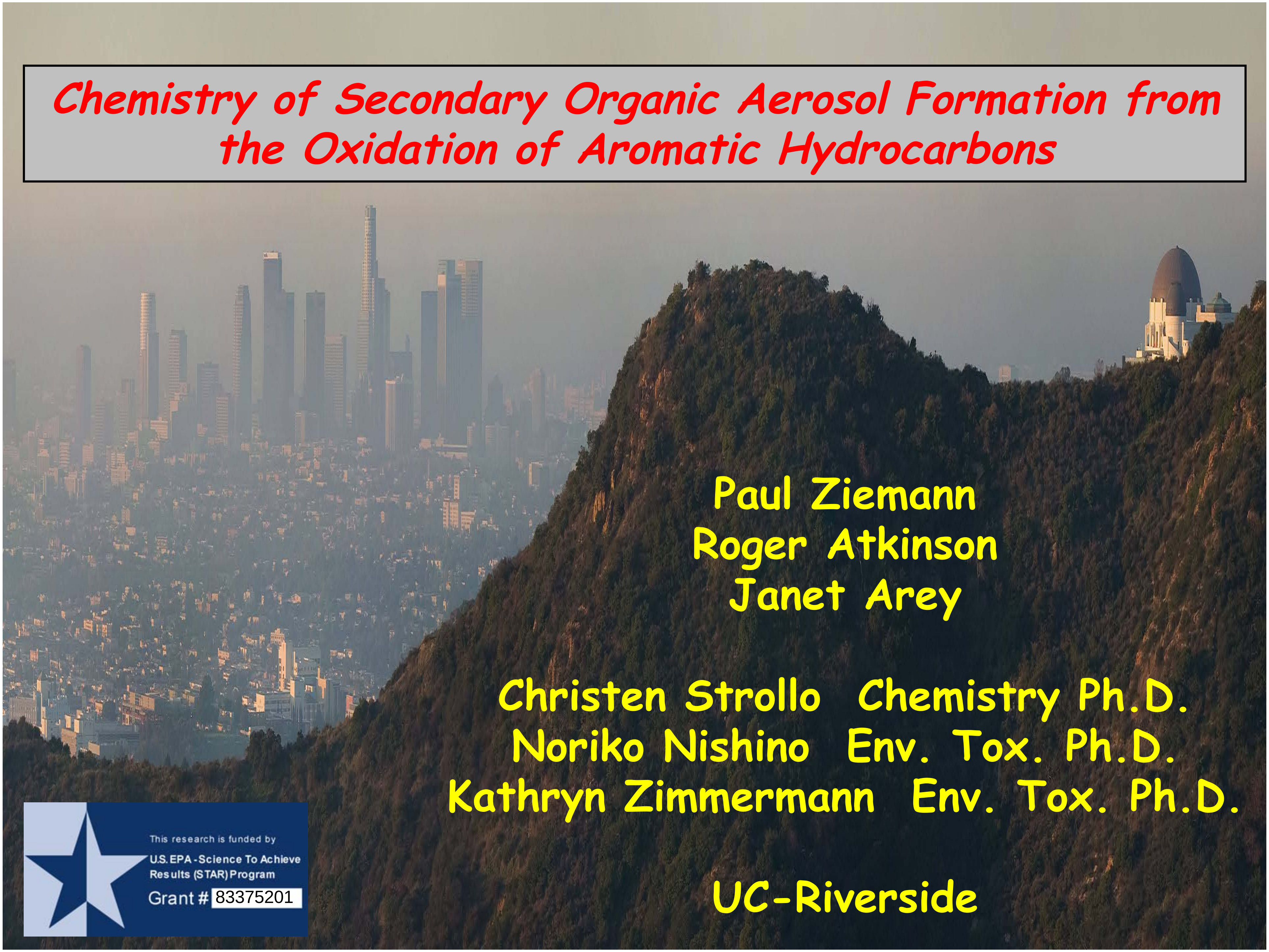
Chemistry of Secondary Organic Aerosol Formation from the Oxidation of Aromatic Hydrocarbons



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UC-Riverside

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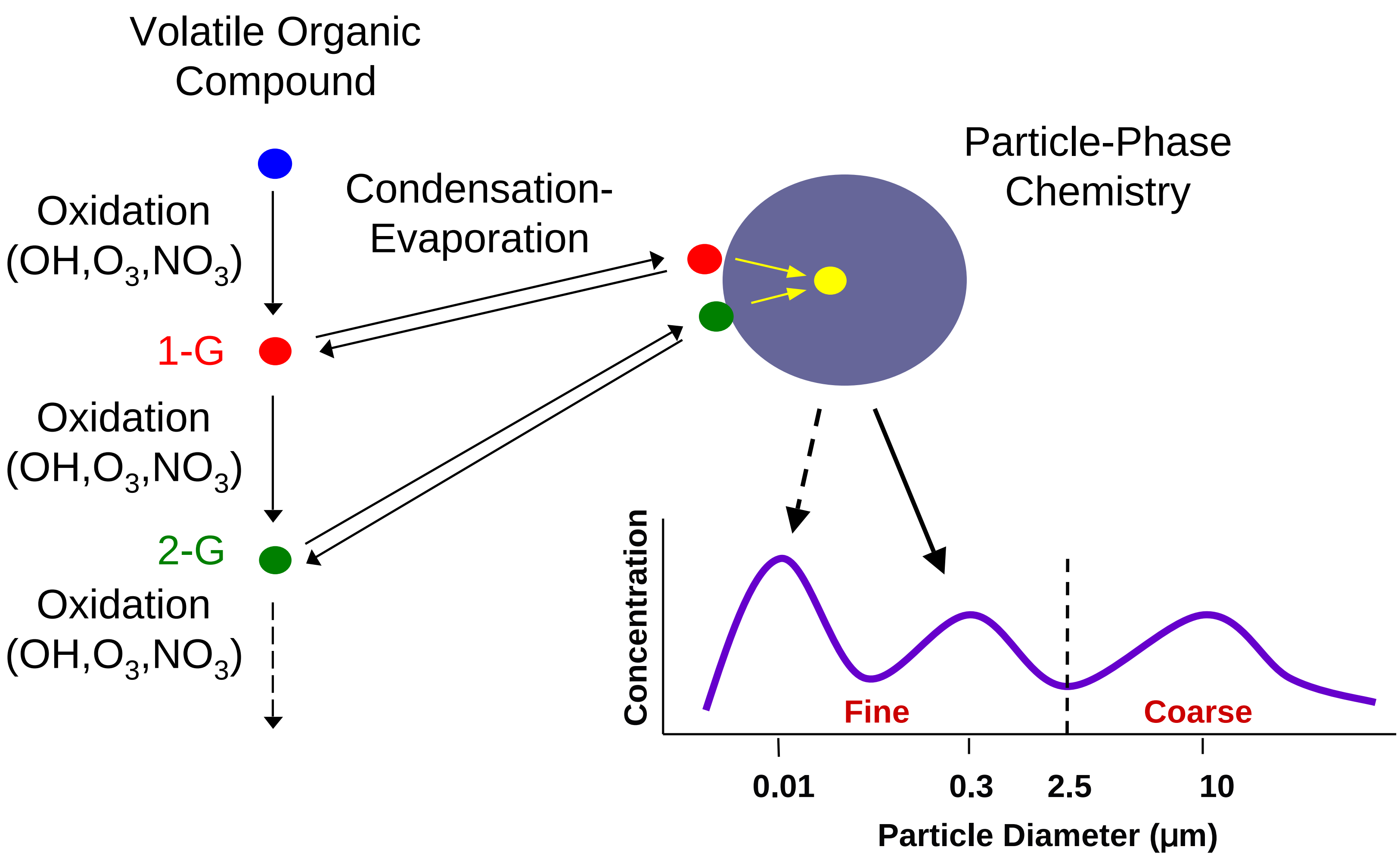
Outline

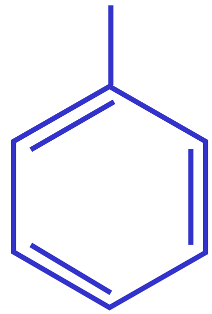
- Background
- Project Objectives & Expected Results
- Experimental Apparatus and Methods
- Reactions of Aromatic Hydrocarbons + OH Radicals
- Results
- Future Plans

Secondary Organic Aerosol (SOA) Formation

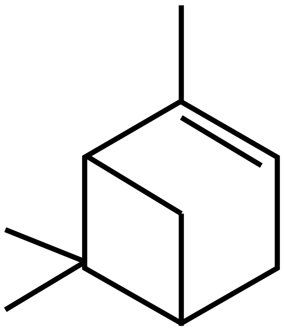


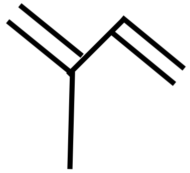
Major Organic Compound Classes

Alkanes
(*n*-decane)



Aromatics
(toluene)





Alkenes
(α-pinene & isoprene)

Major anthropogenic sources of SOA

Major biogenic sources of SOA

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

Atmospheric Chemical Lifetimes of Hydrocarbons

Hydrocarbon	Lifetimes OH	NO_3	O_3
n-decane	1.1 d	240 d	>4500 y
toluene	2.1 d	1.8 y	>4.5 y
m-xylene	6.0 h	180 d	> 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)

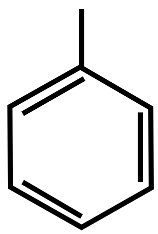
$[O_3]$ = 24-h ave. = 7×10^{11} molecules cm^{-3} (30 ppbv)

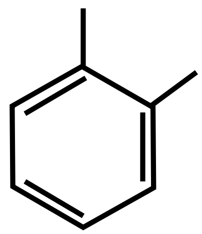
$[NO_3]$ = 12-h nighttime ave. = 5×10^8 molecules cm^{-3} (20 pptv)

