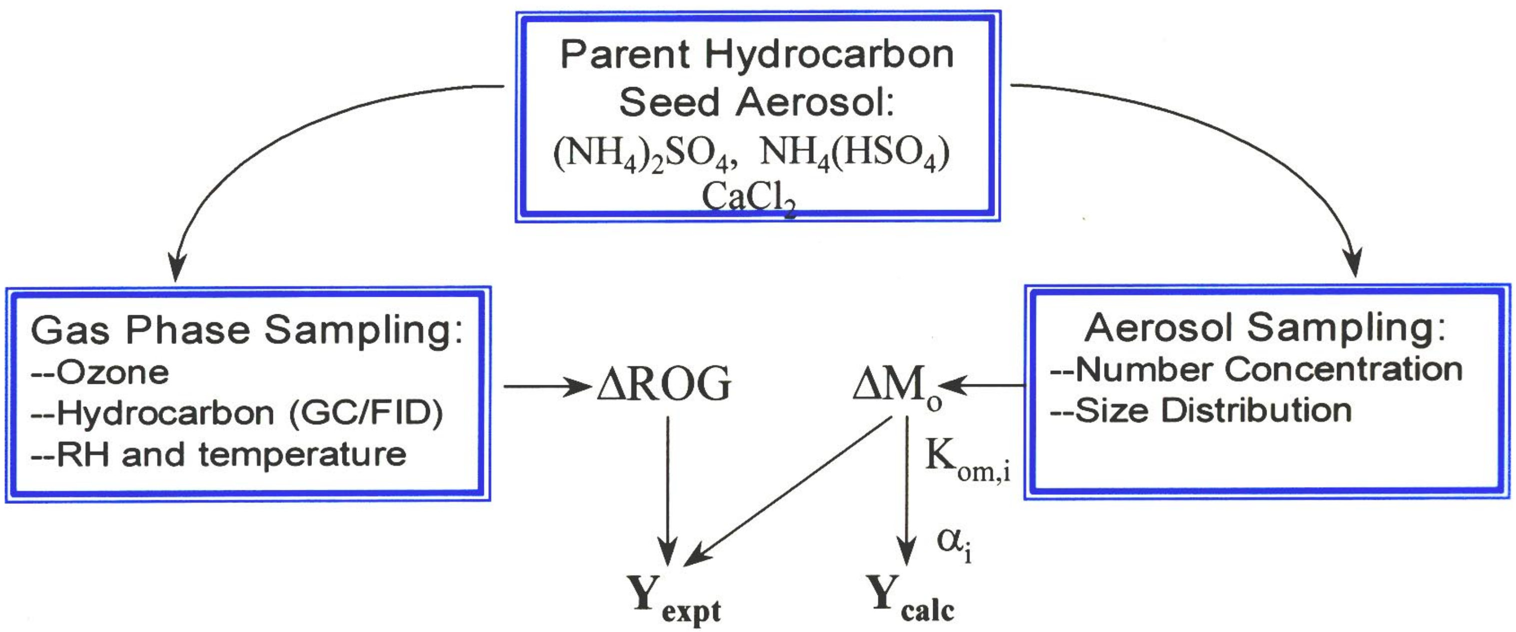
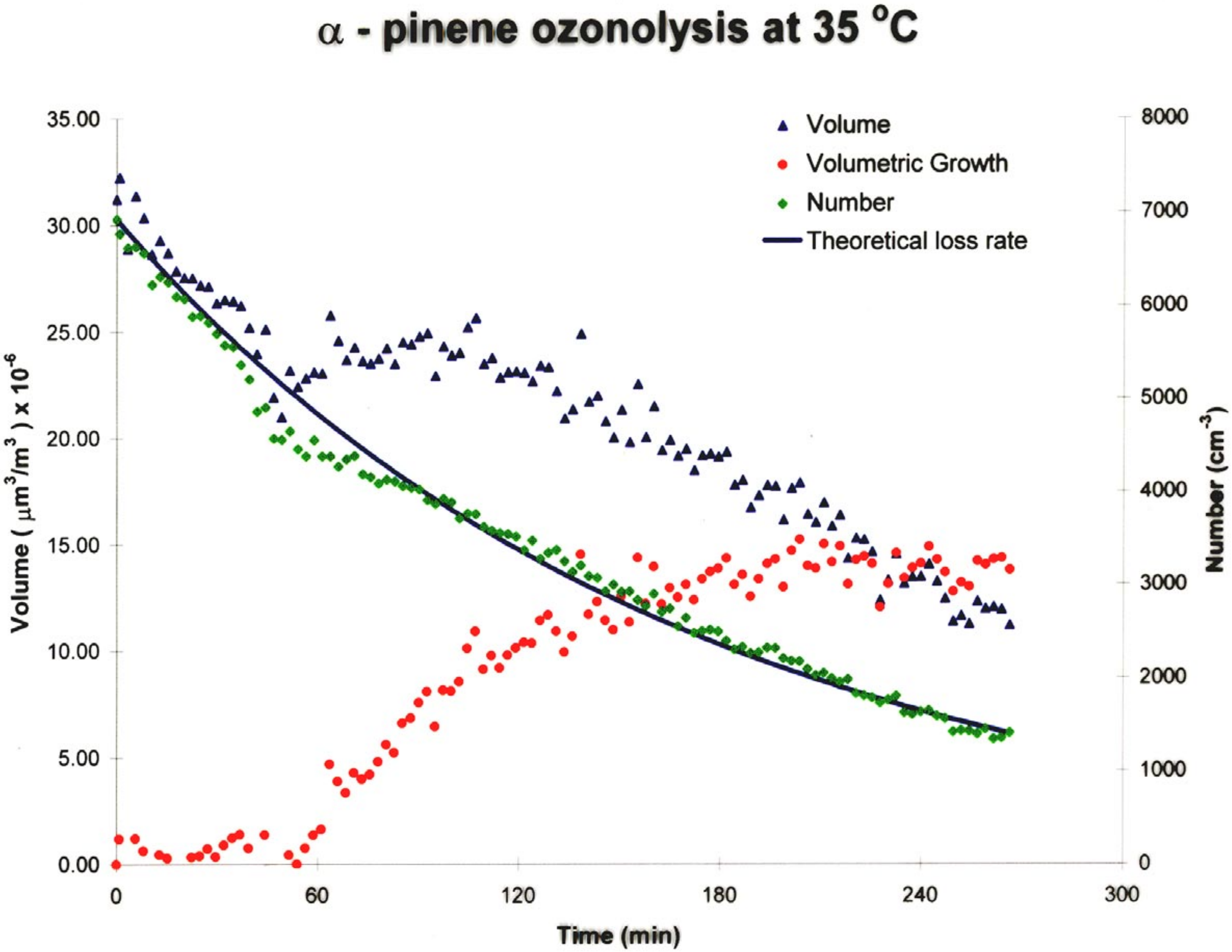
Experimental Protocol

