Chemistry of Secondary Organic Aerosol Formation from the Oxidation of Aromatic Hydrocarbons

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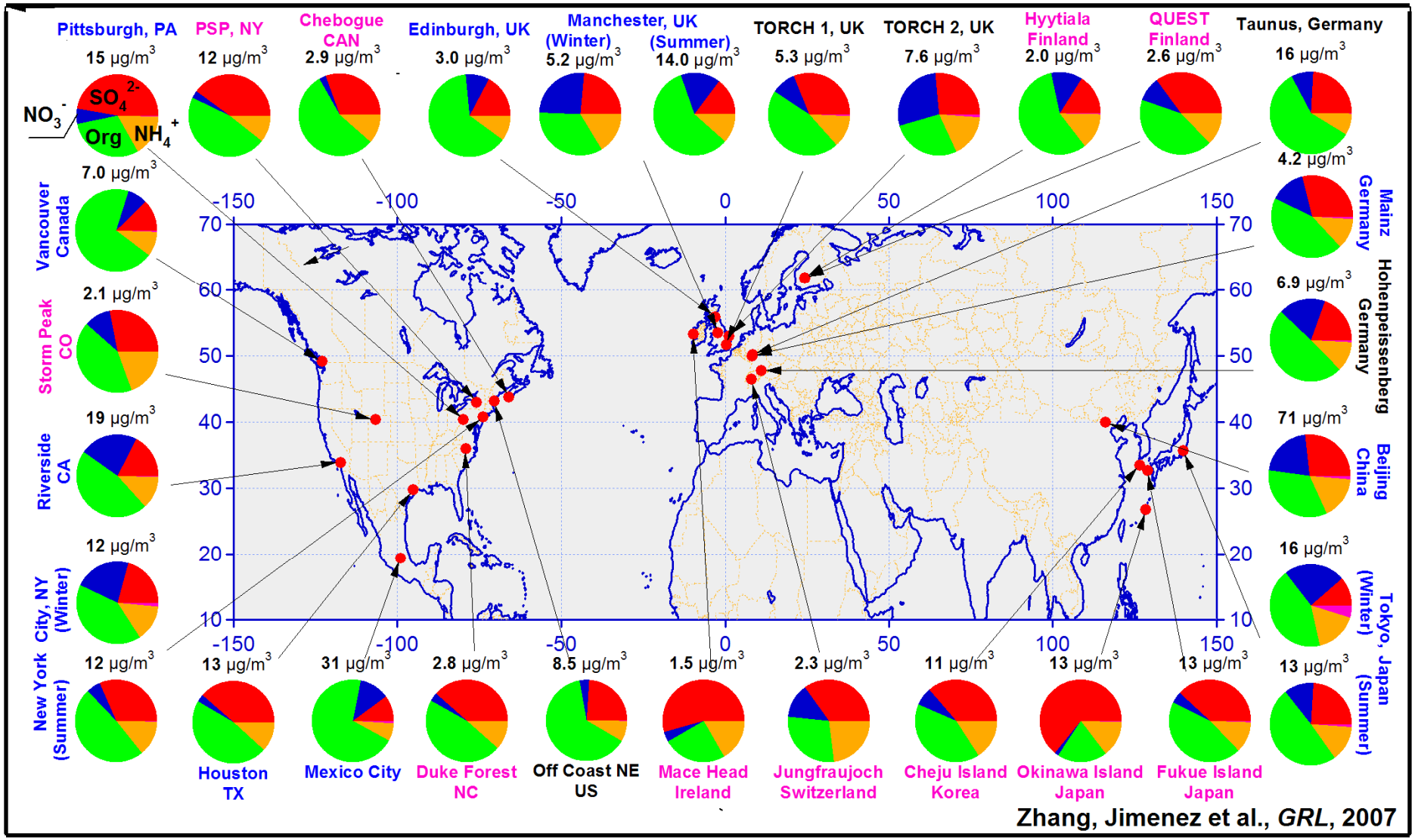
Outline

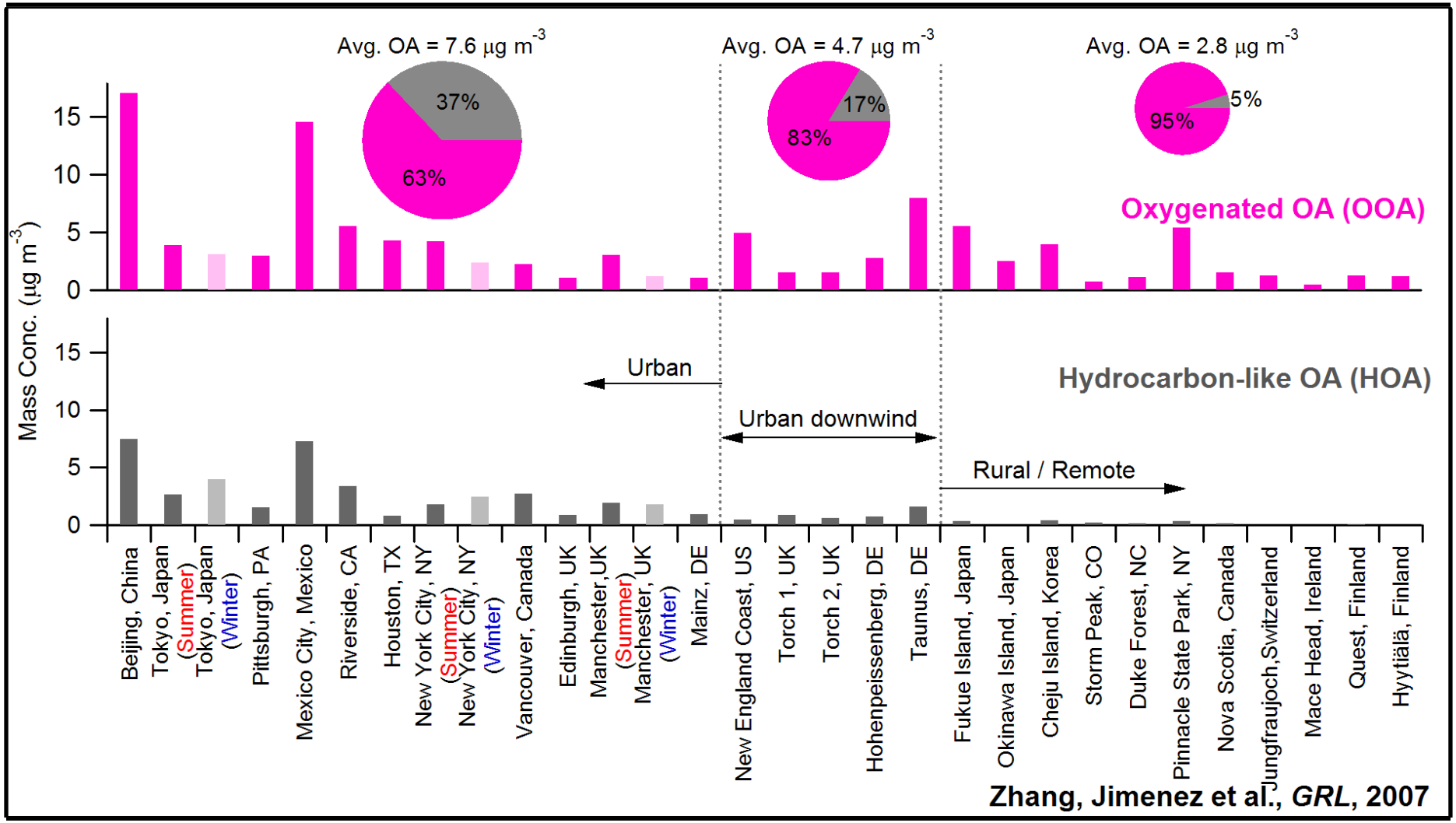
- Secondary Organic Aerosol (SOA) Background
- Reactions of Aromatic Hydrocarbons + OH Radicals
- Project Objectives
- Experimental Apparatus and Methods
- Expected Results