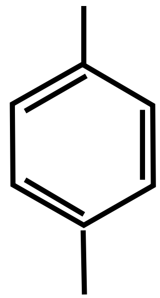

Project Objectives
& Expected Results

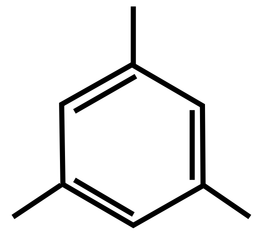
Project Objectives & Expected Results

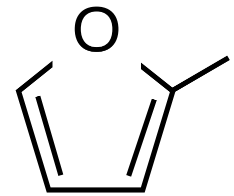
- Identify and quantify first- and multi-generation gas-phase and SOA products and rates of formation from OH radical-initiated reactions for the following systems:


toluene


m-xylene


p-xylene


1,3,5-trimethyl benzene



furans

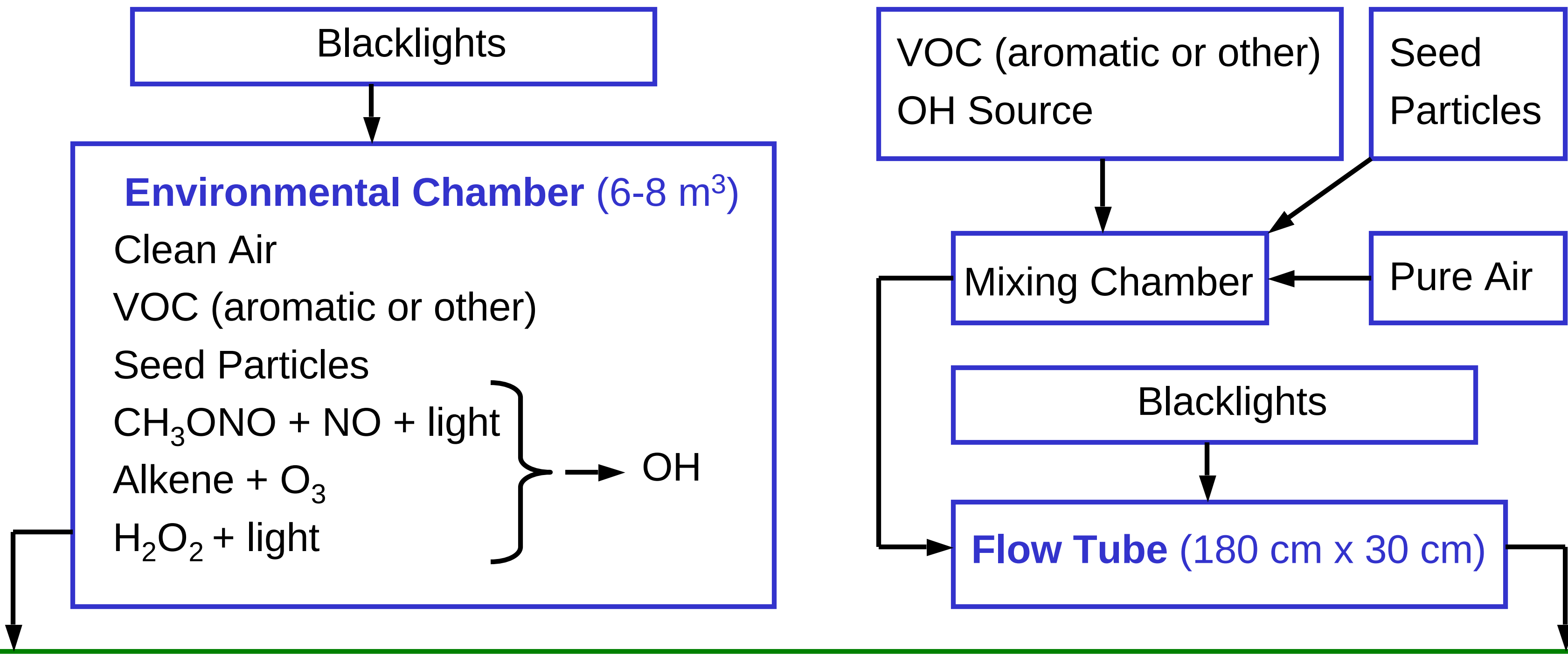
$CH_3C(O)CH{=}CHC(O)CH_3$

$R_1CH{=}CHR_2CH{=}CHR_3$

- Effects of NO_x, RH, particle acidity, NH_3, other VOCs
- Provide quantitative yields & kinetics for development of gas-phase & SOA formation mechanisms for use in atmospheric models