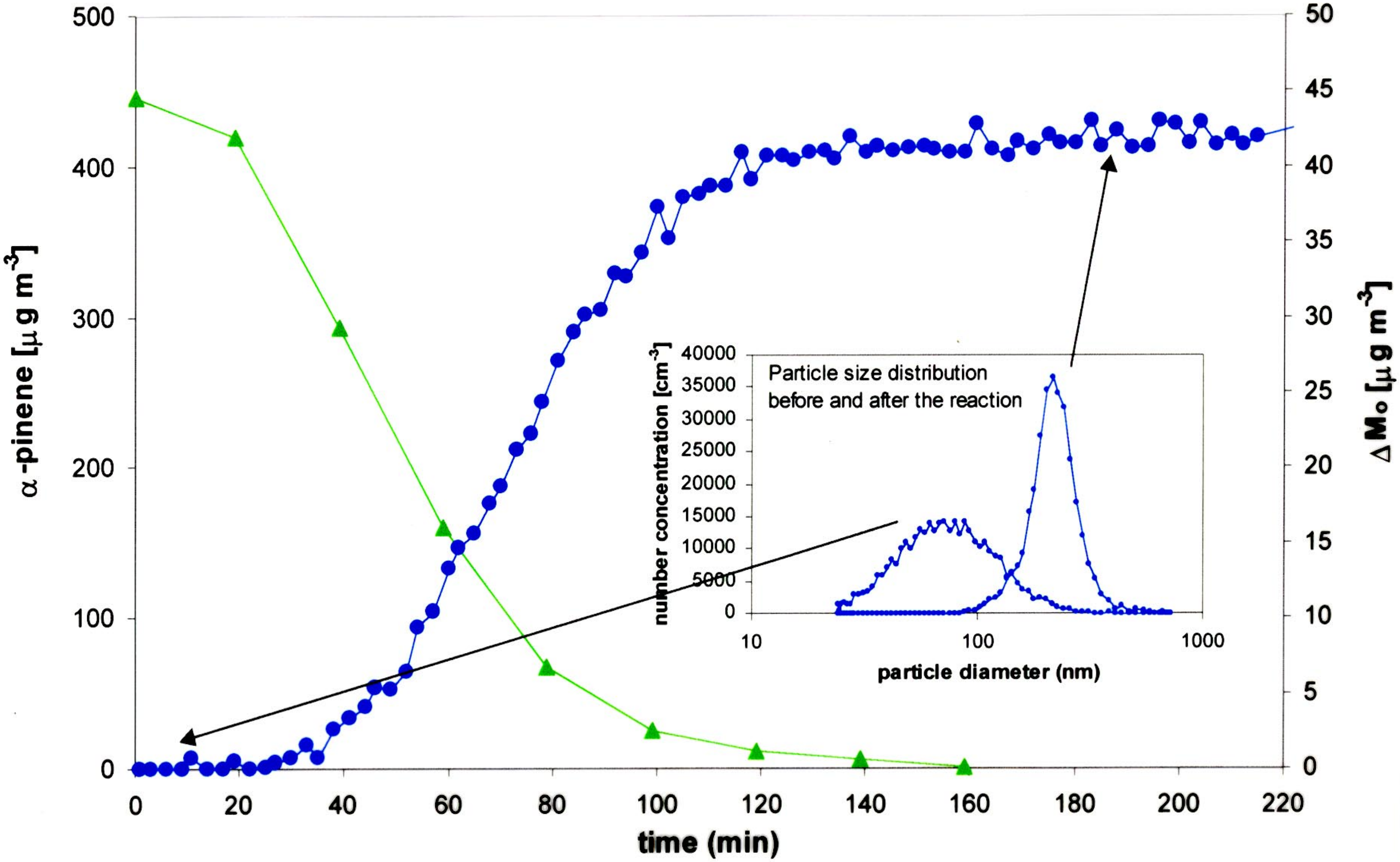
Indoor Teflon Reactor



Two $K_{om.i}$ and α_i values are then varied so that the sum of the residuals between experimental and calculated yields for a single parent is minimized.

$$Yield_{expt} = \Delta M_o / \Delta ROG$$


α - pinene ozonolysis at 35 °C
Volume
Volumetric Growth
Number
Theoretical loss rate
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
Volume (μm³/m³) x 10⁻⁶
8000
7000
6000
5000
4000
3000
2000
1000
0
Number (cm⁻³)
0
60
120
180
240
300
Time (min)



α -pinene [μ g m⁻³]
ΔMo [μ g m⁻³]
time (min)
Particle size distribution
before and after the reaction
number concentration [cm⁻³]
particle diameter (nm)
0
20
40
60
80
100
120
140
160
180
200
220
500
400
300
200
100
50
45
40
35
30
25
20
15
10
5
40000
35000
30000
25000
20000
15000
10000
5000
10
1000

Calculation of Yield

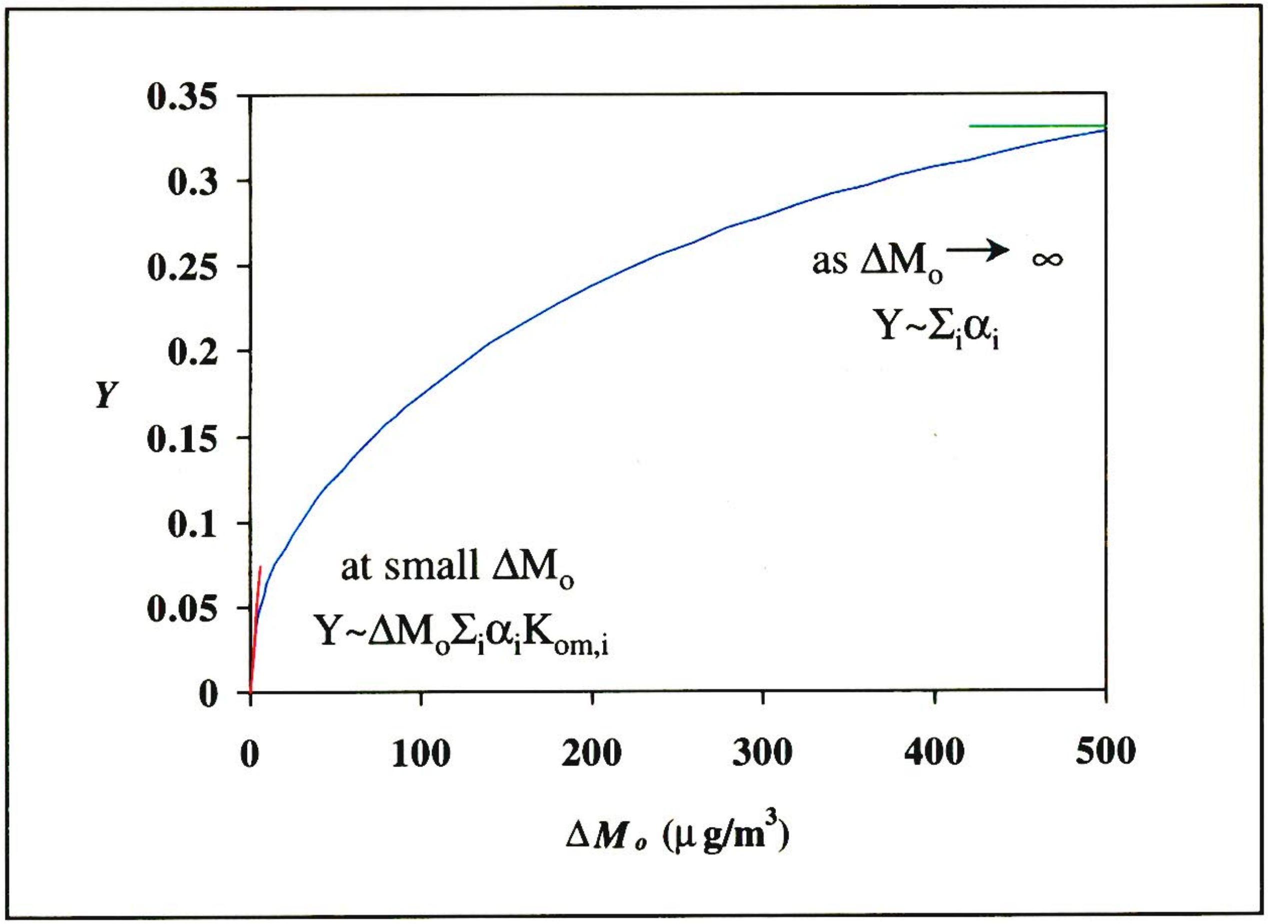
- At low RH, and only semi-volatile products of the parent hydrocarbon partition to the aerosol phase.

$$Yield = \frac{\Delta Mass_{organic}(\mu g/m^3)}{\Delta HC(\mu g/m^3)}$$

- At higher RH, aerosol growth is governed by partitioning of both organic and water to the aerosol phase.