Ambient Organic Aerosol

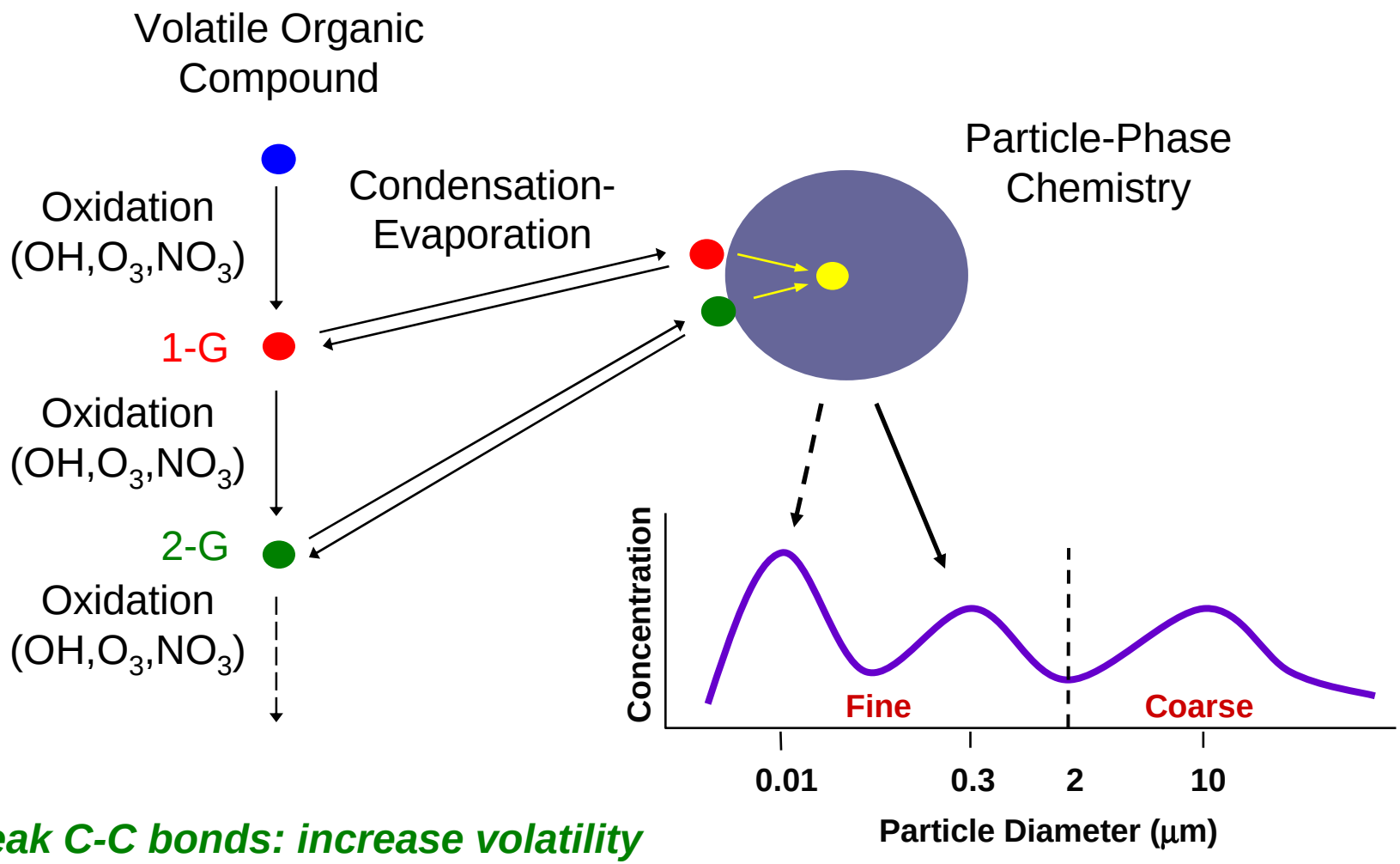


Zhang, Jimenez et al., *GRL*, 2007

Ambient Secondary Organic Aerosol



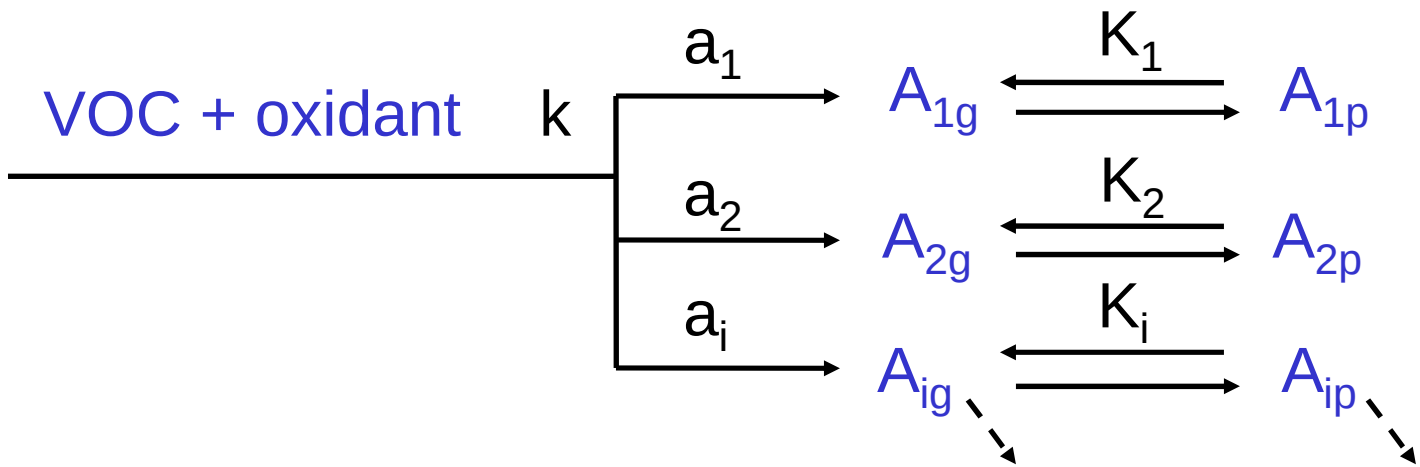
Secondary Organic Aerosol Formation



Break C-C bonds: increase volatility

Add functional groups: decrease volatility

Modeling Secondary Organic Aerosol Formation



more gas- and particle-phase reactions

$$\text{Yield} = C_{pom}\ (\mu g\ m^{-3})/\Delta[VOC]\ (\mu g\ m^{-3})$$

A_i mass yield

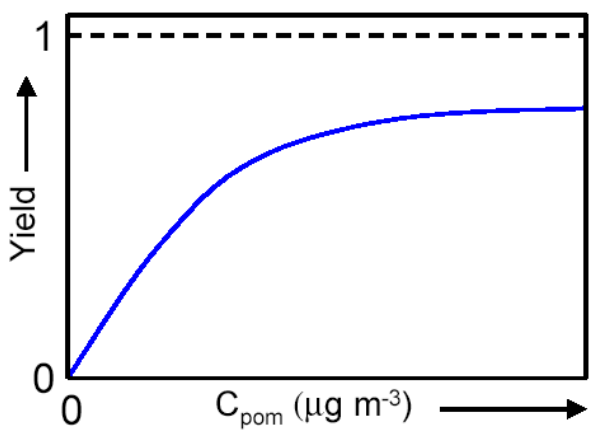
$$\text{Yield} = \sum Y_i = \sum b_i\ [1 + M_{pom}\gamma P_i^o/RTC_{pom}]^{-1}$$

Fraction in particles

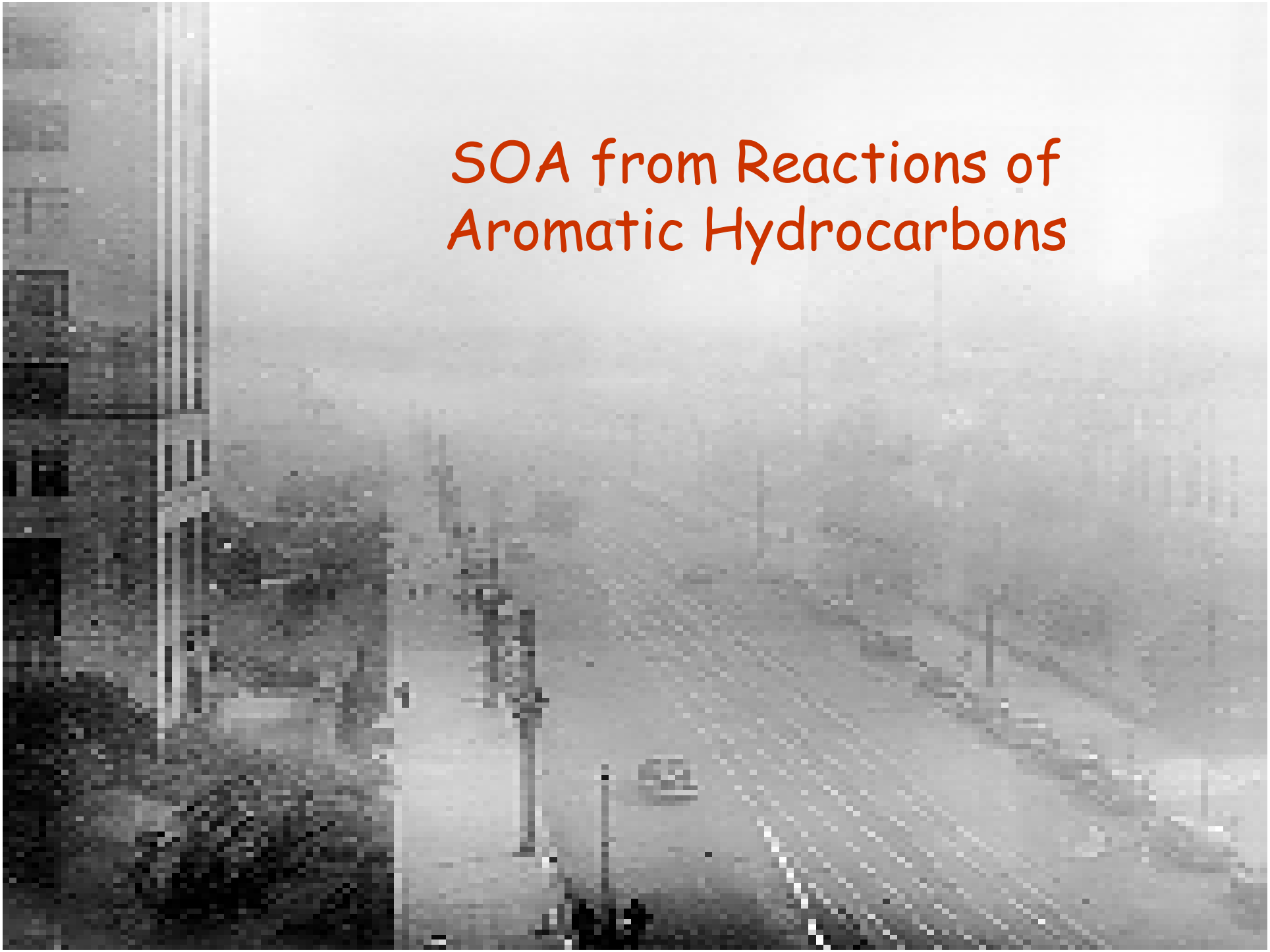
$$a_i = [A_{1g} + A_{1p}]/\Delta[VOC]\ \text{(molar yield)}$$