Experimental Apparatus & Methods

Experimental Apparatus & Methods



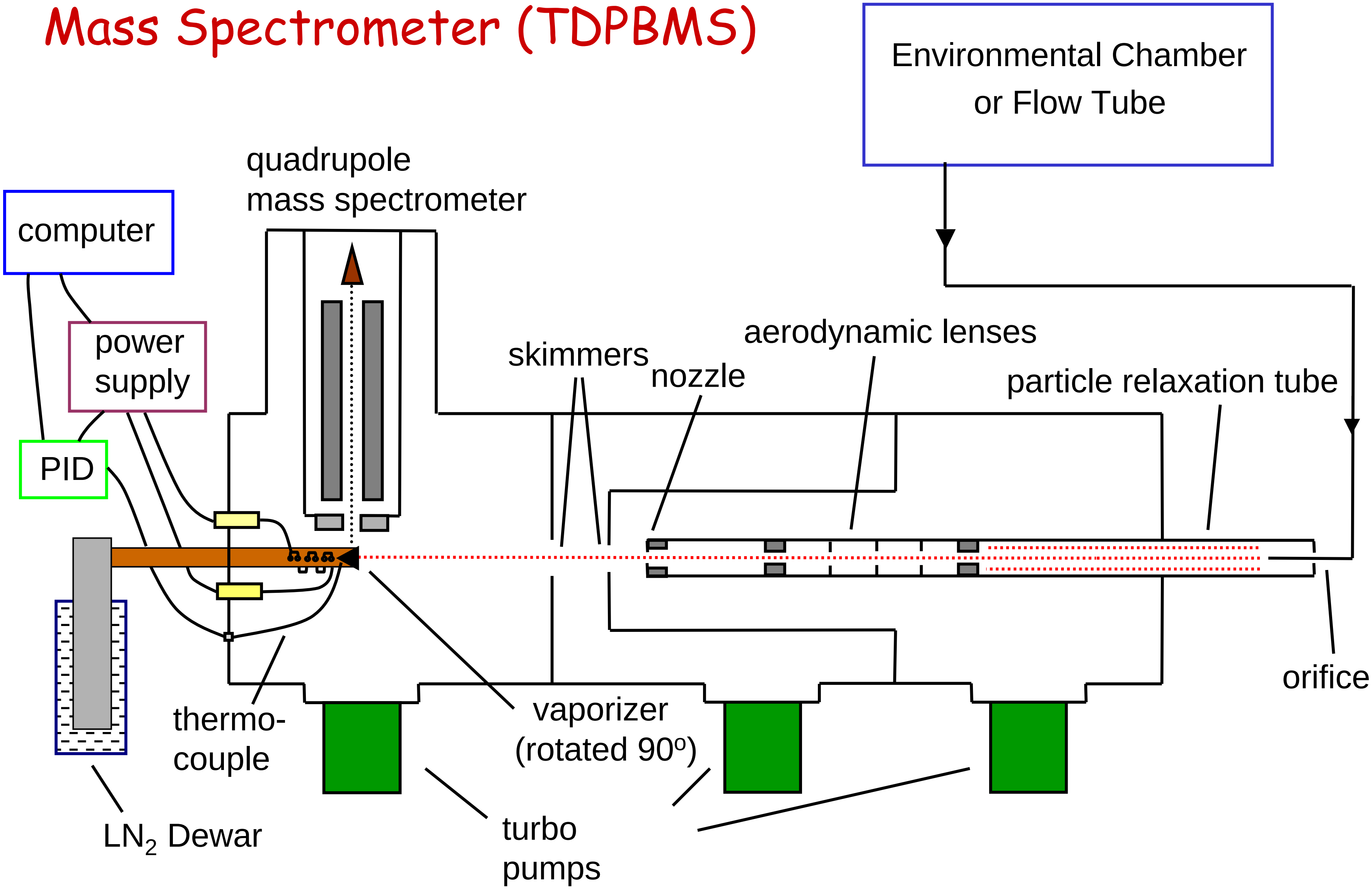
On-Line Analyses

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

Off-Line Analyses

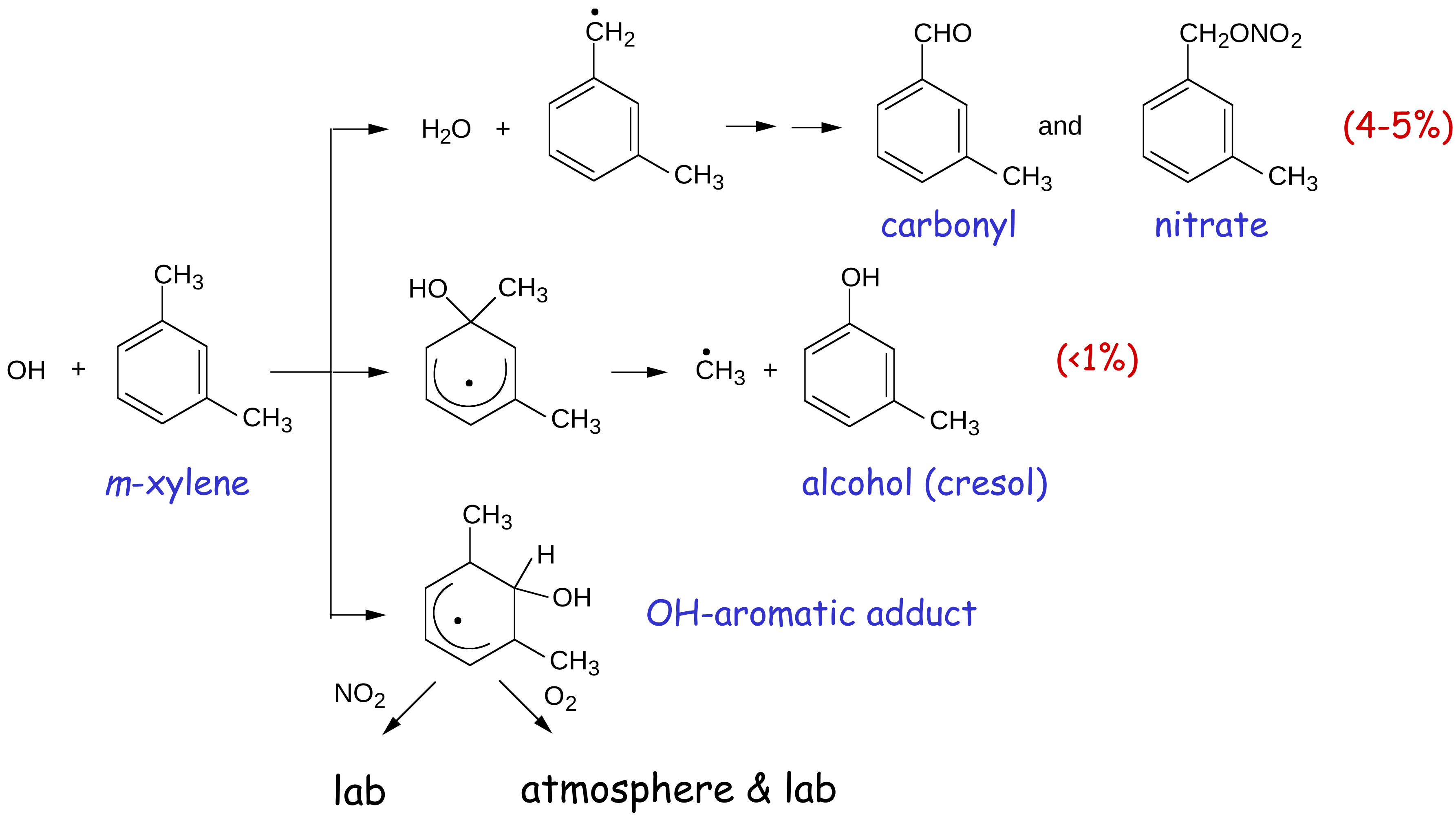
- Denuder (with derivatization), Tenax, Filter Sampling
- Gas and Liquid Chromatography-Mass Spectrometry

Thermal Desorption Particle Beam Mass Spectrometer (TDPBMS)



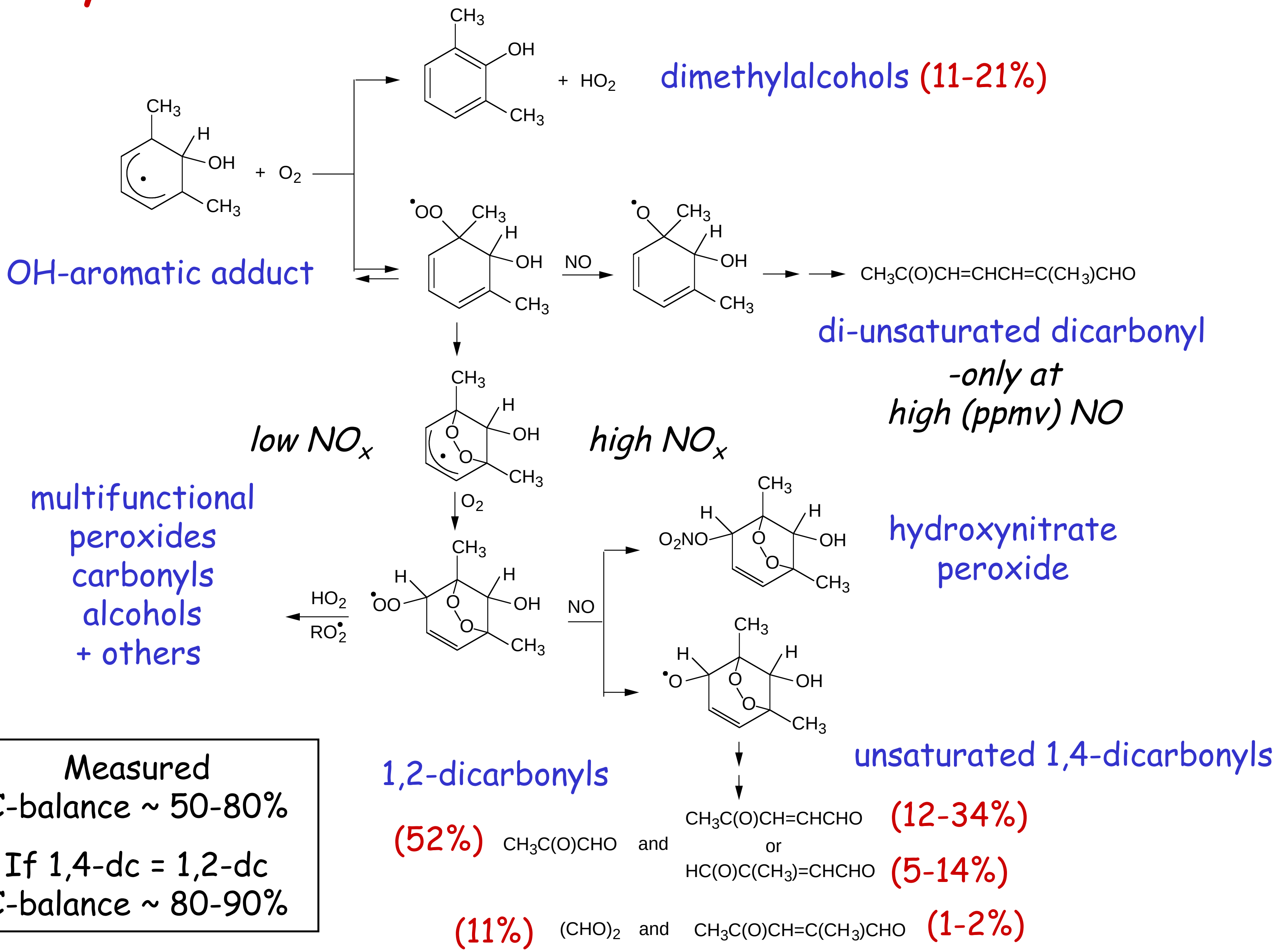
Aromatic Hydrocarbons + OH

m-Xylene + OH



CH2
H2O +
CH3
CHO
and
CH2ONO2
CH3
CH3
(4-5%)
carbonyl
nitrate
OH +
CH3
CH3
m-xylene
HO
CH3
CH3
CH3 +
OH
CH3
(<1%)
alcohol (cresol)
CH3
H
OH
CH3
OH-aromatic adduct
NO2
O2
lab
atmosphere & lab