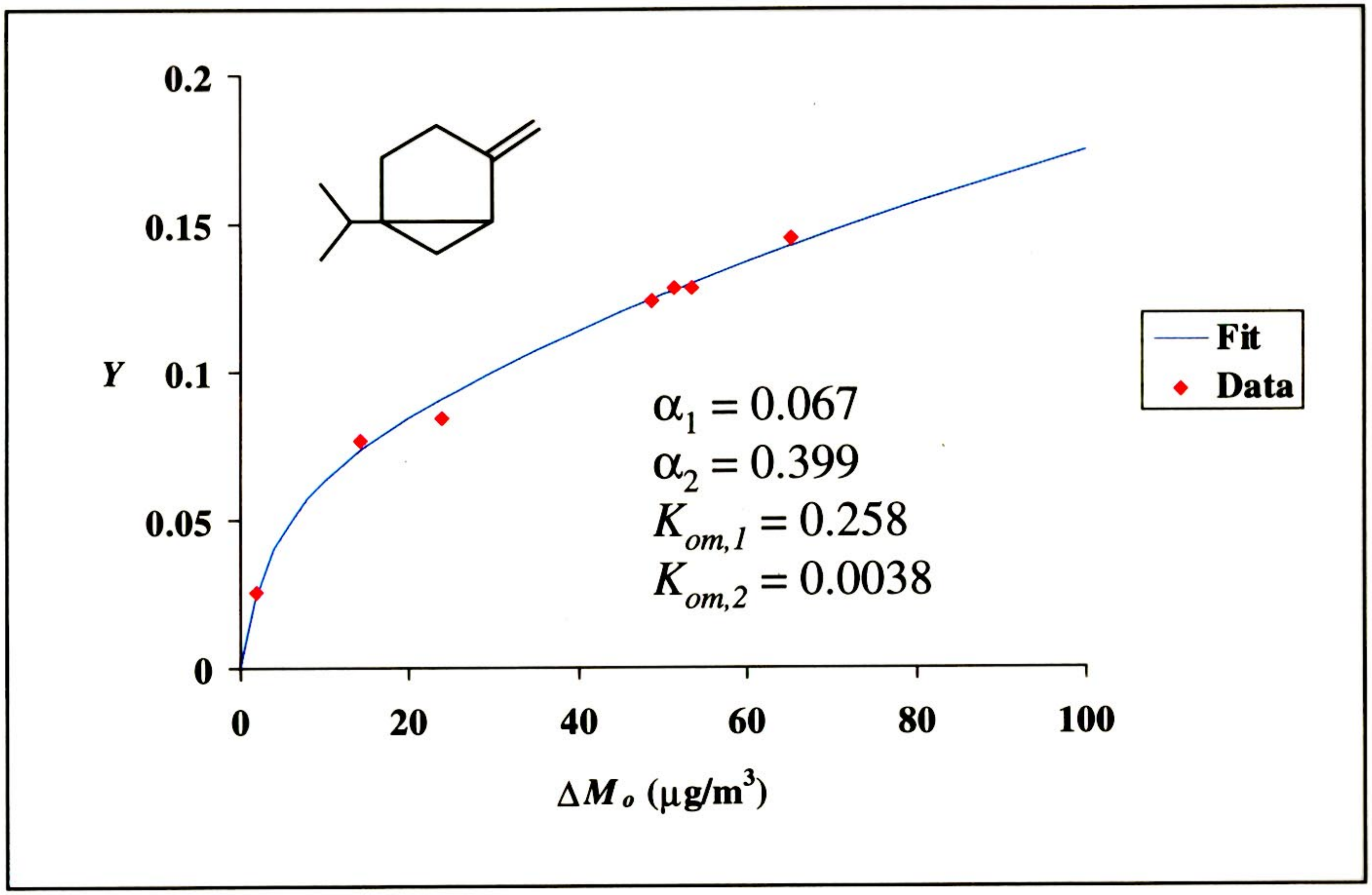
$$Yield^* = \frac{\Delta Mass_{aerosol}(\mu g/m^3)}{\Delta HC(\mu g/m^3)} = \frac{\Delta Mass_{organic}(\mu g/m^3) + \Delta Mass_{water}(\mu g/m^3)}{\Delta HC(\mu g/m^3)}$$

Characteristics of the Aerosol Yield



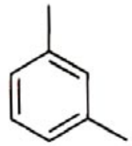
$$Y = \sum_i Y_i = \Delta M_o \sum_i \left(\frac{\alpha_i K_{om,i}}{1 + K_{om,i}\,\Delta M_o} \right)$$

Fitted Curve for Sabinene in Photooxidation Experiments

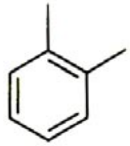


$$Y = \sum_i Y_i = \Delta M_o \sum_i \left(\frac{\alpha_i K_{om,i}}{1 + K_{om,i}\,\Delta M_o} \right)$$

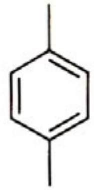
Aromatic Hydrocarbons Previously Studied