$$b_i = a_i[MW_{Ai}/MW_{VOC}]\ \text{(mass yield)}$$

$$K_i = RT/M_{pom}\gamma P_i^o$$

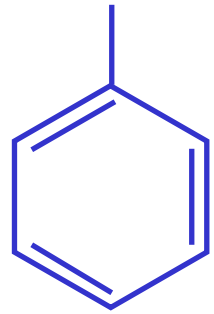


SOA from Reactions of Aromatic Hydrocarbons

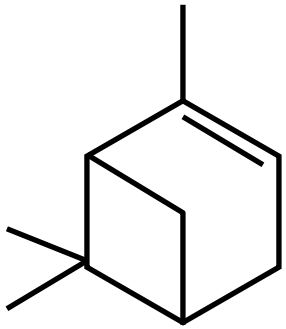


Major Organic Compound Classes

Alkanes
(*n*-decane)



Aromatics
(toluene)



Alkenes/Monoterpenes
(α-pinene)

Major source of urban SOA

Major source of global SOA

Models
(using Caltech SOA yields)

Urban Areas

Alkanes ~40%
Aromatics ~20-30%
Alkenes ~10%
Oxygenates & Unidentified

Atmospheric Chemical Lifetimes of Hydrocarbons

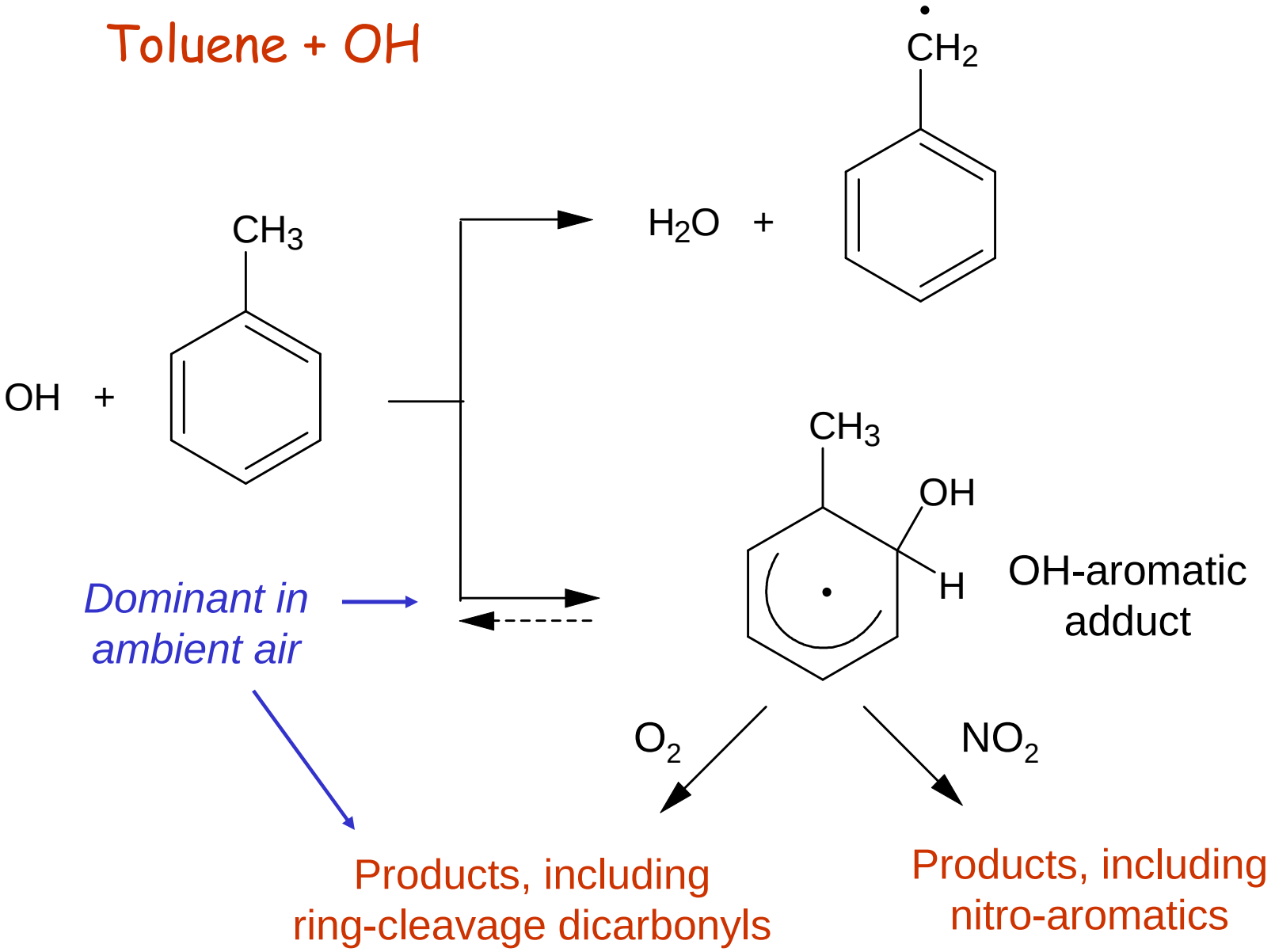
	Lifetimes		
Hydrocarbon	OH	NO_3	O_3
n-decane	1.1 d	240 d	>4500 y
toluene	2.1 d	1.8 y	>4.5 y
α-pinene	2.7 h	5.4 min	4.7 h

[OH] = 12-h daytime ave. = 2.0×10^{6} molecules cm^{-3} (0.08 pptv)

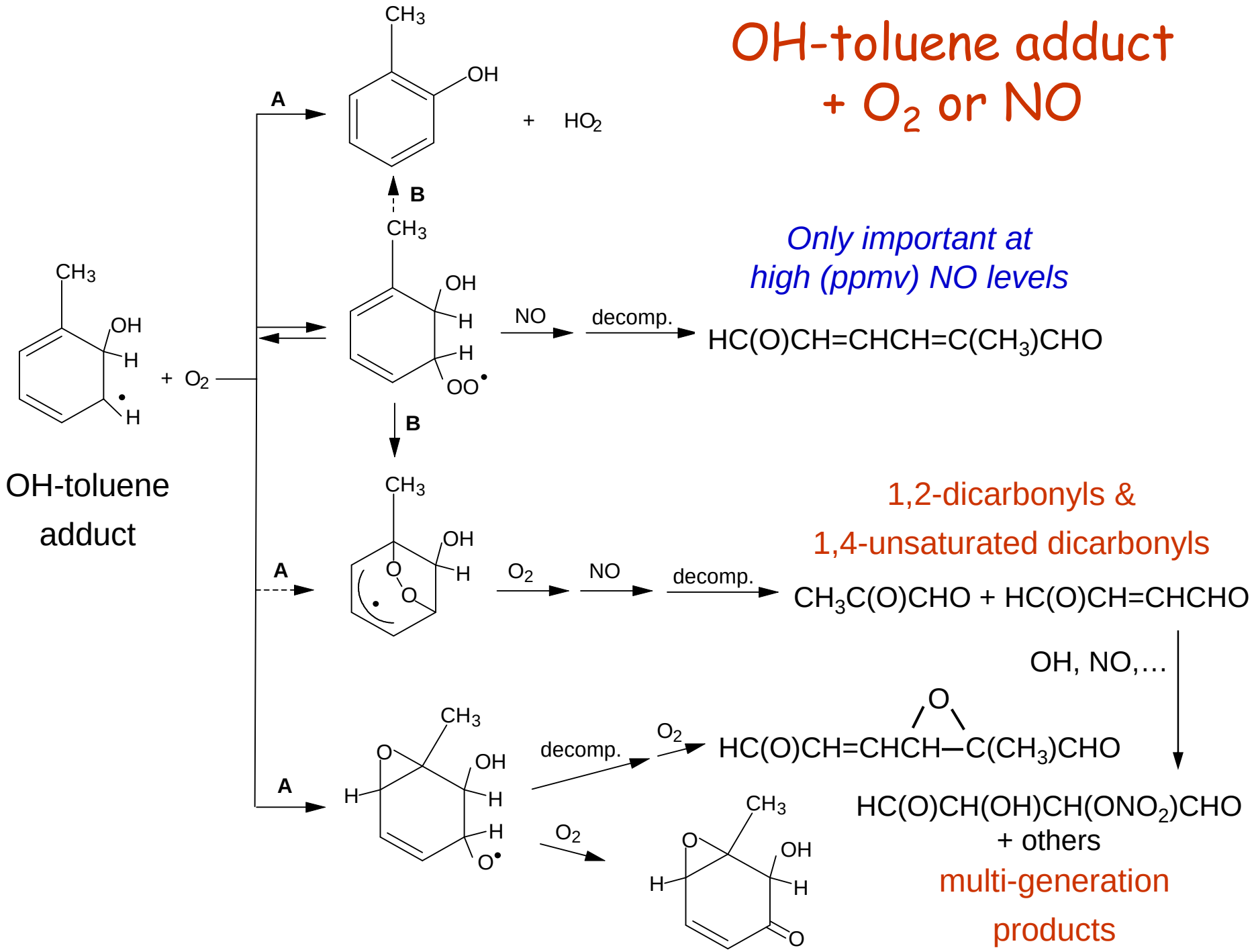
$[O_3]$ = 24-h ave. = 7×10^{11} molecules cm^{-3} (30 ppbv)