m-Xylene + OH



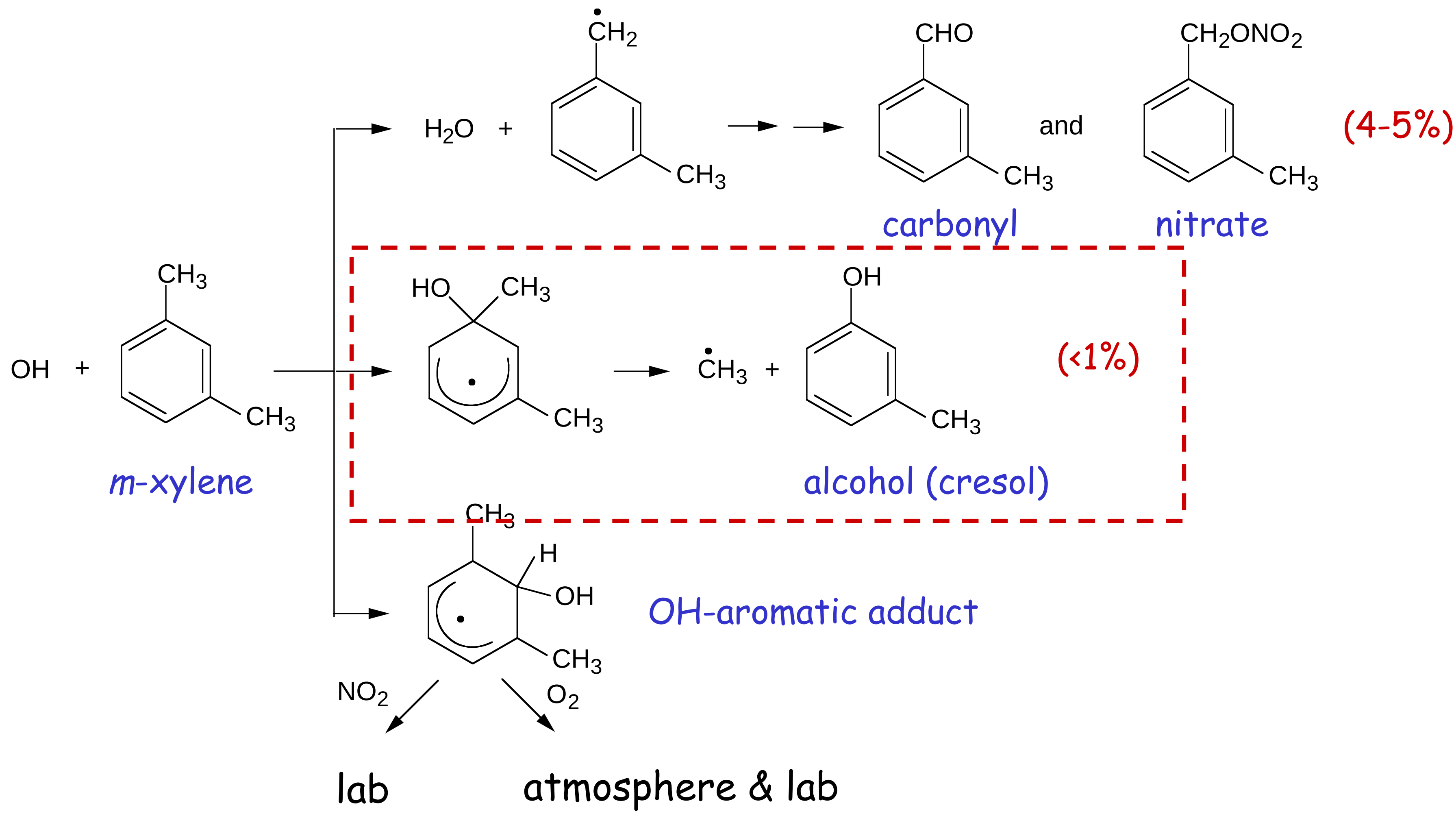
Measured
C-balance ~ 50-80%

If 1,4-dc = 1,2-dc
C-balance ~ 80-90%

Presented Results

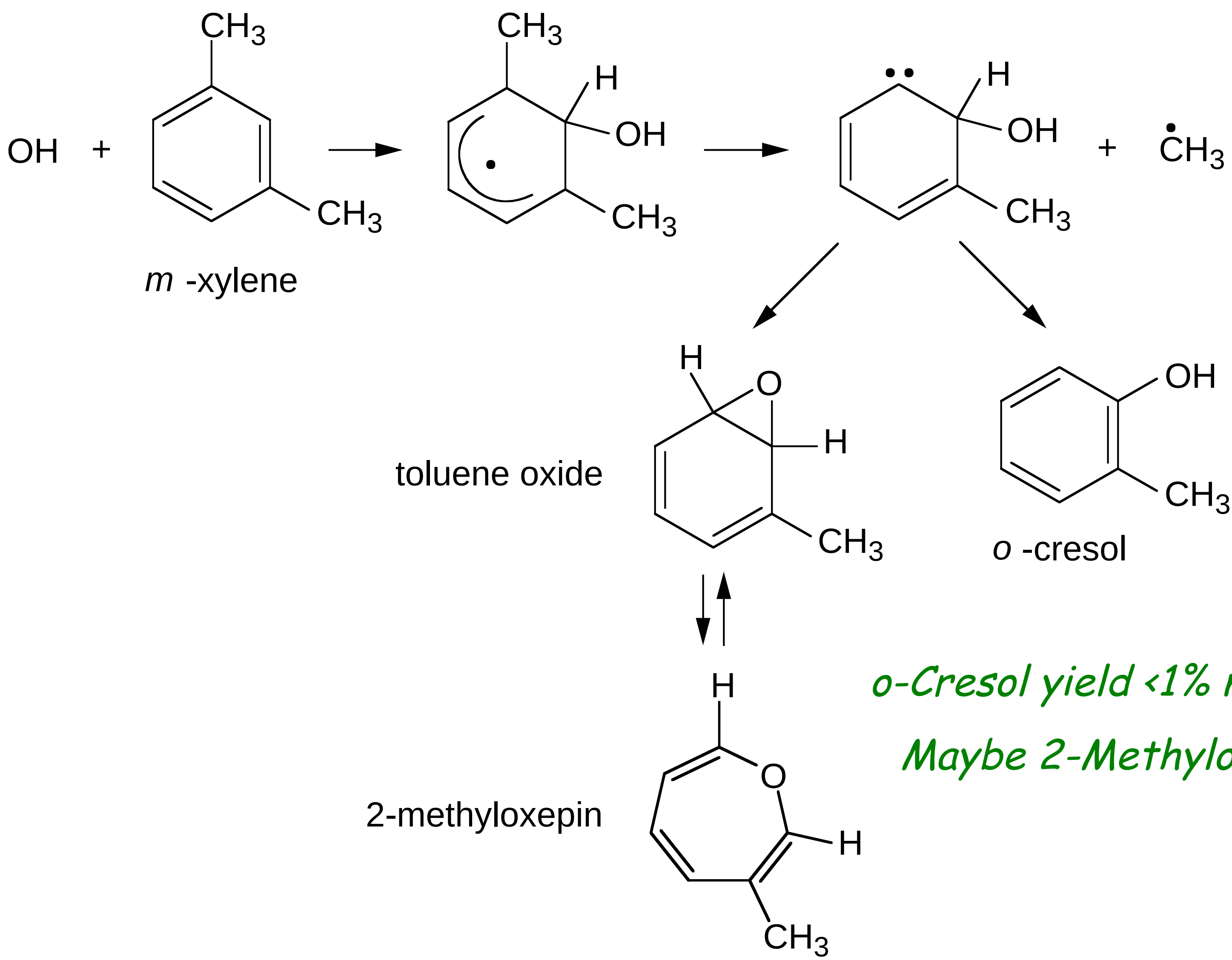
- Cresol yield
- Effect of NO_2 on 1,2-dicarbonyl yields
- Peroxide SOA yields
- Identification & quantification of unsaturated 1,4-dicarbonyls
- Contributions of unsaturated 1,4-dicarbonyl reaction products, 1,2-dicarbonyls, and dimethylalcohols to SOA
- SOA functional group and elemental composition

m-Xylene + OH



OH +
CH3
CH3
m-xylene
H2O +
CH2
CH3
CHO
CH3
and
CH2ONO2
CH3
(4-5%)
carbonyl
nitrate
HO
CH3
CH3
CH3 +
OH
CH3
(<1%)
alcohol (cresol)
CH3
H
OH
CH3
OH-aromatic adduct
NO2
O2
lab
atmosphere & lab

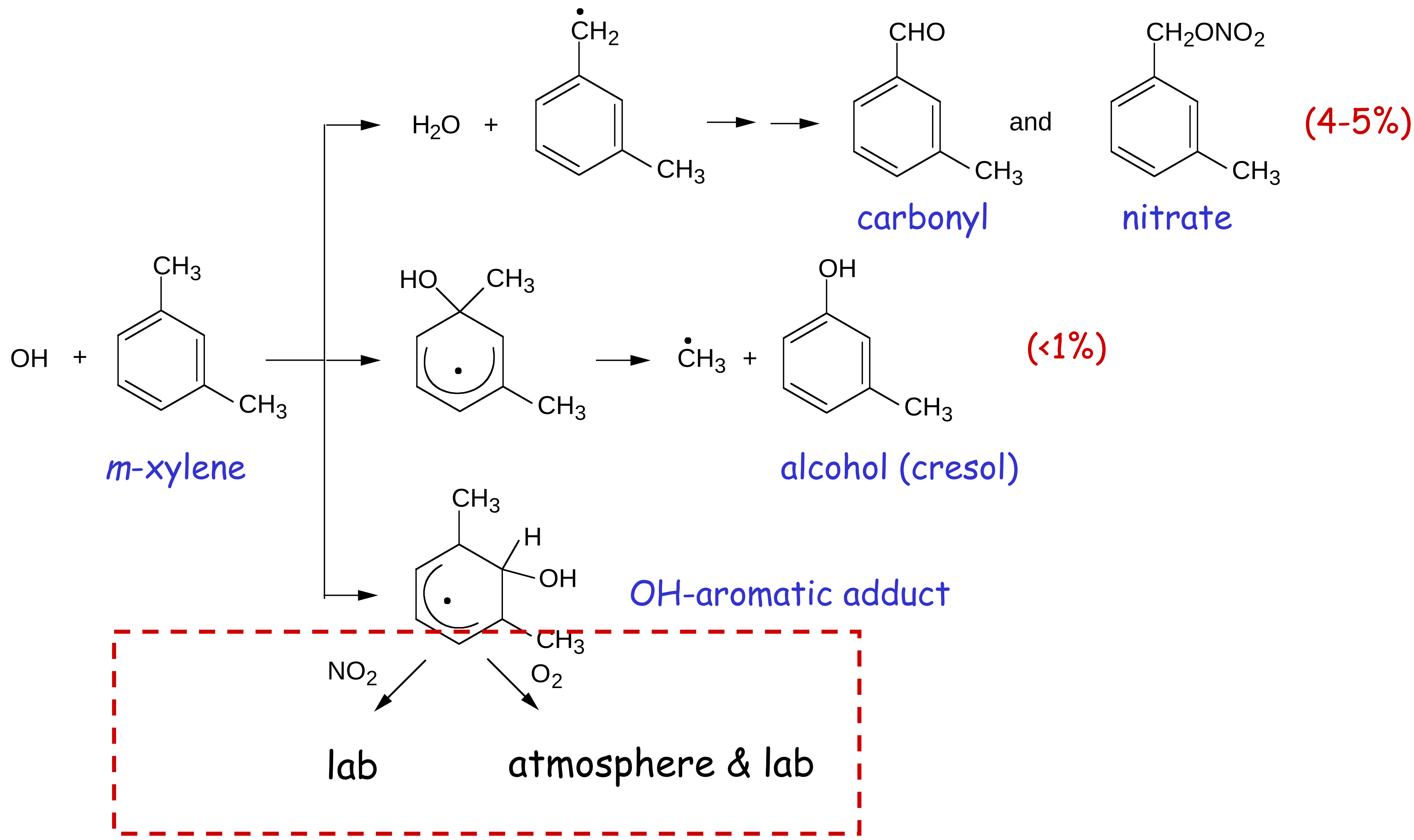
Cresol (Alcohol) Yield from *m*-Xylene + OH