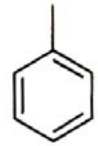
m-xylene



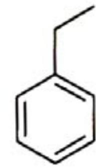
o-xylene



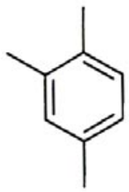
p-xylene



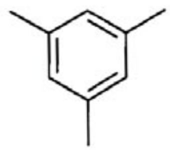
toluene



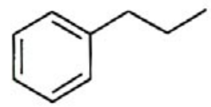
ethylbenzene



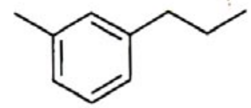
1,2,4-trimethylbenzene



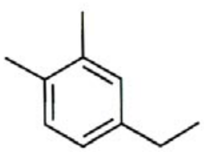
1,3,5-trimethylbenzene



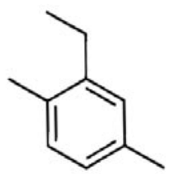
n-propylbenzene



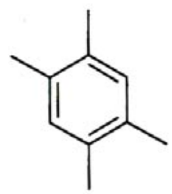
1-methyl-3-n-propylbenzene



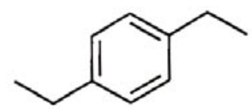
1,2-dimethyl-4-ethylbenzene



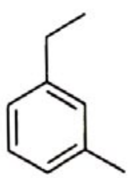
1,4-dimethyl-2-ethylbenzene



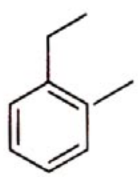
1,2,4,5-tetramethylbenzene



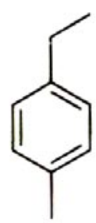
p-diethylbenzene



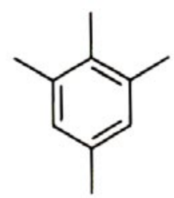
m-ethyltoluene



o-ethyltoluene



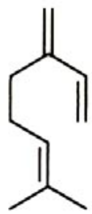
p-ethyltoluene



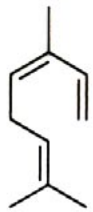
1,2,3,5-tetramethylbenzene

Biogenic Hydrocarbons Previously Studied

Acyclic Triolefins

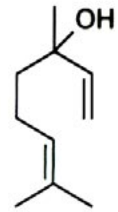


Myrcene

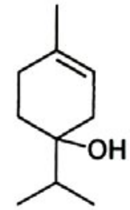


Ocimene

Oxygenated Terpenes

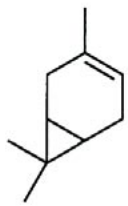


Linalool

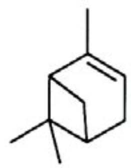


Terpinene-4-ol

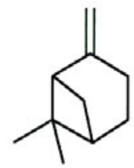
Bicyclic Olefins



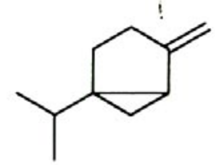
Δ³-Carene



α-Pinene

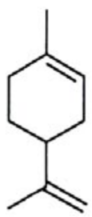


β-Pinene

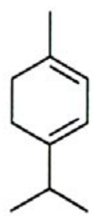


Sabinene

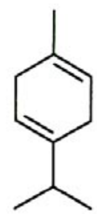
Cyclic Diolefins



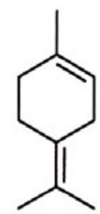
Limonene



α-Terpinene

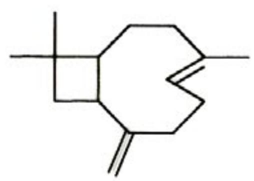


γ-Terpinene

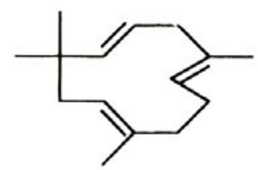


Terpinolene

Sesquiterpenes

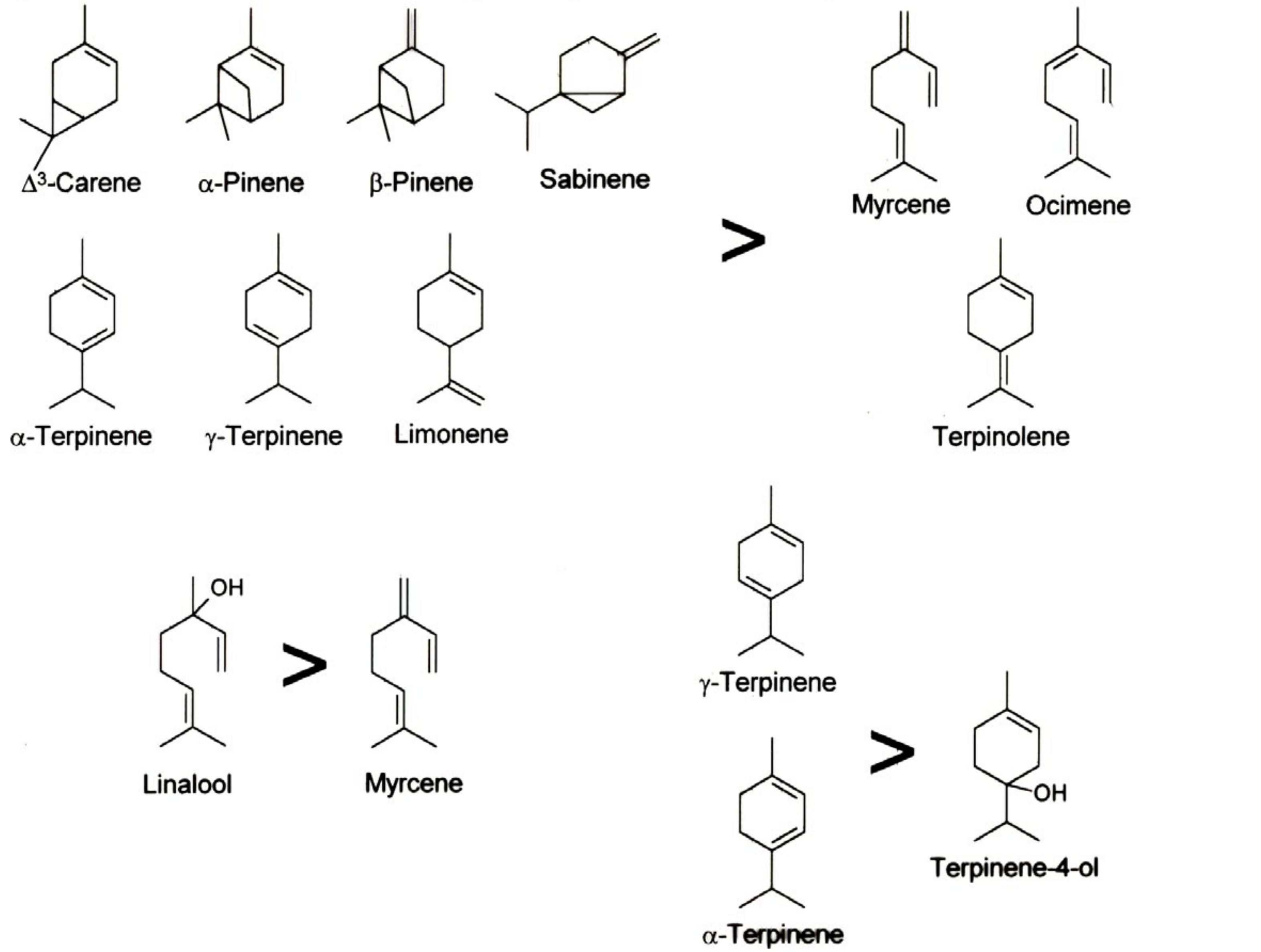


β-Caryophyllene

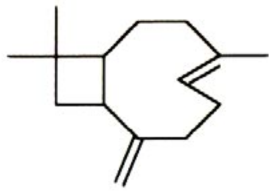


α-Humulene

Cyclic structures have higher yields than open chain compounds

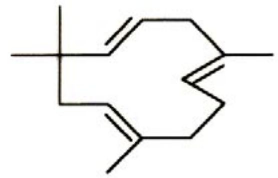


Sesquiterpenes have highest yield due to carbon number



β-Caryophyllene

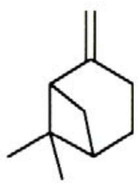
$C_{15}C_{24}$



α-Humulene

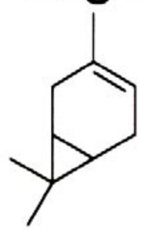
vs. $C_{10}C_{24}$ monoterpenes

Location of double bonds and number of carbon in secondary ring important: photooxidation



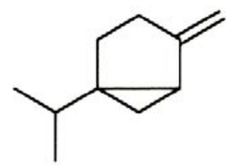
β-Pinene

>



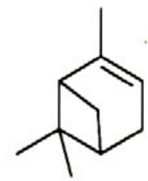
Δ^3-Carene

>



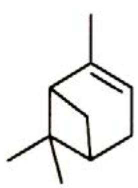
Sabinene

>



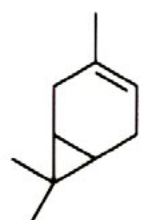
α-Pinene

As well as type of oxidant: ozone reaction



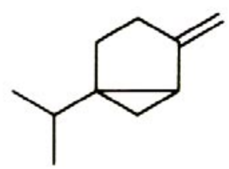
α-Pinene

>



Δ^3-Carene

>



Sabinene

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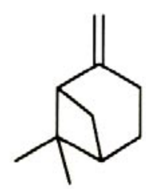
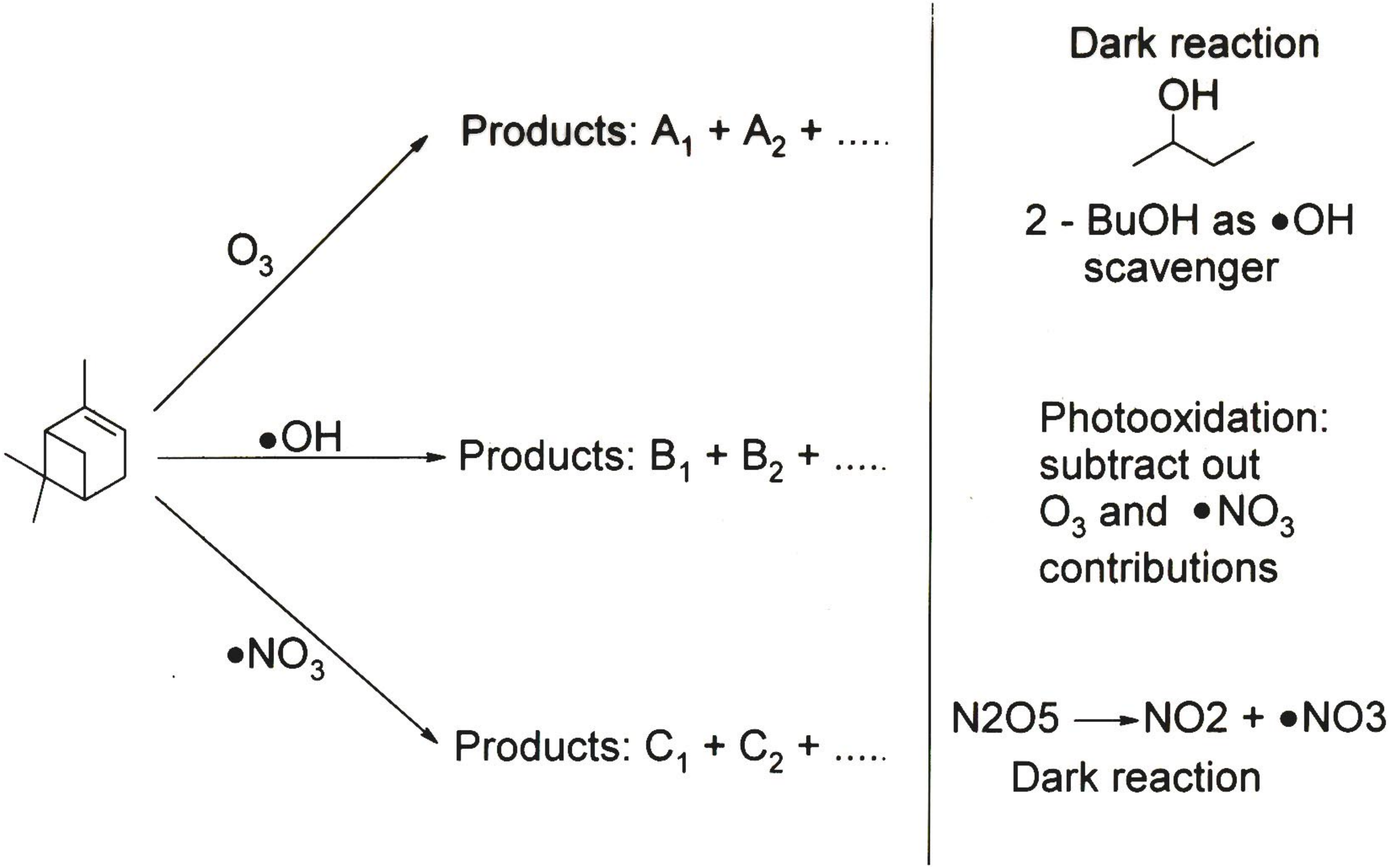
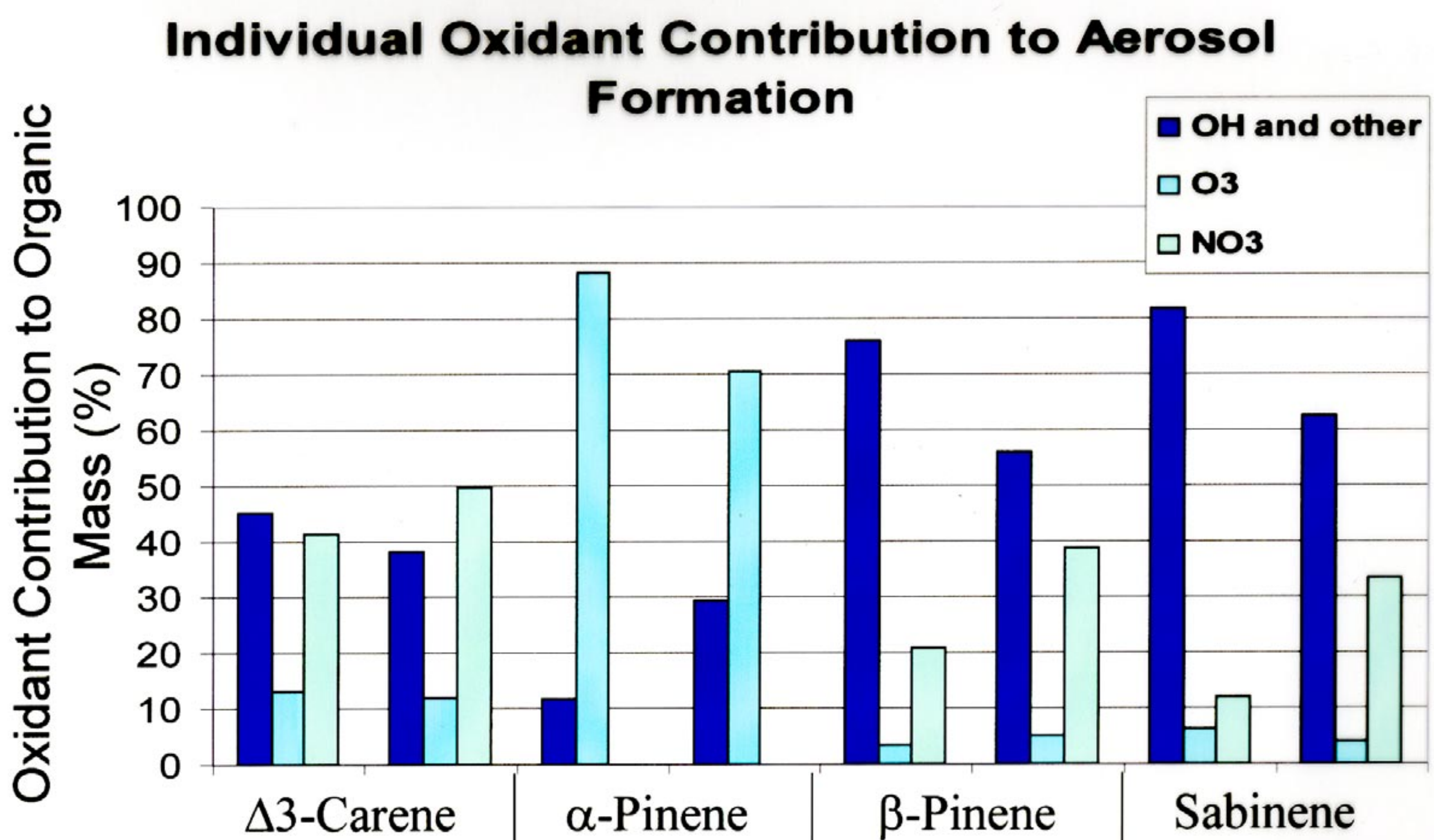