$[NO_3]$ = 12-h nighttime ave. = 5×10^{8} molecules cm^{-3} (20 pptv)

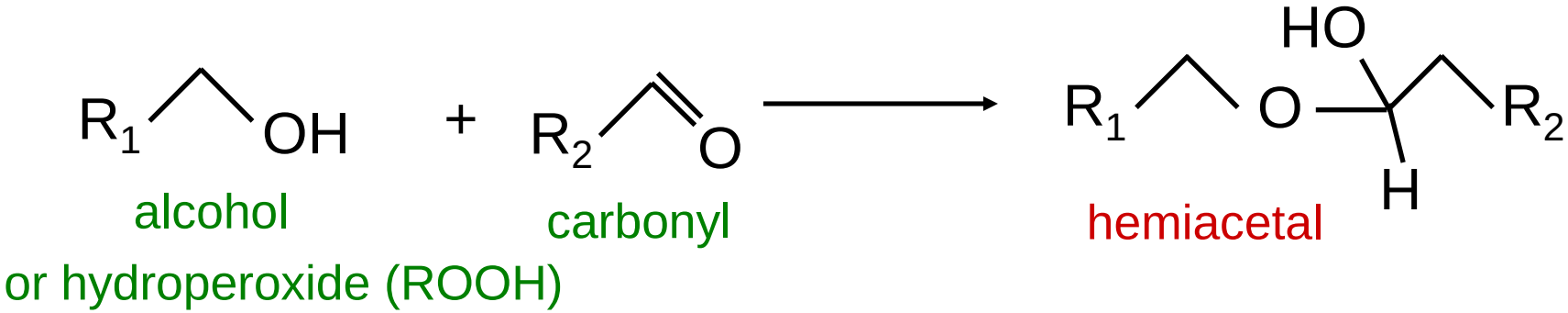
Toluene + OH

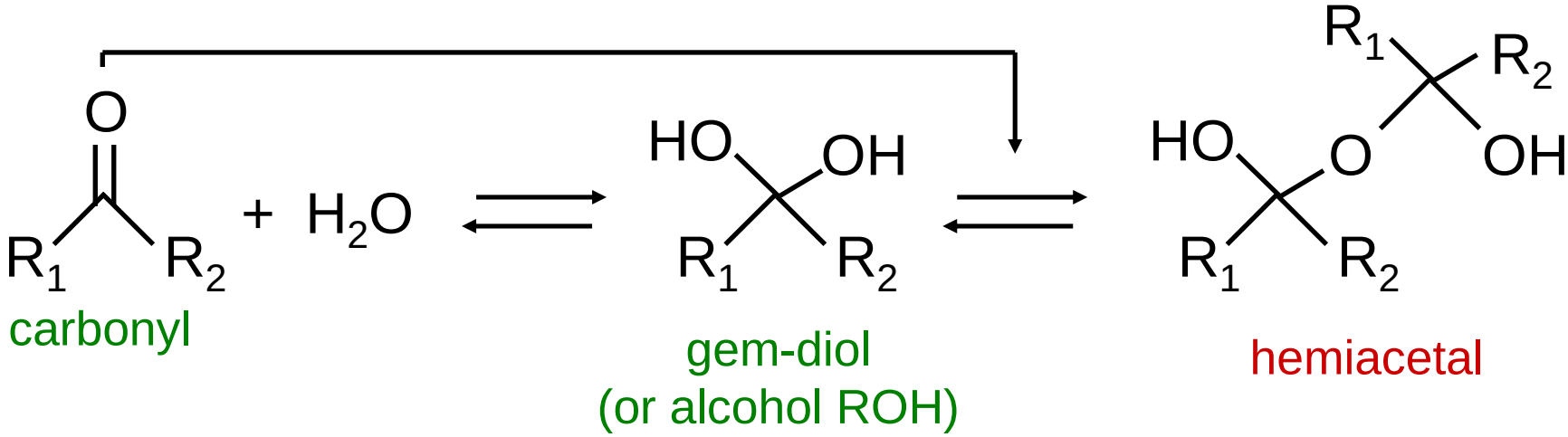

CH2
H2O +
CH3
OH +
CH3
OH
H
OH-aromatic adduct
Dominant in ambient air
O2
NO2
Products, including ring-cleavage dicarbonyls
Products, including nitro-aromatics

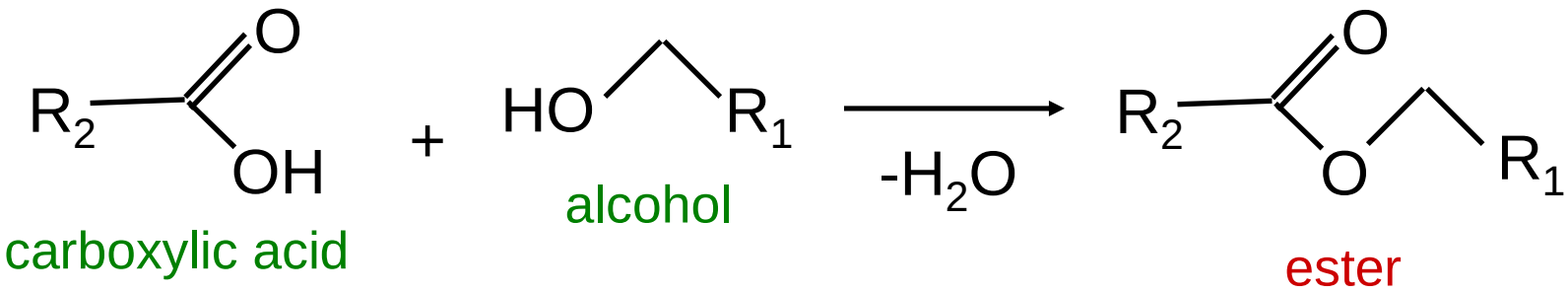
OH-toluene adduct + O_2 or NO



Oligomer Formation



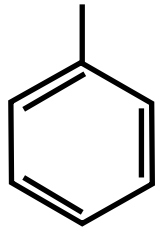




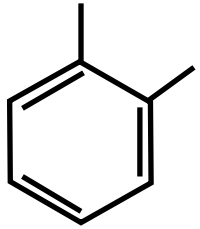
Project
Objectives

Project Objectives

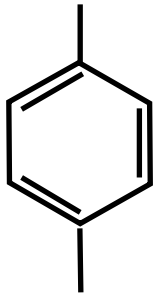
- Identify and quantify first- and multi-generation gas-phase and SOA products and rates of formation from OH radical-initiated reactions for the following systems:



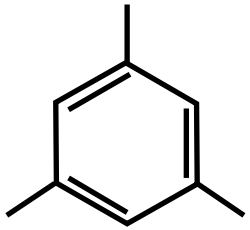
toluene



m-xylene



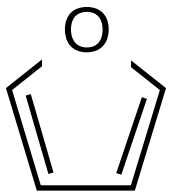
p-xylene



1,3,5-trimethyl benzene

$CH_3C(O)CH{=}CHC(O)CH_3$

$R_1CH{=}CHR_2CH{=}CHR_3$



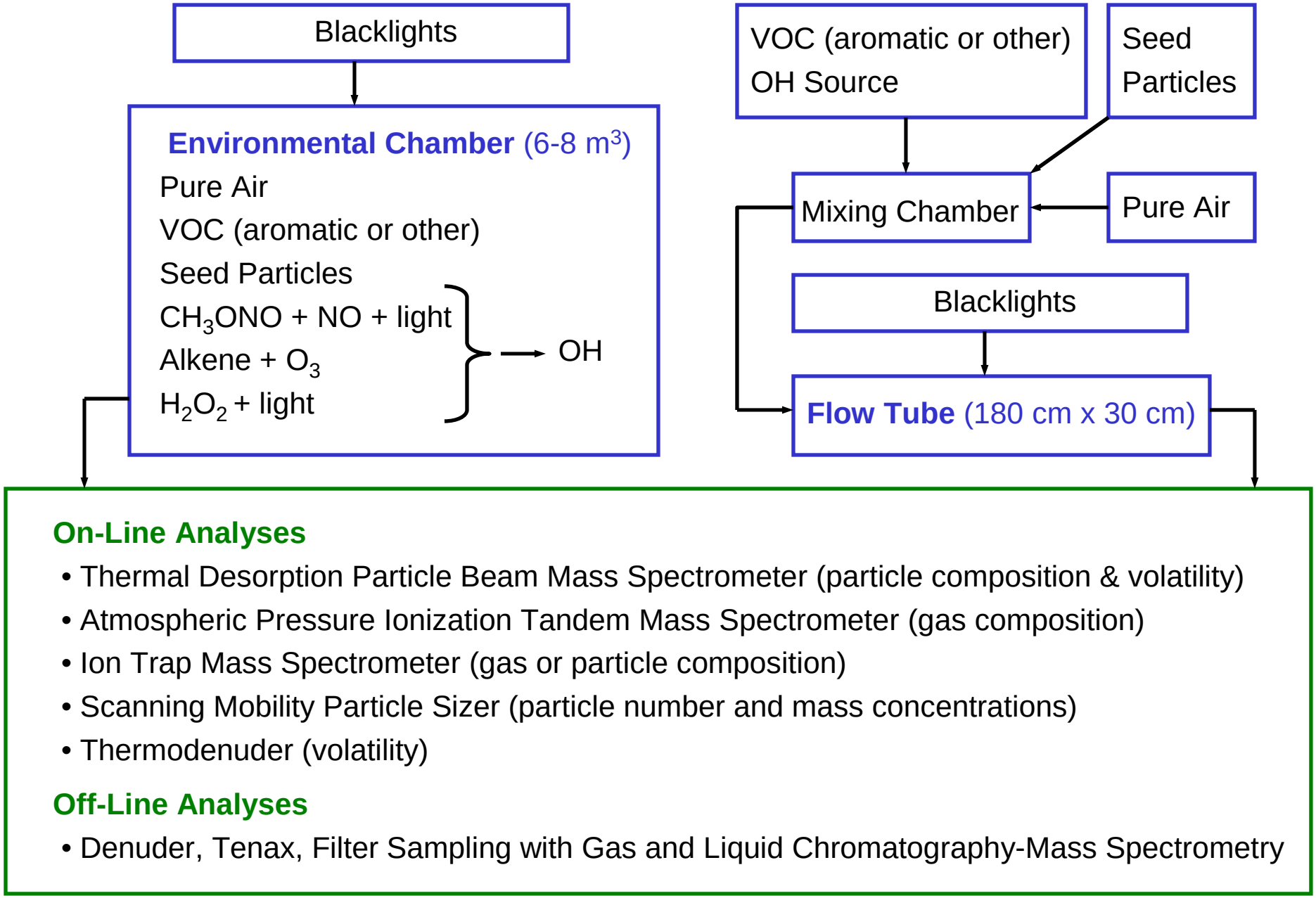
furan

- Effects of NO_x

- Effects of humidity, particle acidity, ammonia, other VOCs

Experimental Apparatus & Methods

Experimental Apparatus & Methods



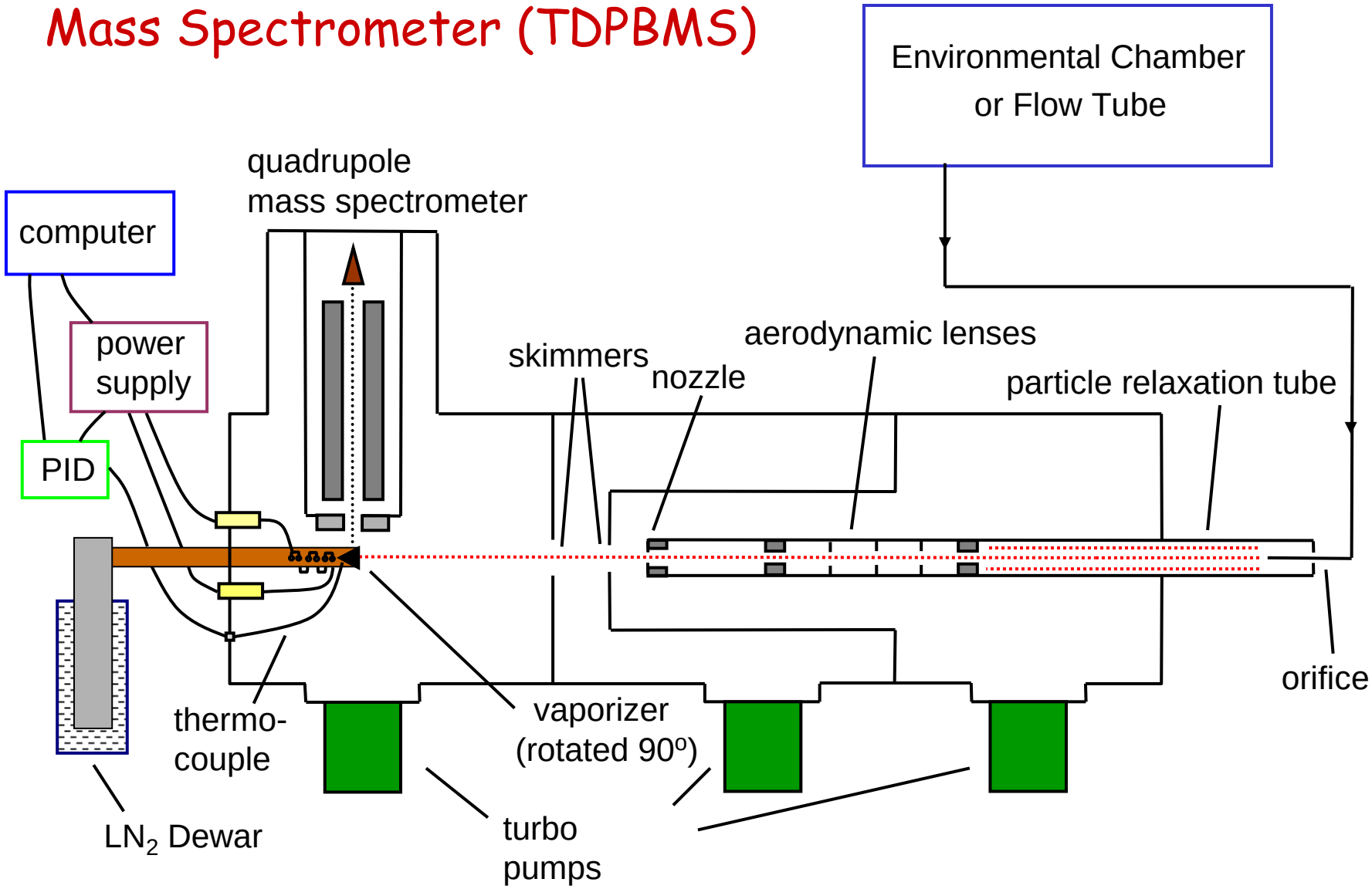
On-Line Analyses

- Thermal Desorption Particle Beam Mass Spectrometer (particle composition & volatility)
- Atmospheric Pressure Ionization Tandem Mass Spectrometer (gas composition)
- Ion Trap Mass Spectrometer (gas or particle composition)
- Scanning Mobility Particle Sizer (particle number and mass concentrations)
- Thermodenuder (volatility)

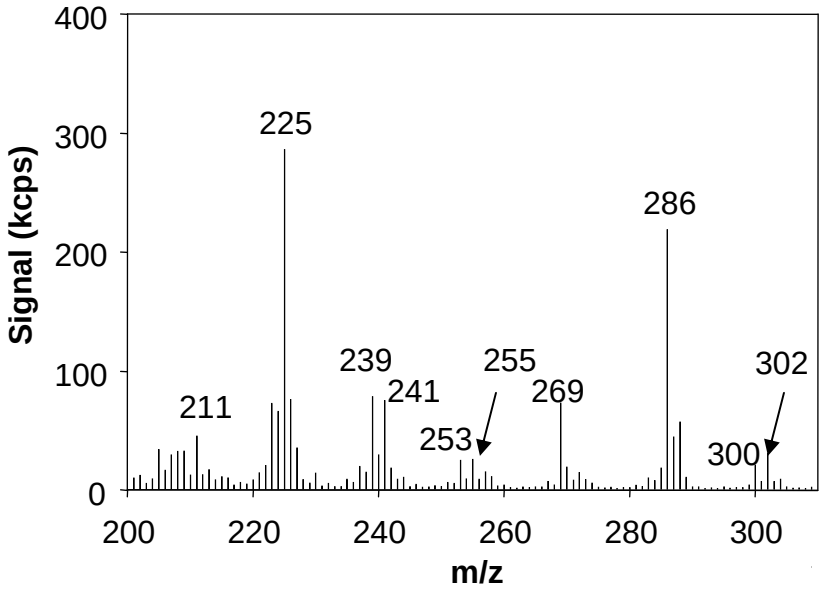
Off-Line Analyses

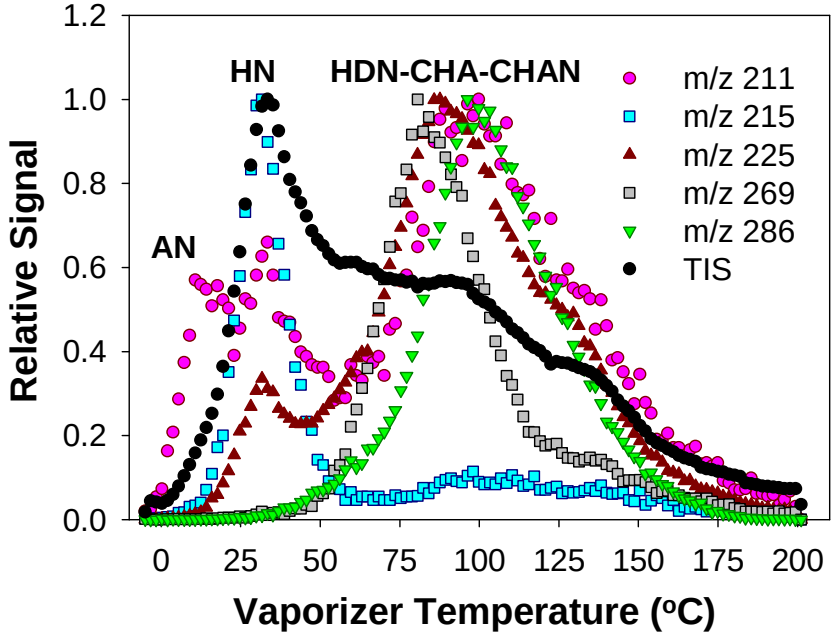
- Denuder, Tenax, Filter Sampling with Gas and Liquid Chromatography-Mass Spectrometry