o-Cresol yield <1% not 11%

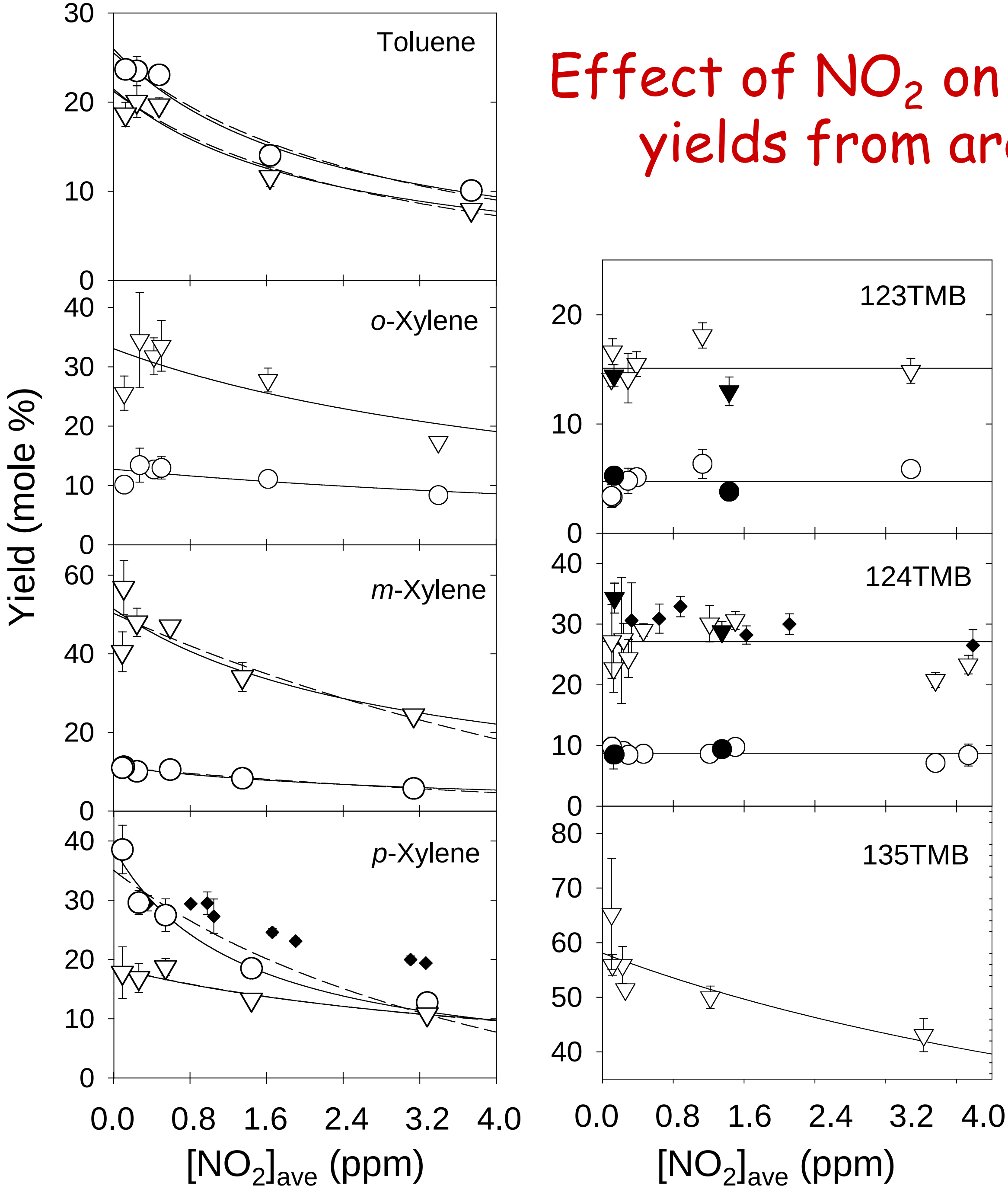
Maybe 2-Methyloxepin

m-Xylene + OH



OH +
CH3
CH3
m-xylene
H2O +
CH2
CH3
CHO
CH3
and
CH2ONO2
CH3
(4-5%)
carbonyl
nitrate
HO
CH3
CH3
CH3 +
OH
CH3
(<1%)
alcohol (cresol)
CH3
H
OH
CH3
OH-aromatic adduct
NO2
O2
lab
atmosphere & lab

Effect of NO_2 on glyoxal/methylglyoxal yields from aromatics + OH/NO_x



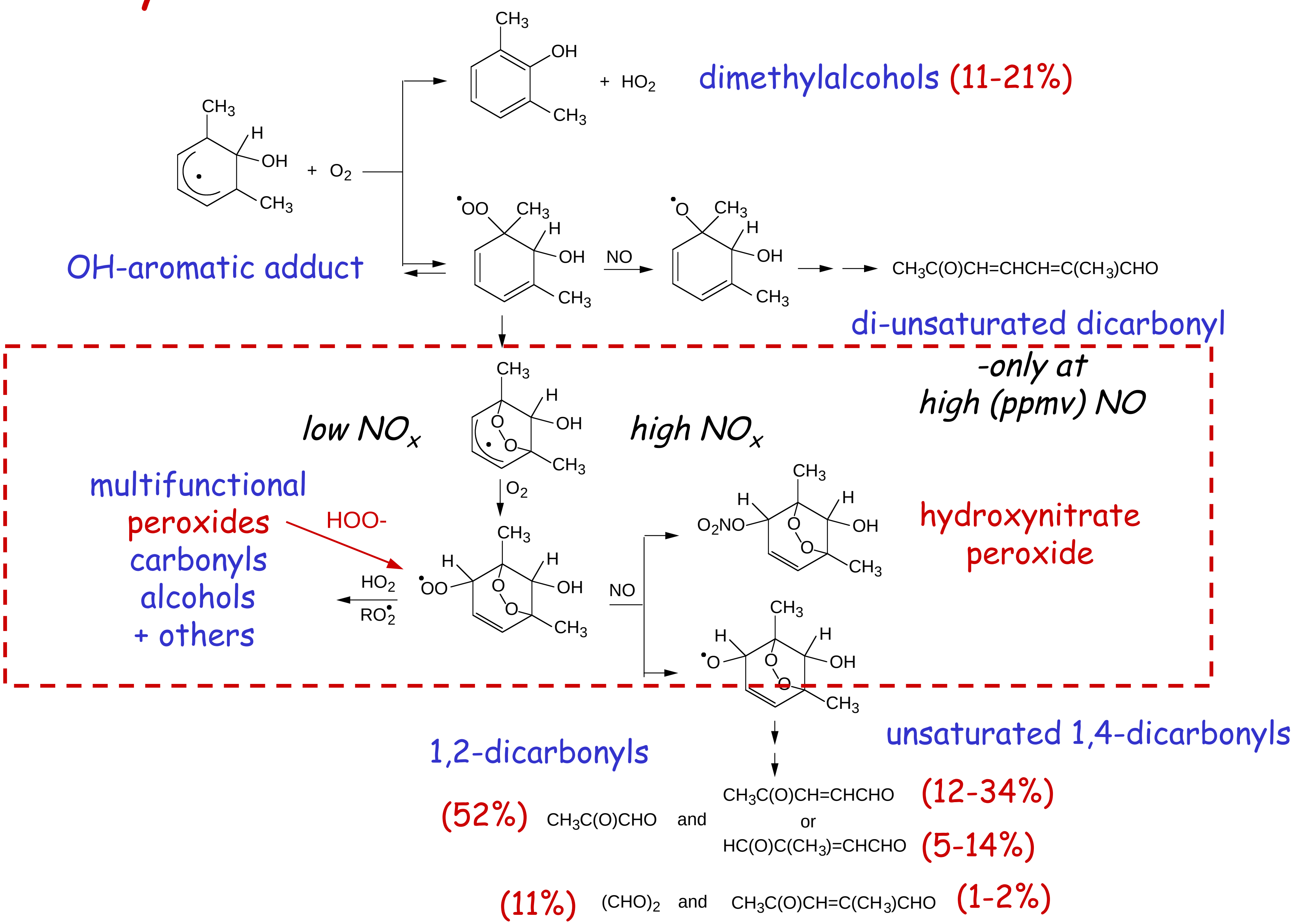
○, ● - Glyoxal

▽, ▼- Methylglyoxal

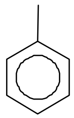
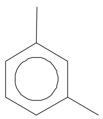
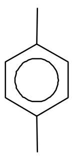
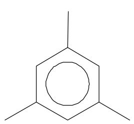
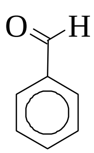
◆ - 3-Hexene-2,5-dione