β-Pinene



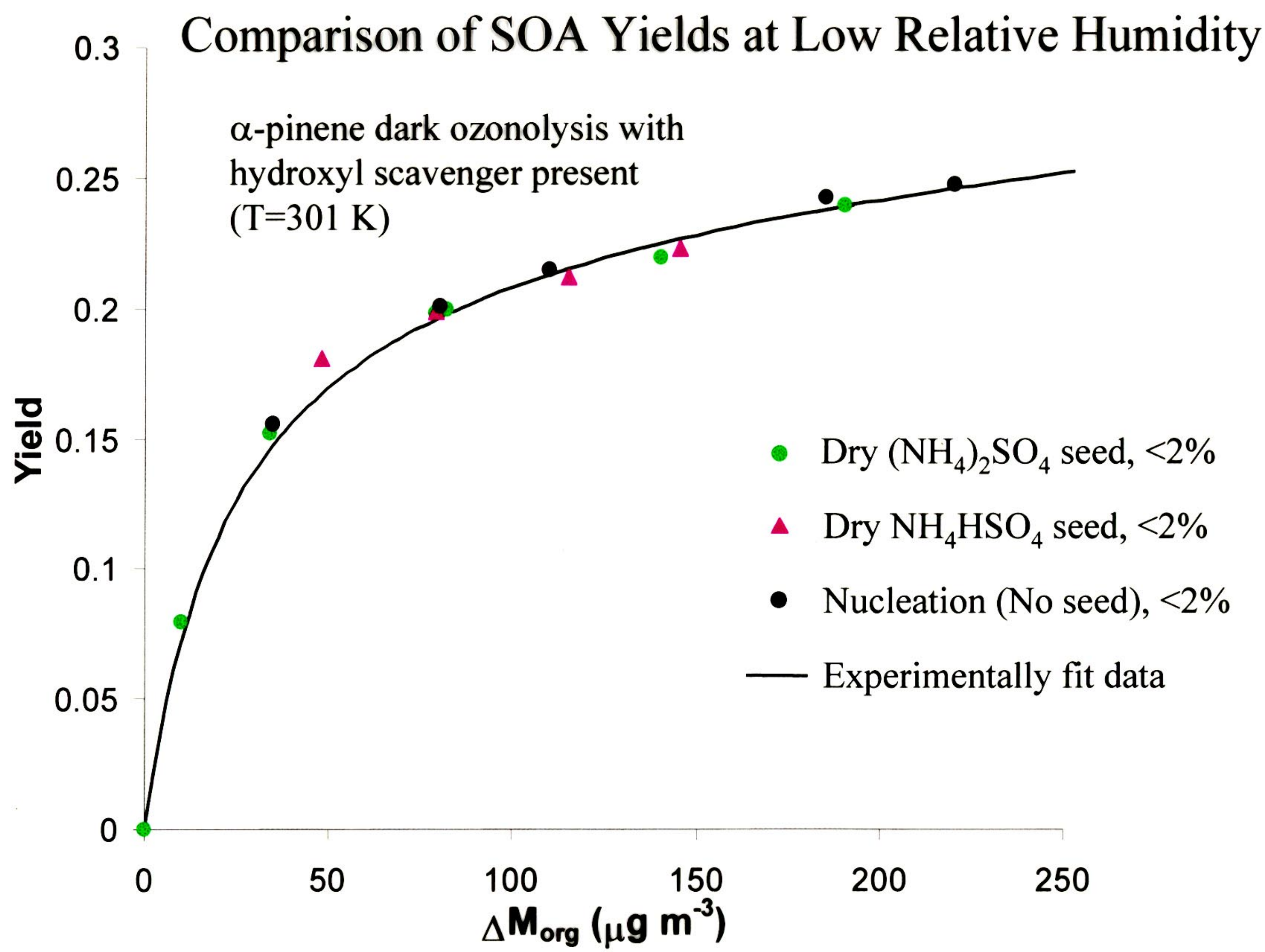
O3
Products: A1 + A2 + ...
•OH
Products: B1 + B2 + ...
•NO3
Products: C1 + C2 + ...
Dark reaction
OH
2 - BuOH as •OH scavenger
Photooxidation: subtract out O3 and •NO3 contributions
N2O5 → NO2 + •NO3
Dark reaction