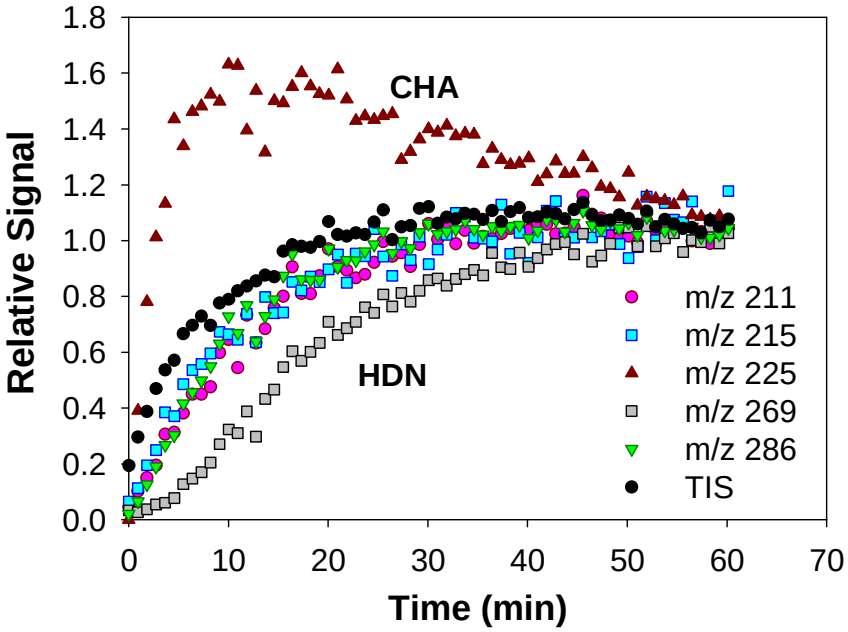
Thermal Desorption Particle Beam Mass Spectrometer (TDPBMS)