No glyoxal/methylglyoxal from OH-aromatic + NO_2
-maybe 123 & 124 TMB

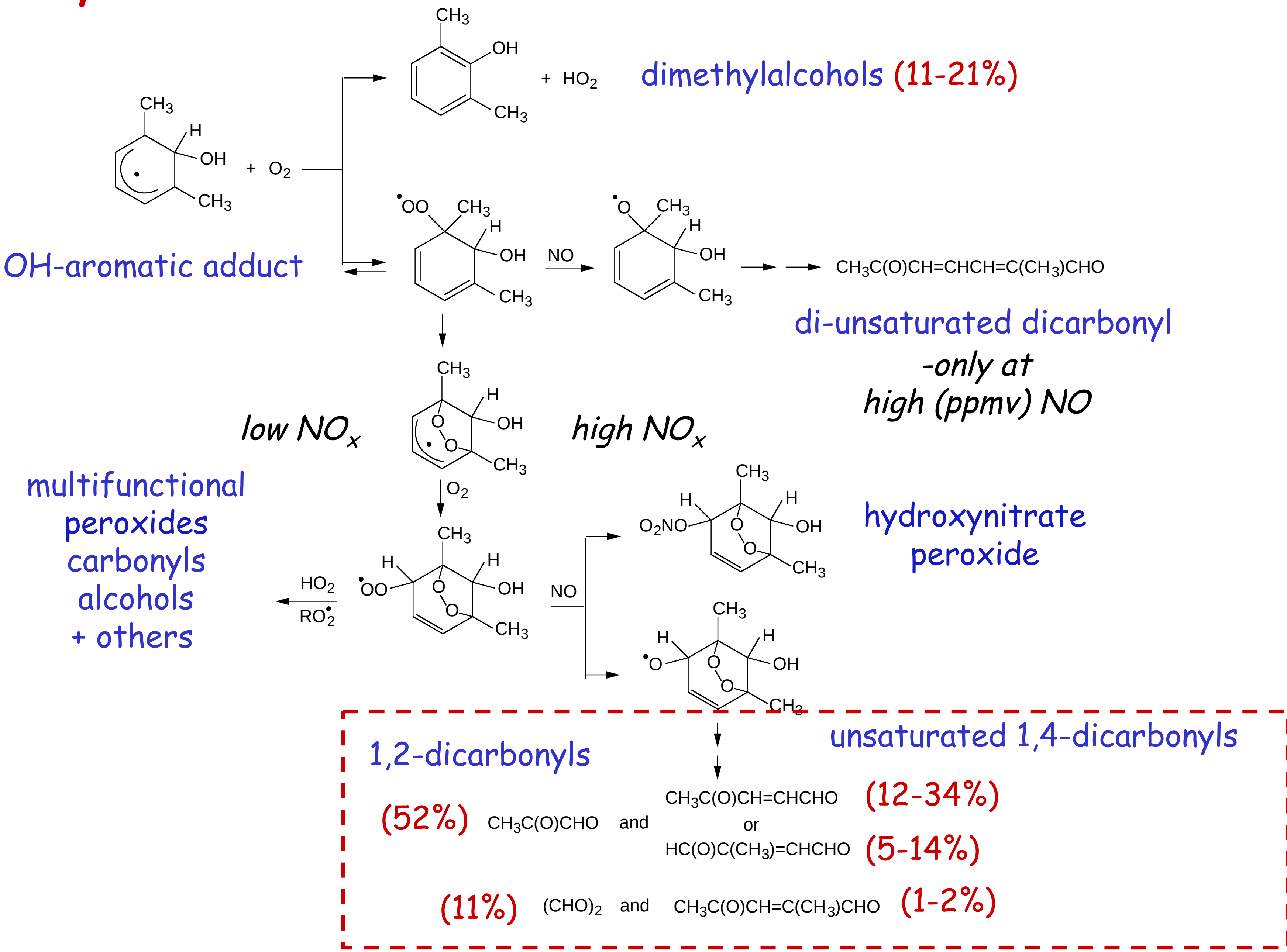
m-Xylene + OH



CH_3
OH
CH_3
+ HO_2
dimethylalcohols (11-21%)
CH_3
H
OH
CH_3
+ O_2
OH-aromatic adduct
OO
CH_3
H
OH
CH_3
NO
O
CH_3
H
OH
CH_3
$CH_3C(O)CH{=}CHCH{=}C(CH_3)CHO$
di-unsaturated dicarbonyl
-only at
high (ppmv) NO
low NO_x
high NO_x
CH_3
H
O
O
OH
CH_3
O_2
multifunctional
peroxides
carbonyls
alcohols
+ others
HOO-
HO_2
RO_2
H
OO
CH_3
H
O
O
OH
CH_3
NO
CH_3
H
O_2NO
H
O
O
OH
CH_3
hydroxynitrate
peroxide
CH_3
H
O
H
O
O
OH
CH_3
1,2-dicarbonyls
unsaturated 1,4-dicarbonyls
(52%) $CH_3C(O)CHO$ and
$CH_3C(O)CH{=}CHCHO$ (12-34%)
or
$HC(O)C(CH_3){=}CHCHO$ (5-14%)
(11%) $(CHO)_2$ and $CH_3C(O)CH{=}C(CH_3)CHO$ (1-2%)

OH + Aromatic	with NO_x				without NO_x			
	HC (ppm)	MN/NO (ppm)	SOA Yield (%)	Peroxide (mass %)	HC (ppm)	TME/O_3 (ppm/ppm)	SOA Yield (%)	Peroxide (mass %)
 toluene	1	1	6.8	5.7	2	2/1	17.0	19.7
 m-xylene	4	4	33.6	6.2	4	2/1	36.2	14.6
 p-xylene	2	2	21.2	6.8	2	2/1	36.2	21.3
 1,3,5-trimethylbenzene	4	4	17.0	6.4	2	2/1	31.4	21.0
 benzaldehyde	10	10	3.4	NM	10	50/10	13.0	16.4

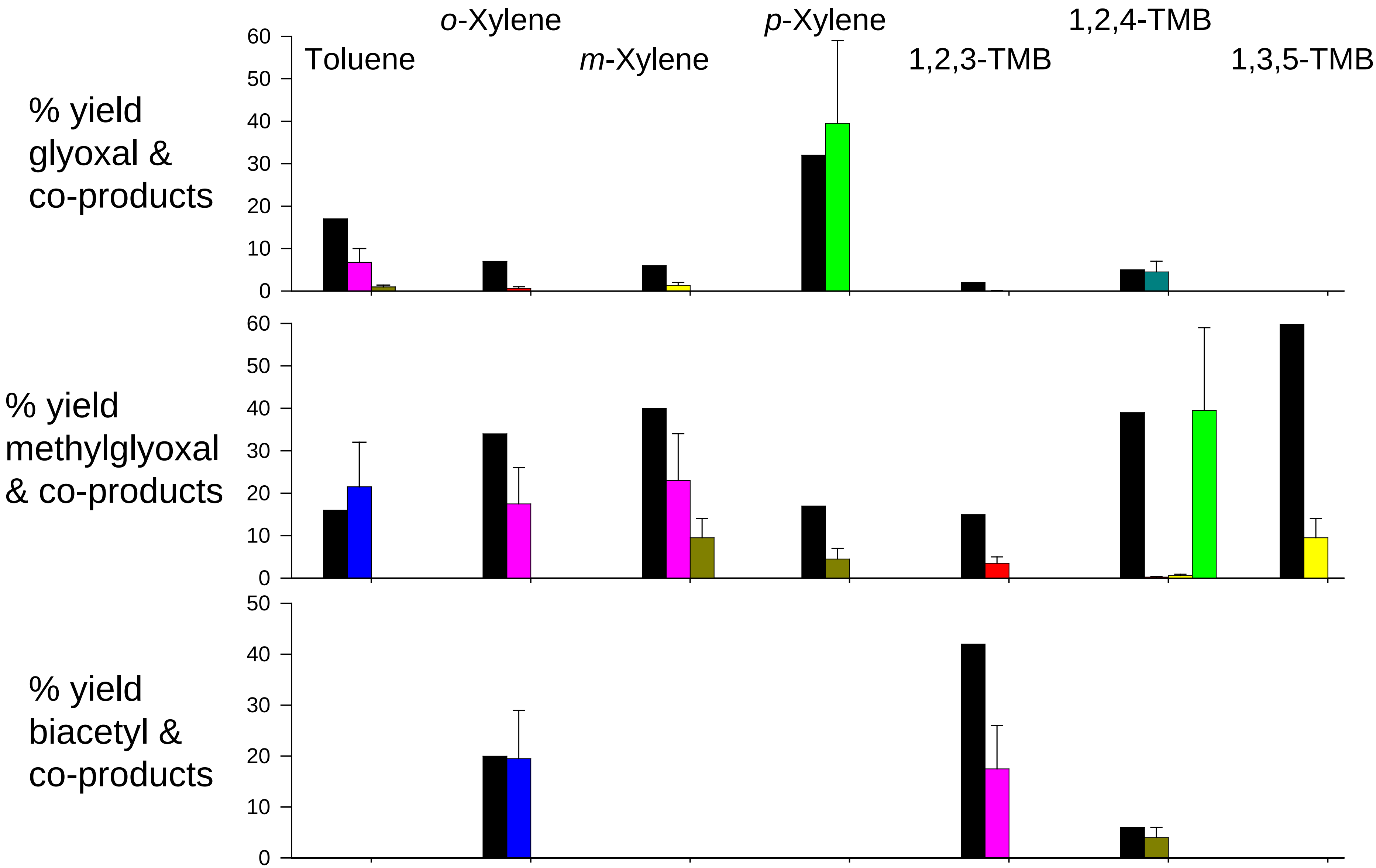
m-Xylene + OH


CH3
OH
CH3
+ HO2
dimethylalcohols (11-21%)
CH3
H
OH
CH3
+ O2
OH-aromatic adduct
•OO
CH3
H
OH
CH3
NO
•O
CH3
H
OH
CH3
CH3C(O)CH=CHCH=C(CH3)CHO
di-unsaturated dicarbonyl
-only at
high (ppmv) NO
low NOx
high NOx
CH3
H
O
O
OH
CH3
O2
multifunctional
peroxides
carbonyls
alcohols
+ others
HO2
RO2•
•OO
H
CH3
H
O
O
OH
CH3
NO
O2NO
H
CH3
H
O
O
OH
CH3
hydroxynitrate
peroxide
•O
H
CH3
H
O
O
OH
CH3
1,2-dicarbonyls
unsaturated 1,4-dicarbonyls
(52%)
CH3C(O)CHO
and
CH3C(O)CH=CHCHO
(12-34%)
or
HC(O)C(CH3)=CHCHO
(5-14%)
(11%)
(CHO)2
and
CH3C(O)CH=C(CH3)CHO
(1-2%)