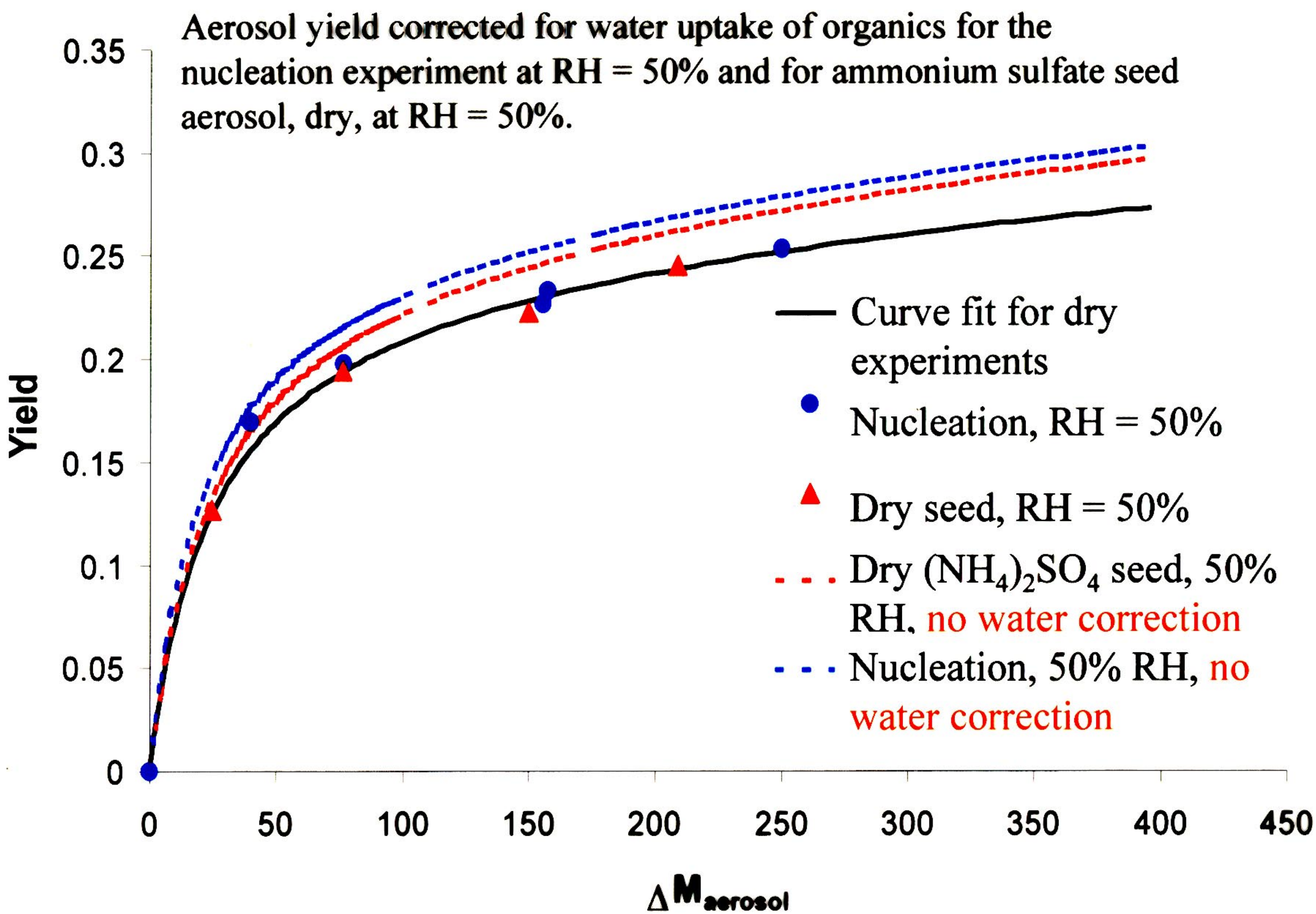


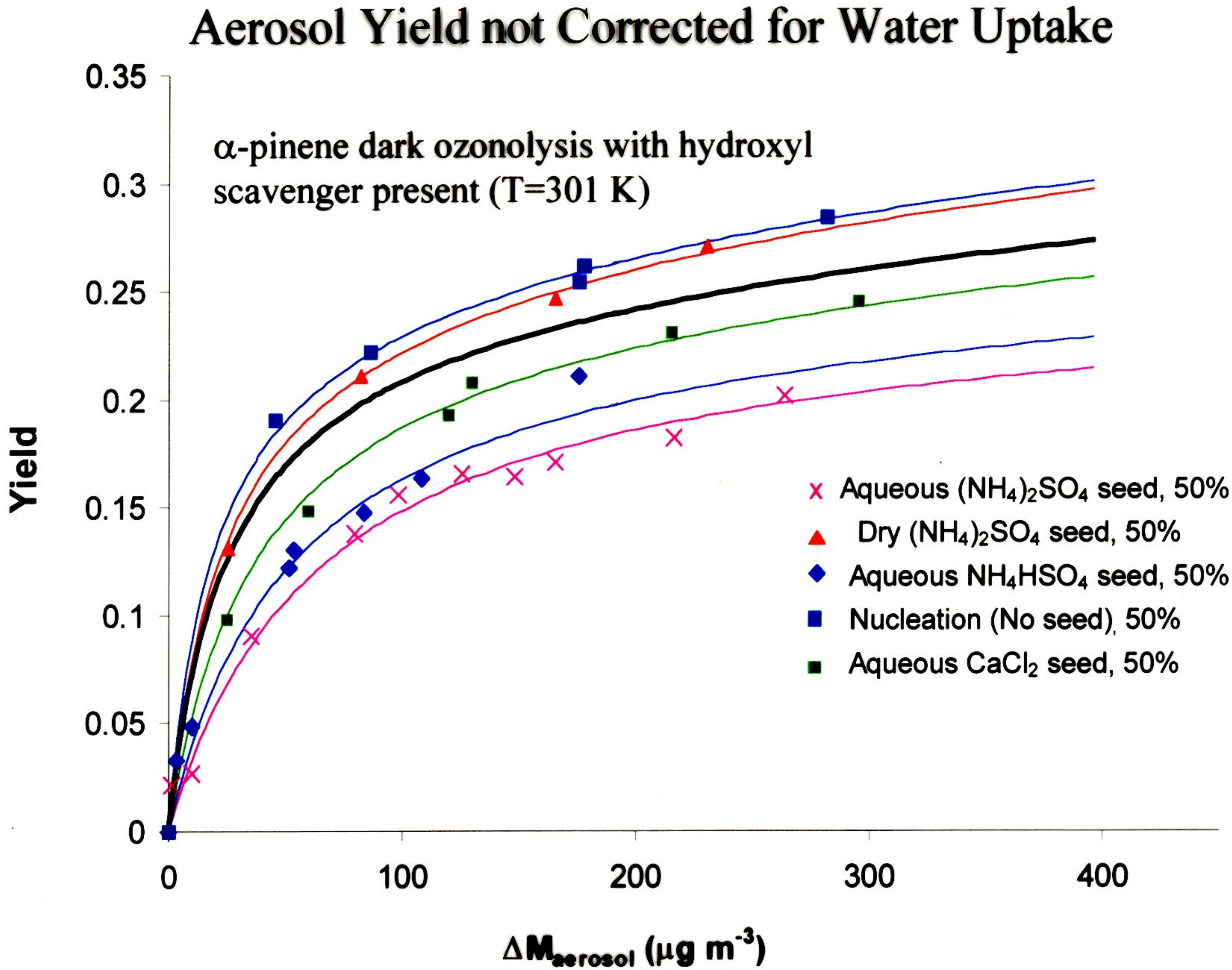
	Δ3-Carene		α-Pinene		β-Pinene		Sabinene	
C_o (ppb)	72.5	104.6	72.4	94.8	32.3	79.0	34.9	83.3
NO_x level (ppb)	128	162	203	124	135	153	102	199
M_o (μg/ml)	54.6	99.7	22.7	39.3	20.4	109.4	14.8	65.2
Yield	14.2%	17.9%	5.9%	7.7%	11.8%	26.0%	6.4%	14.5%