SOA Mass Spectra and Desorption Profiles from Pentadecane + OH/NO_x



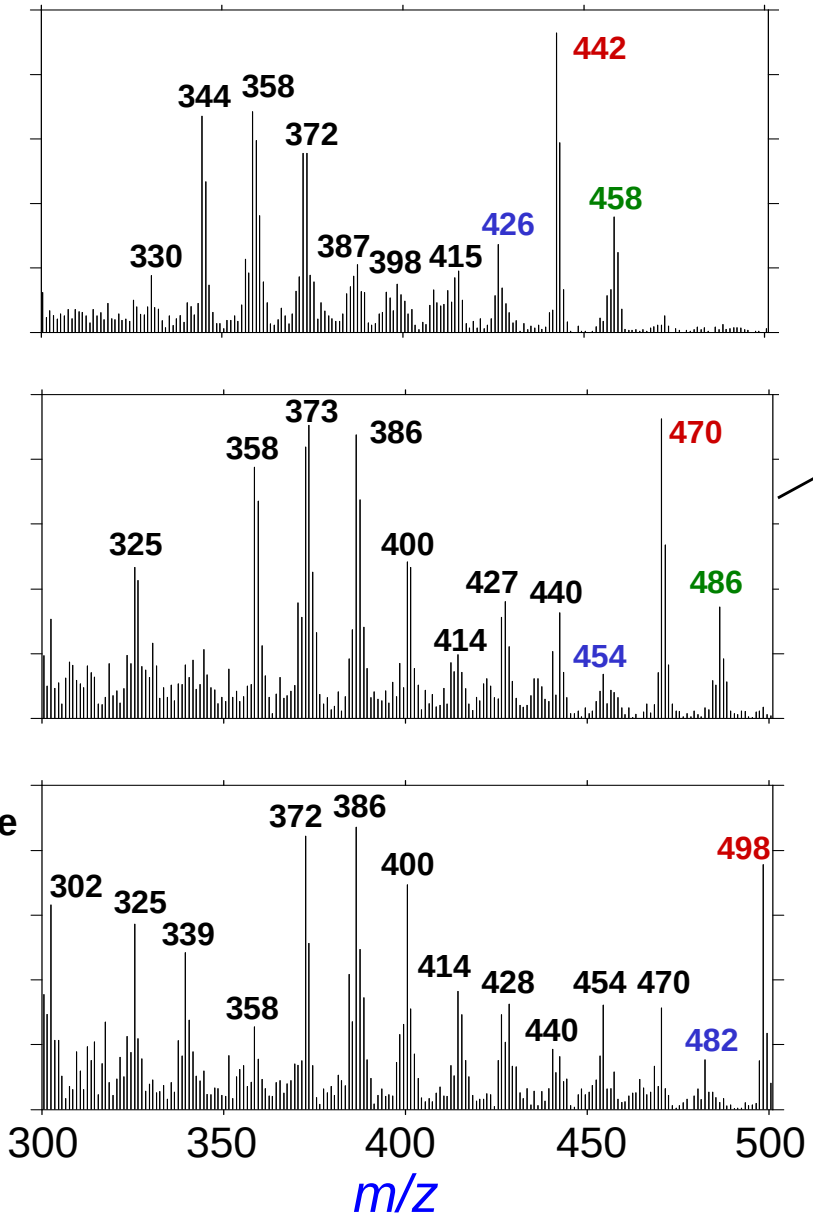




High MW SOA Products from 1-Alkenes + OH/NO_x

1-tridecene

C_{13} MW =182

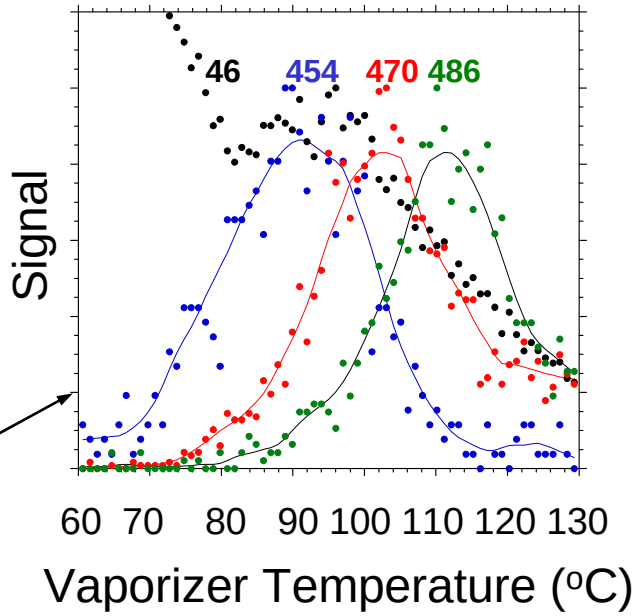


1-tetradecene

C_{14} MW =196

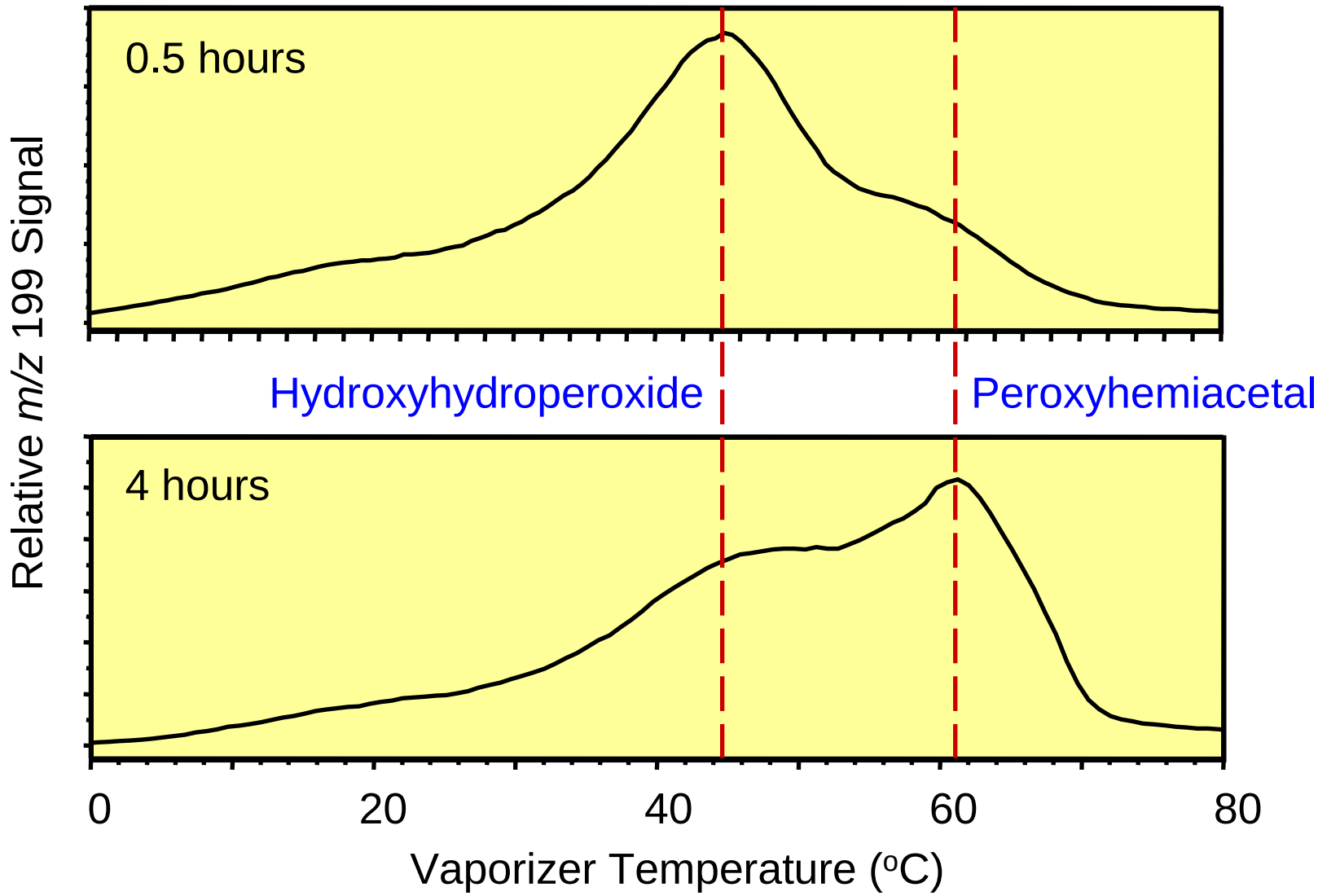
1-pentadecene

C_{15} MW =210

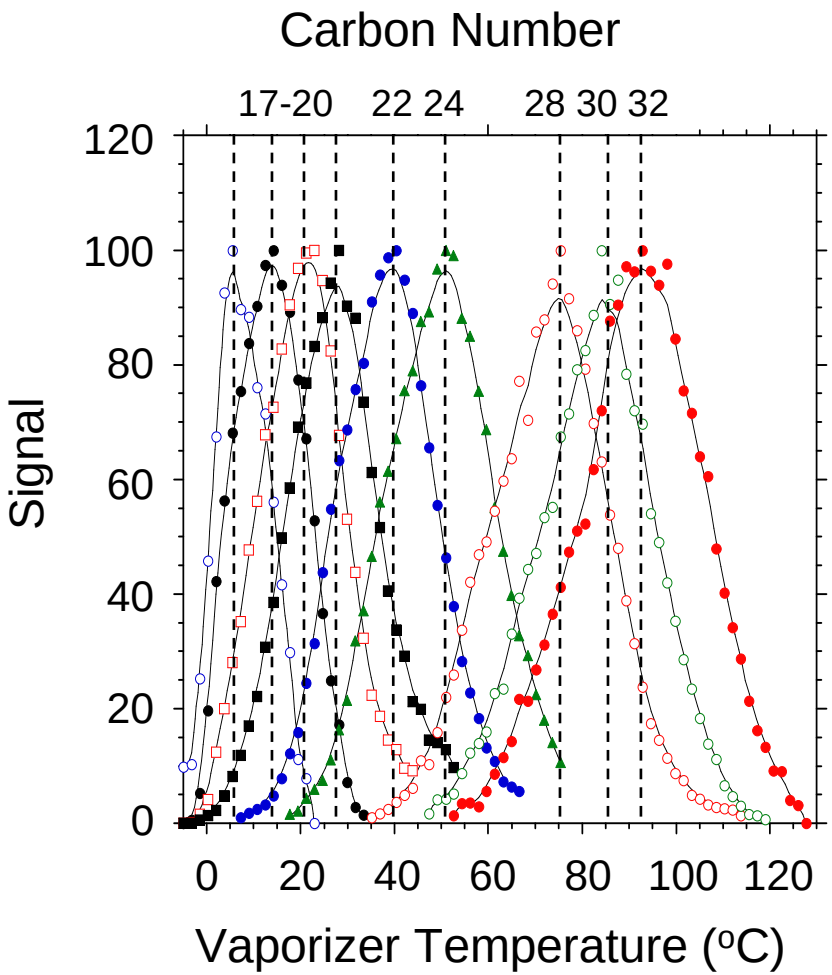


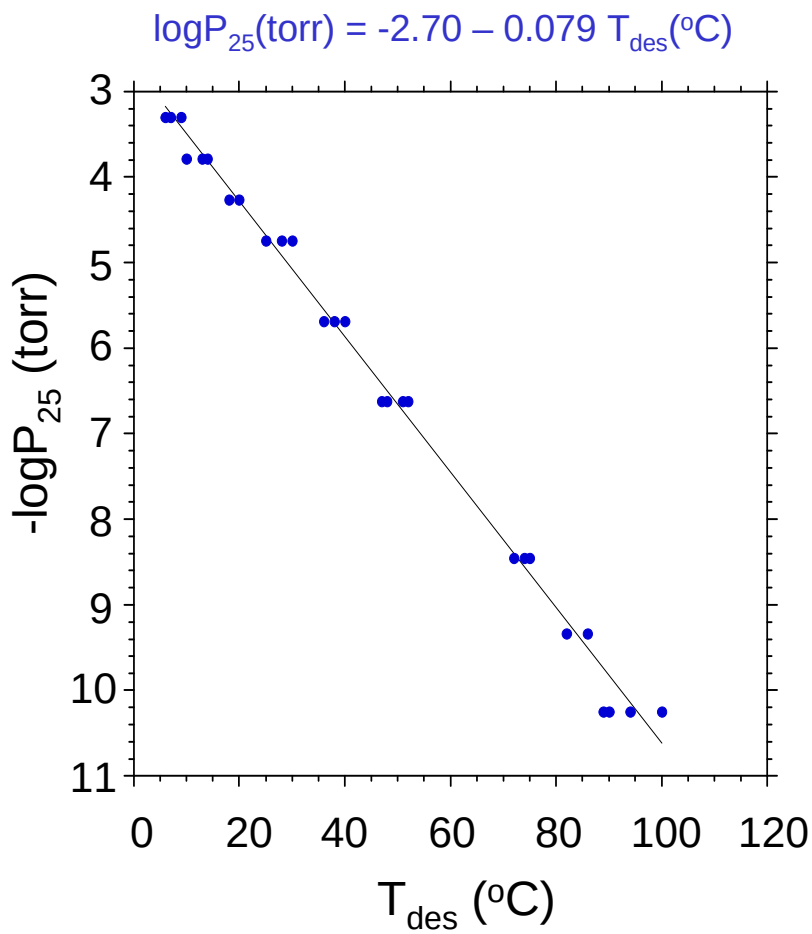
	C13	C14	C15
Δ14	344	358	372
Δ28	426	454	482
Δ28	442	470	498
Δ28	458	486	[514]