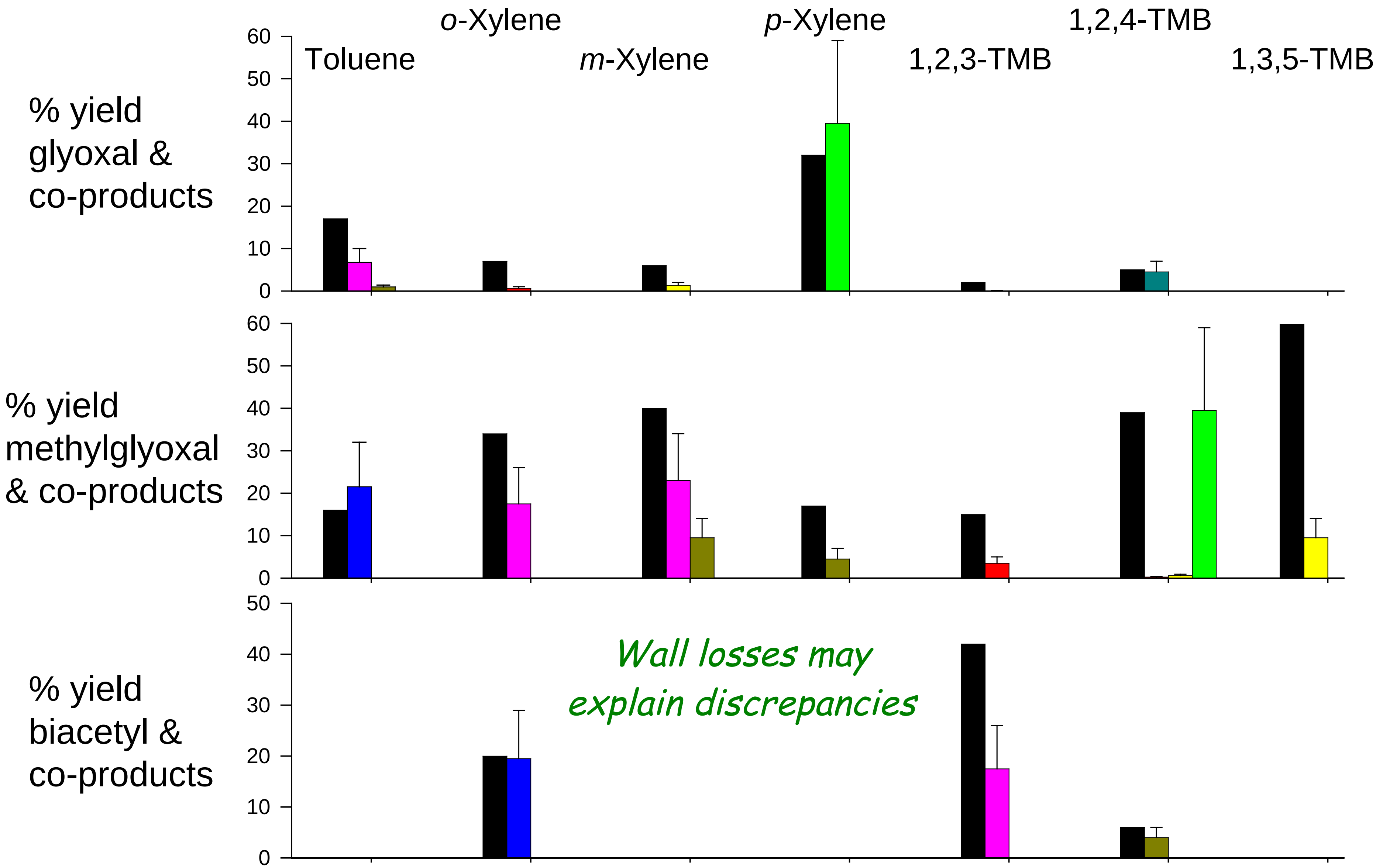
Identified 1,2-Dicarbonyls and Unsaturated 1,4-Dicarbonyls

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	

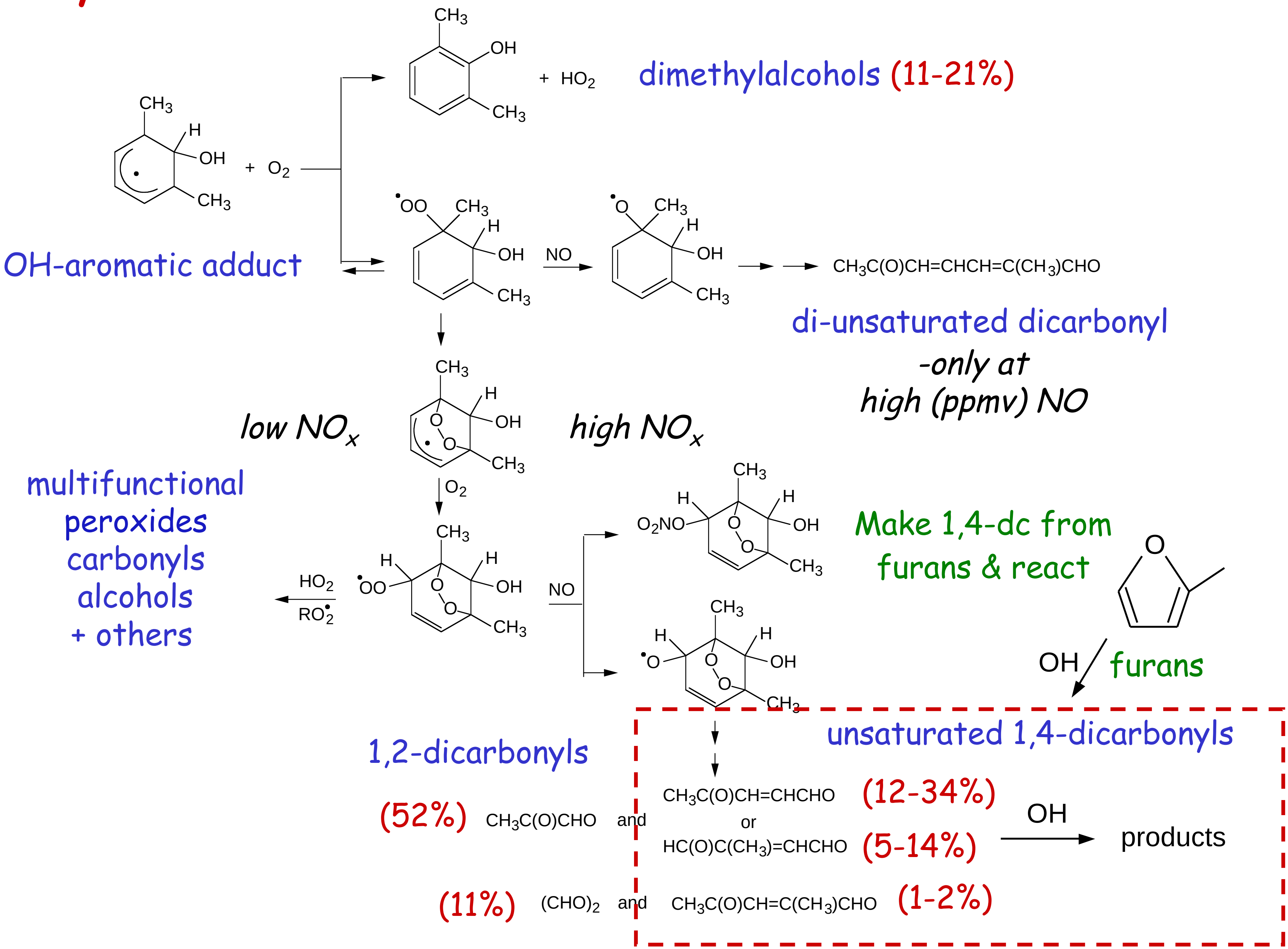
Quantified 1,2-Dicarbonyls and Unsaturated 1,4-Dicarbonyls



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



m-Xylene + OH


CH3
OH
+ HO2
dimethylalcohols (11-21%)
CH3
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+ O2
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OH-aromatic adduct
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CH3C(O)CH=CHCH=C(CH3)CHO
di-unsaturated dicarbonyl
-only at
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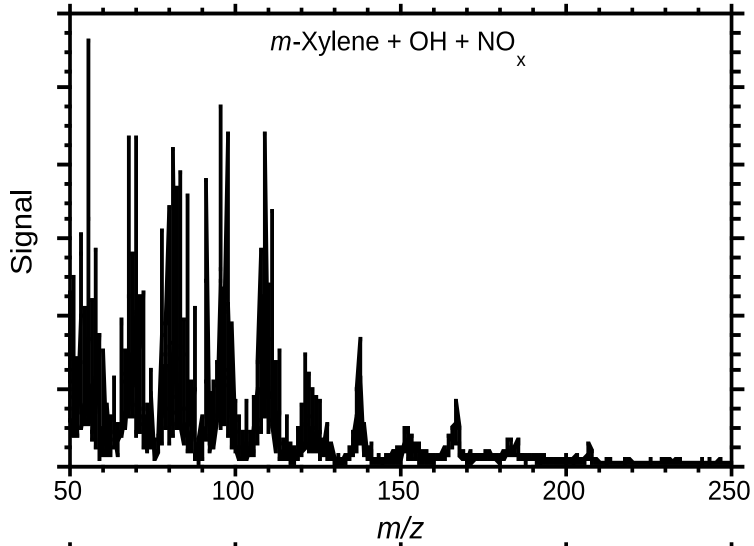
low NOx
high NOx
O2
multifunctional
peroxides
carbonyls
alcohols
+ others
HO2
RO2•
O2NO
Make 1,4-dc from
furans & react
OH
furans
1,2-dicarbonyls
unsaturated 1,4-dicarbonyls
(52%) CH3C(O)CHO and
CH3C(O)CH=CHCHO (12-34%)
or
HC(O)C(CH3)=CHCHO (5-14%)
OH
products
(11%) (CHO)2 and CH3C(O)CH=C(CH3)CHO (1-2%)