Types of Experiments

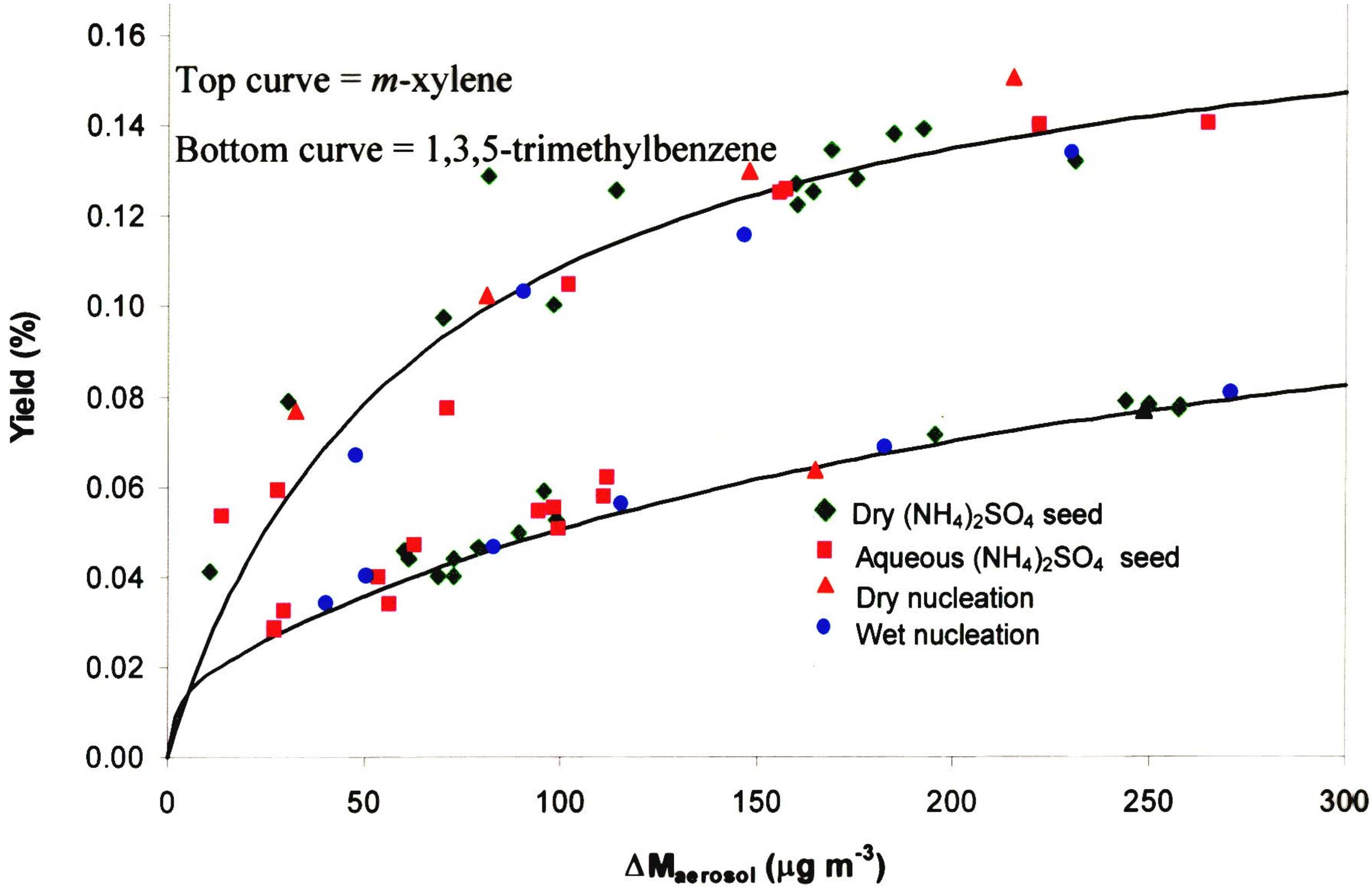
- Nucleation-no seed
  - RH<2%
  - RH=50%
- Dry seed
  - RH<2% $(NH_4)_2(SO_4)$, $(NH_4)HSO_4$
  - RH=50% $(NH_4)_2(SO_4)$
- Aqueous seed
  - RH=50% $(NH_4)_2(SO_4)$, $(NH_4)HSO_4$, $CaCl_2$


Comparison of SOA Yields at Low Relative Humidity
α-pinene dark ozonolysis with
hydroxyl scavenger present
(T=301 K)
Yield
0.3
0.25
0.2
0.15
0.1
0.05
0
0
50
100
150
200
250
ΔM_{org} ($\mu g\ m^{-3}$)
Dry $(NH_4)_2SO_4$ seed, <2%
Dry NH_4HSO_4 seed, <2%
Nucleation (No seed), <2%
Experimentally fit data

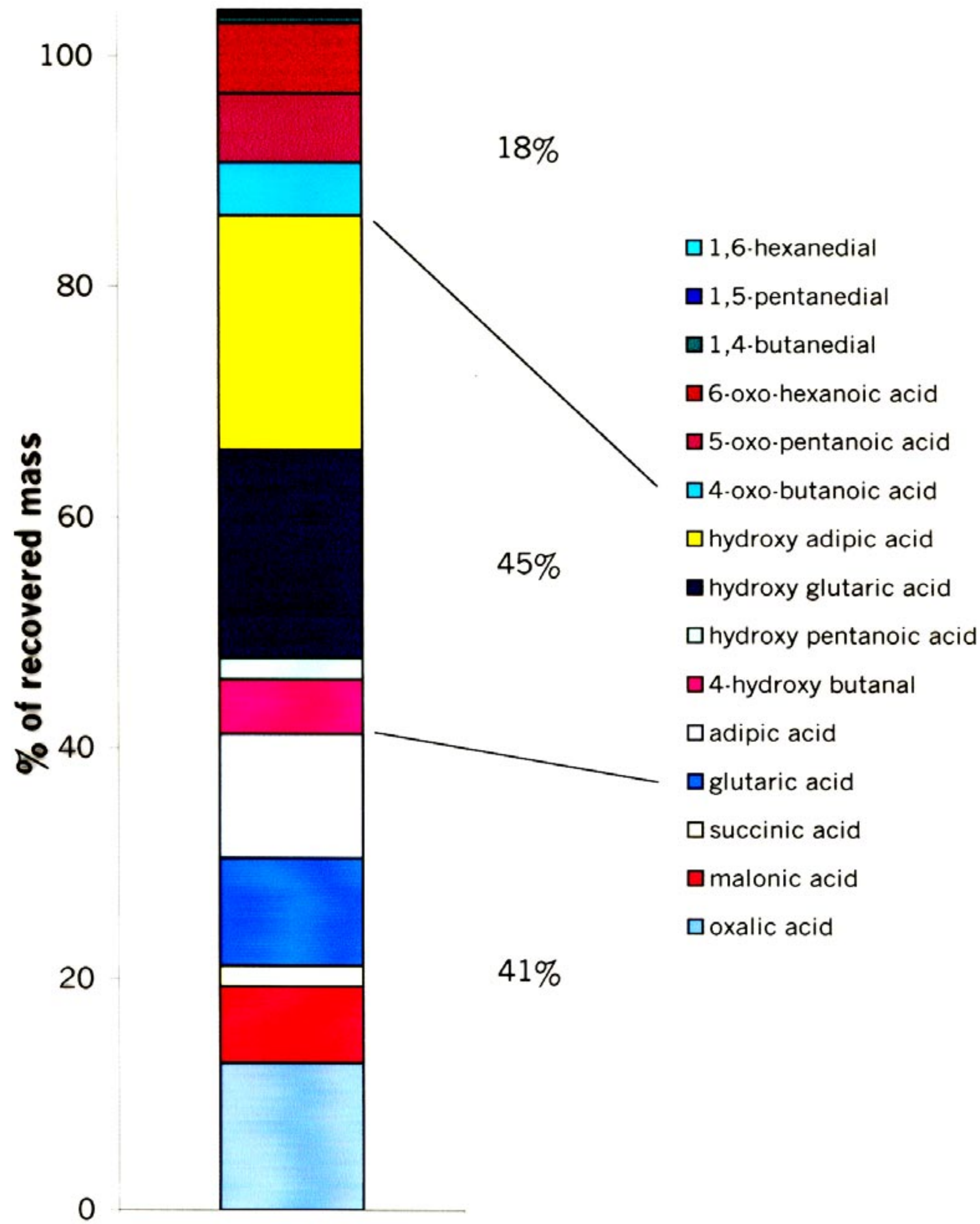

Aerosol yield corrected for water uptake of organics for the nucleation experiment at RH = 50% and for ammonium sulfate seed aerosol, dry, at RH = 50%.
Yield
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
50
100
150
200
250
300
350
400
450
ΔM aerosol
Curve fit for dry experiments
Nucleation, RH = 50%
Dry seed, RH = 50%
Dry (NH4)2SO4 seed, 50% RH, no water correction
Nucleation, 50% RH, no water correction



Aerosol Yield not Corrected for Water Uptake
α-pinene dark ozonolysis with hydroxyl
scavenger present (T=301 K)
Yield
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
100
200
300
400
ΔM aerosol (µg m⁻³)
Aqueous (NH4)2SO4 seed, 50%
Dry (NH4)2SO4 seed, 50%
Aqueous NH4HSO4 seed, 50%
Nucleation (No seed), 50%
Aqueous CaCl2 seed, 50%



Top curve = m-xylene
Bottom curve = 1,3,5-trimethylbenzene
Dry (NH4)2SO4 seed
Aqueous (NH4)2SO4 seed
Dry nucleation
Wet nucleation
Yield (%)
ΔMaerosol (μg m-3)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
50
100
150
200
250
300


% of recovered mass
100
80
60
40
20
0
18%
45%
41%
1,6-hexanedial
1,5-pentanedial
1,4-butanedial
6-oxo-hexanoic acid
5-oxo-pentanoic acid
4-oxo-butanoic acid
hydroxy adipic acid
hydroxy glutaric acid
hydroxy pentanoic acid
4-hydroxy butanal
adipic acid
glutaric acid
succinic acid
malonic acid
oxalic acid

Overall Goals of the Experiments

- Continue establishing aerosol forming potential of atmospheric organics
- Provide data to test theoretical models of SOA formation and aerosol thermodynamics

Phase 1

- Effects of RH, inorganic salt seed composition, and seed state (dry/aqueous) on SOA yield through ozone oxidation of hydrocarbons

- Characterize the composition of the aerosol phase (functional groups, OC/OM, etc.)