SOA Desorption Profiles from 1-Tetradecene + O_3

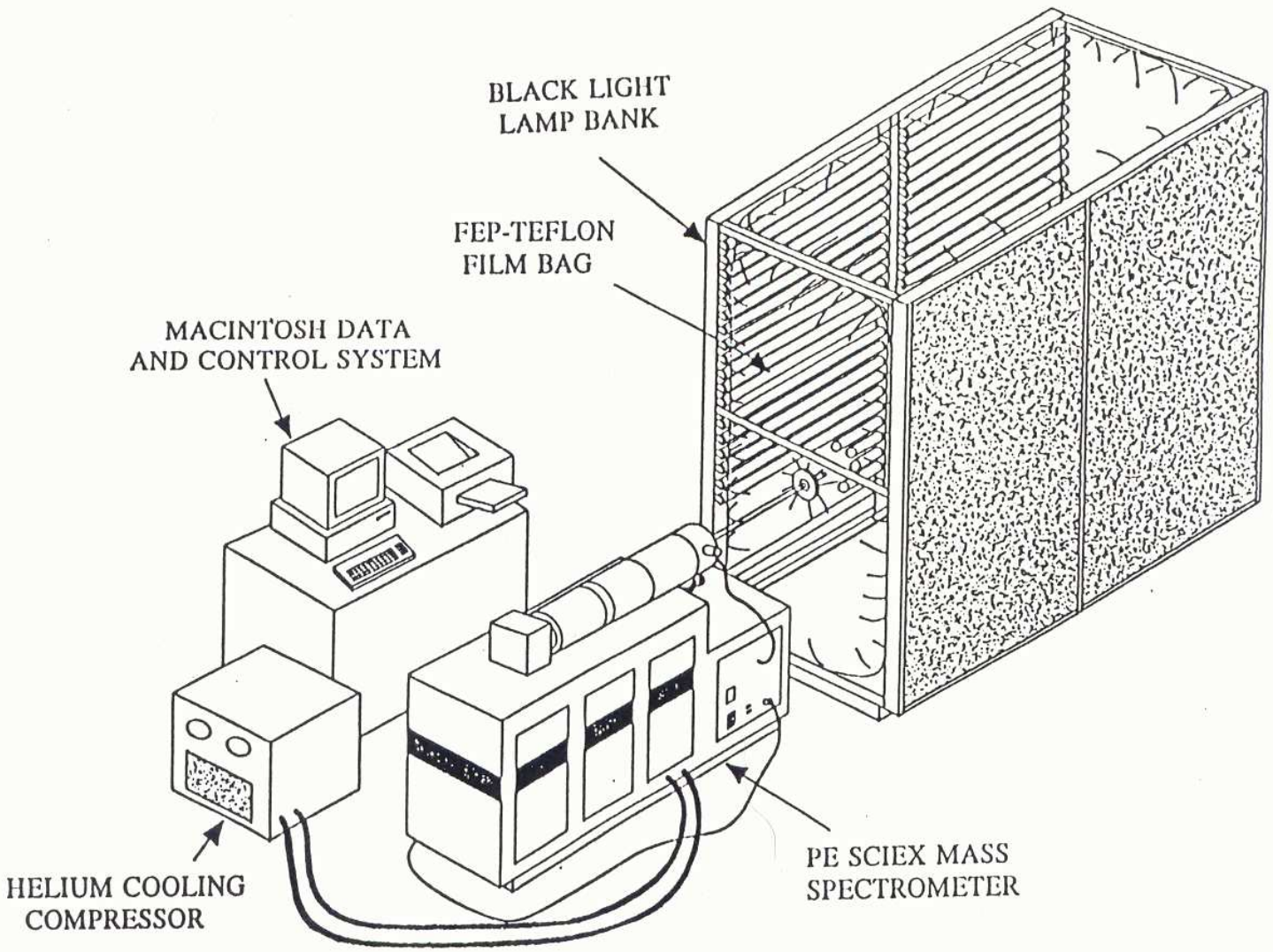


Desorption Profiles and Vapor Pressures of *n*-Alkanes





Atmospheric Pressure Ionization-Tandem Mass Spectrometer (API-TMS)



Gas-Phase Carbonyls from Aromatics + OH/NO_x

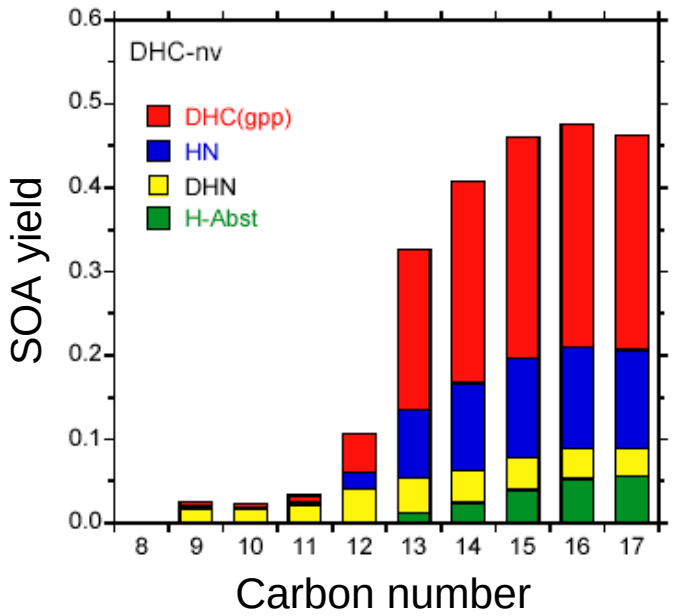
- 7000 L Teflon chamber
- $[aromatic]_0$, $[CH_3ONO]_0$, $[NO]_0$ = 1ppmv
- 19-27% aromatic reacted
- $[NO_2]_f$ = 0.4-0.8 ppmv
- [aromatics]: Tenax w/GC-FID
- [carbonyls]: PBFHA derivatives from coated XAD-4 resin denuder, solvent extraction, GC-MS with positive CI.

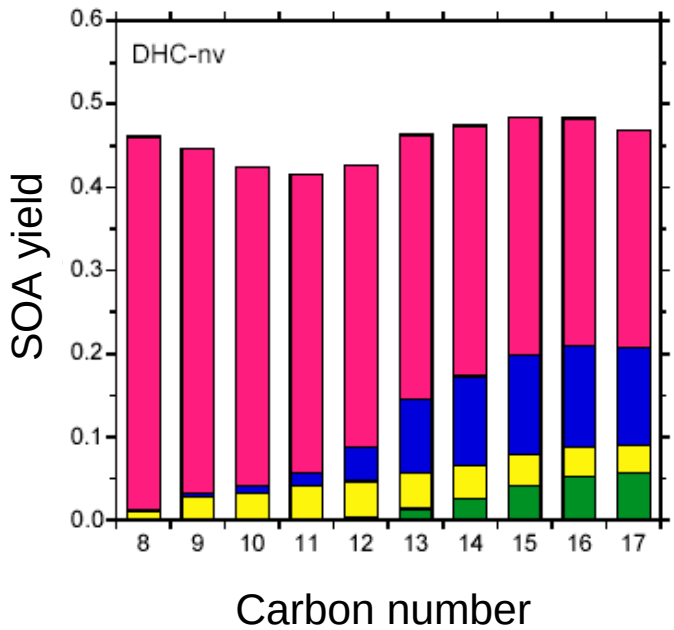
- All predicted 1,2-dicarbonyls and 1,4-unsaturated* dicarbonyls detected
- When scaled to literature yields for 1,2-dicarbonyls get ~60-70% mass balance

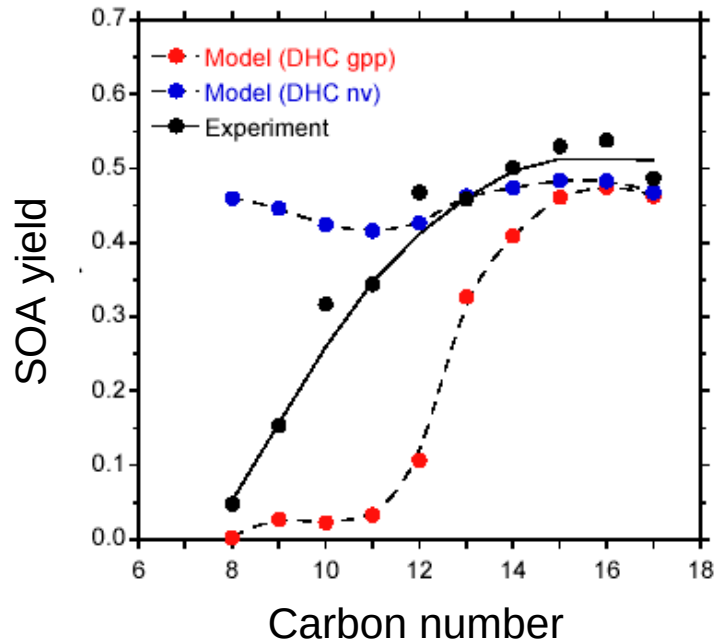
Identified 1,2-Dicarbonyls and 1,4-Unsaturated Dicarbonyls

ring-opened product	toluene	xylene			trimethylbenzene		
		o-	*m*-	*p*-	1,2,3-	1,2,4-	1,3,5-
$(CHO)_2$	X	X	X	X	X	X	
$CH_3C(O)CHO$	X	X	X	X	X	X	X
$CH_3C(O)C(O)CH_3$		X			X	X	
$HC(O)CH{=}CHCHO$	X	X					
$CH_3C(O)CH{=}CHCHO$	X	X	X		X		
$HC(O)C(CH_3){=}CHCHO$	X		X	X		X	
$CH_3C(O)C(CH_3){=}CHCHO$		X			X	X	
$CH_3C(O)CH{=}C(CH_3)CHO$			X			X	X
$CH_3C(O)CH{=}CHC(O)CH_3$				X		X	
$HC(O)C(CH_3){=}C(CH_3)CHO$[a]		a				a	
$CH_3C(O)C(CH_3){=}C(CH_3)CHO$					X		
$CH_3C(O)C(CH_3){=}CHC(O)CH_3$						X	

Modeling and Measurements of SOA from 1-Alkenes + OH/NO_x







Expected Results

- Identity and quantity of gas-phase and particle-phase reaction products and rates of formation for aromatics + OH
- Effects of NO_x, humidity, particle acidity, ammonia, VOCs
- Quantitative gas-phase reaction mechanisms
- Quantitative particle-phase reaction mechanisms
- Estimated product vapor pressures
- Models with reaction mechanisms and vapor pressures compared with laboratory results
- Experimental and modeling results provided to scientific community for development of regional and global models of atmospheric chemistry of aromatic hydrocarbons and SOA formation