Phase 2

- Can aerosol yield for a series of similar hydrocarbons be correlated with aspects of hydrocarbon structure, such as location of double bonds and ring size?

Analytical Instruments Used

Samples from two 28-m^3 indoor Teflon chambers are drawn to be analyzed by:

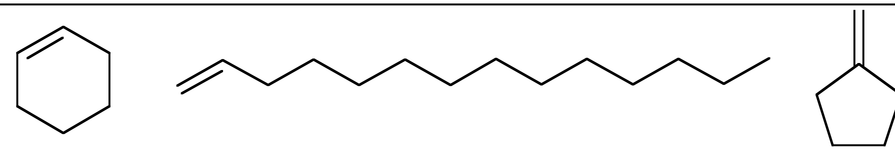
Instrument	Analytical Information	On/off-line	Sampled Chamber
DMA (Differential Mobility Analyzer)	- Size distribution - Number, mass, and volume concentrations	On-line	Both (dedicated)
H-TDMA (Humidity Tandem DMA)	Hygroscopicity of the aerosol	On-line	Both (switching)
CNC (Condensation Nucleus Counter)	Number concentration (>3 nm and >10 nm)	On-line	Both (dedicated)
GC-FID (Gas Chromatograph)	Reactant hydrocarbon concentration	On-line	Both (switching)
AMS (Aerosol Mass Spectrometer)	Aerosol phase composition and mass distribution	On-line	High-conc. run only
CIMS (Chemical Ionization Mass Spec.)	Gas phase composition	On-line	High-conc. run only
Ozone/NO_x analyzers	Ozone, NO_x concentrations	On-line	Both (dedicated)
Filter Samples - GC/MS and LC/MS - OC analysis	- Aerosol phase composition - OM/OC ratio for organics	Off-line	High-conc. run only

Experimental Protocols (Phase 1)

<u>Phase 1</u>: *Effect of RH and seed on gas-particle conversion and aerosol yield*

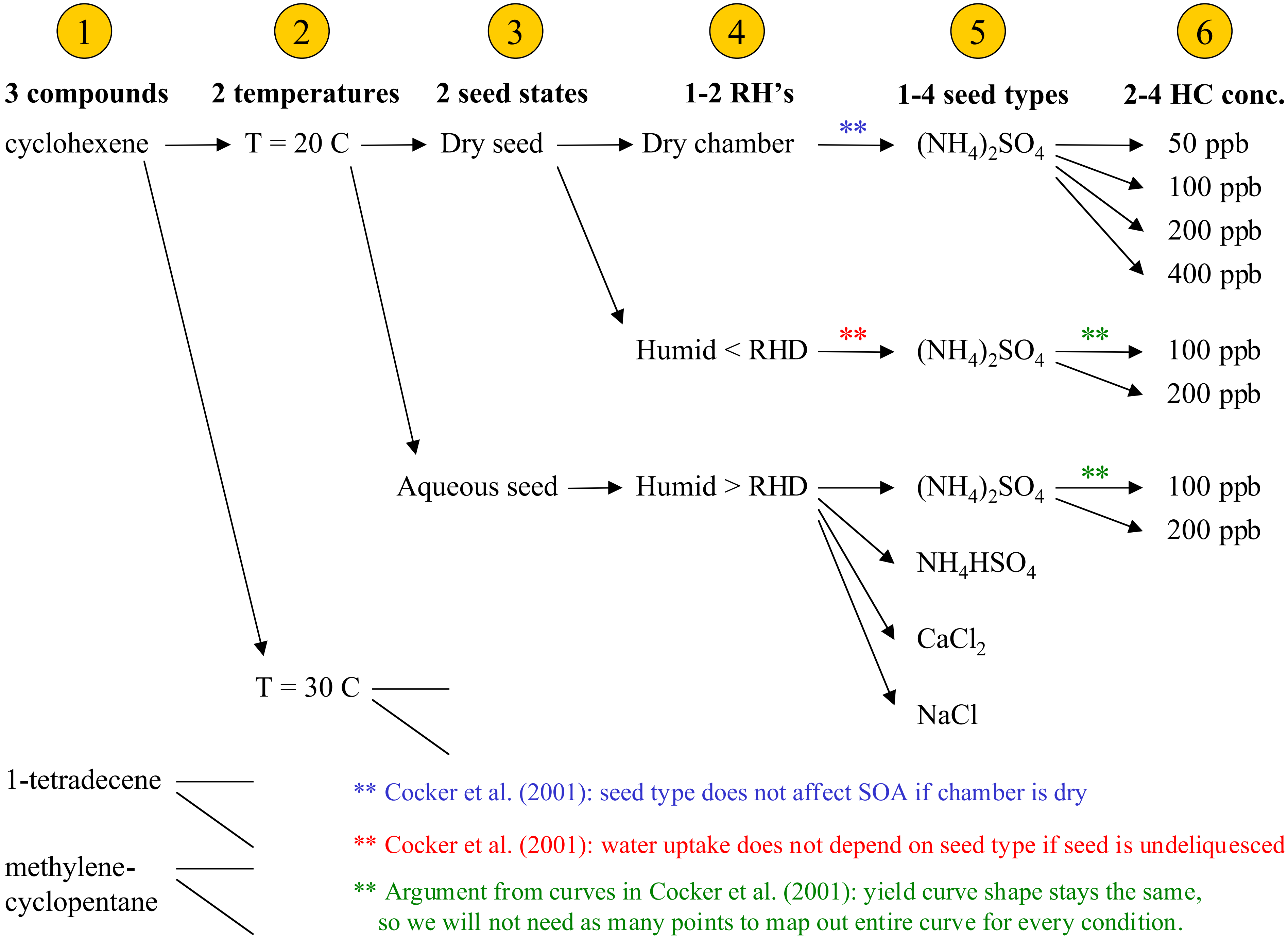
React parent HC's with ozone in a dark chamber. Each experiments uses a different combinations of the following parameters:

- Parent HC (3):



cyclohexene, 1-tetradecene, methylene-cyclopentane

- Initial HC concentration (2-4): {100, 200 ppb} <u>or</u> {50, 100, 200, 400 ppb}
- Chamber RH/Seed state (3): dry chamber / dry seed; humid chamber < RHD / dry seed; humid chamber > RHD / aqueous seed
- Seed species (4): $(NH_4)_2SO_4$, NH_4HSO_4, $CaCl_2$, NaCl *
- Temperature (2): 20 ϒC, 30 ϒC



** Cocker et al. (2001): seed type does not affect SOA if chamber is dry

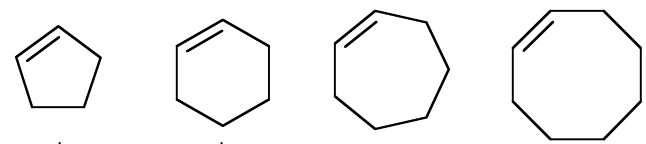
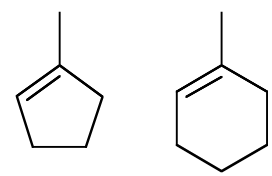
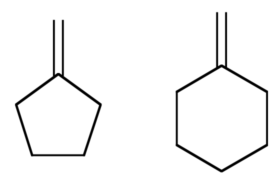
** Cocker et al. (2001): water uptake does not depend on seed type if seed is undeliquesced

** Argument from curves in Cocker et al. (2001): yield curve shape stays the same, so we will not need as many points to map out entire curve for every condition. We will use 2 points to get the scaling.

Experimental Protocols (Phase 2)

Phase 2: *Chemistry of the reactive organic gas*

Perform a series of HC + ozone experiments in a dark chamber with dry environment and one type of seed to study how the aerosol yield varies with HC structure. Parameters to vary:

- Parent HC (8):
  - Effect of number of carbon atoms: 
  - Steric effect: 
  - Effect of double bond position: 
  - Other possibilities: effect of HC shape, effect of ring-breaking vs. staying intact, effect of conjugated double bonds, etc.
- Initial HC concentration (3)
- Temperature (2)