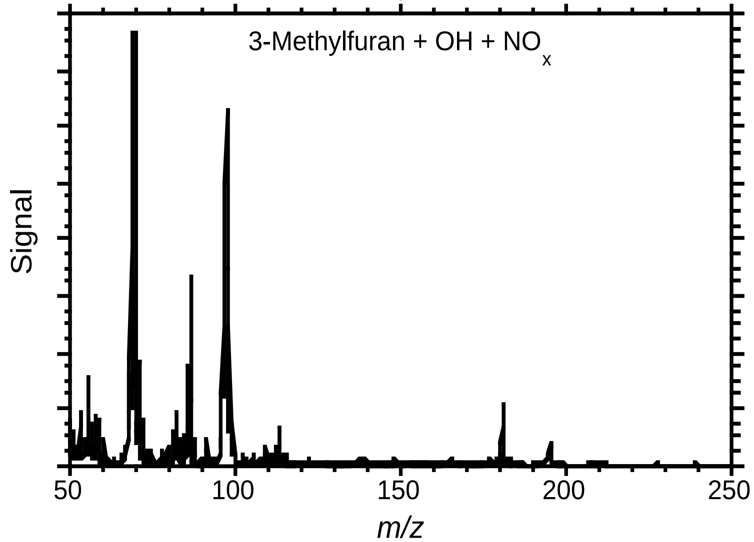
SOA Yields: per Reacted VOC & Reacted Unsaturated 1,4-Dicarbonyl

NO	NO_2 (ppm)	ΔVOC (ppm)	*m*-xylene	3-methylfuran	2-methylfuran
			SOA/ΔVOC (SOA/ΔUDC)		
Y	0.6	0.5 / 0.4 / 0.4	1.4 (15)	0.3 (1.8)	0.5 (3.8)
N	2.4	2.6 / 1.0 / 1.0	26 (50)	3.5 (2.9)	5.5 (5.8)
Y	0.8	0.4 / 0.5 / 0.4	3.1 (43)	0.4 (2.2)	0.2 (2.3)
Y	1.7	1.8 / 0.8 / 0.7	4.6 (22)	0.5 (0.7)	0.5 (1.1)
Y	3.7	2.7 / 1.0 / 1.0	30 (55)	4.6 (1.9)	5.8 (7.2)

SOA/ΔUDC for m-xylene >> methylfurans:
UDC reaction products not major SOA source

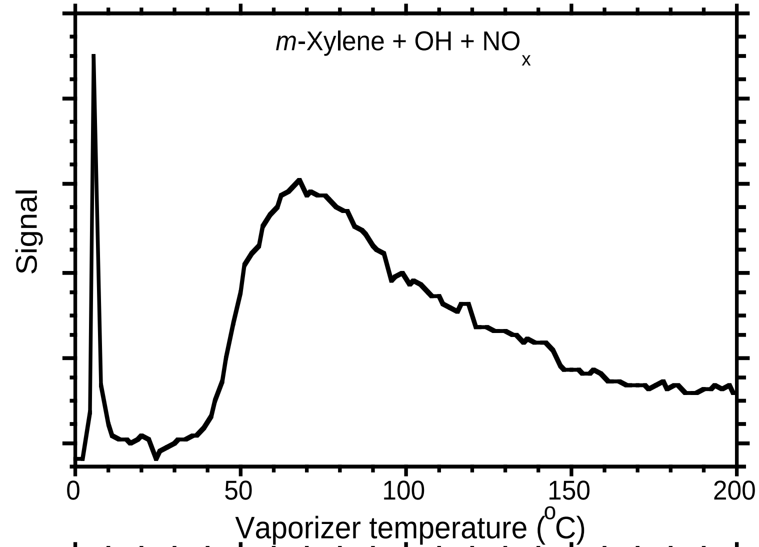
Real-time TDPBMS

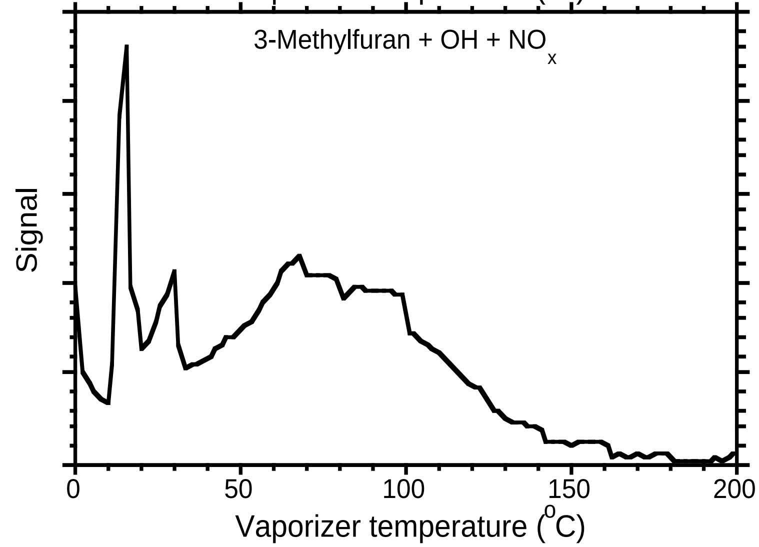




Very different spectra:
UDC reaction products not major SOA source

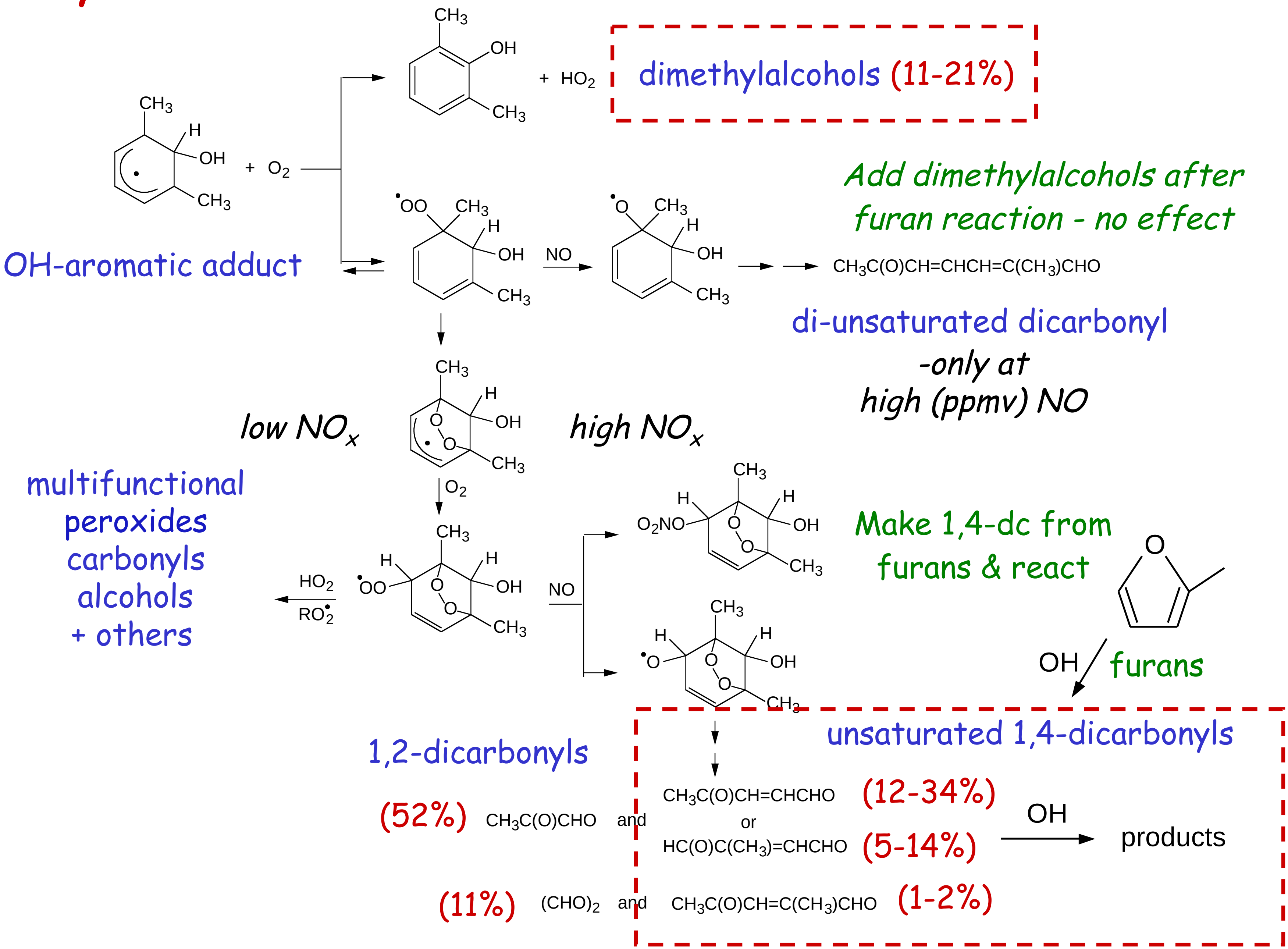
TPTD





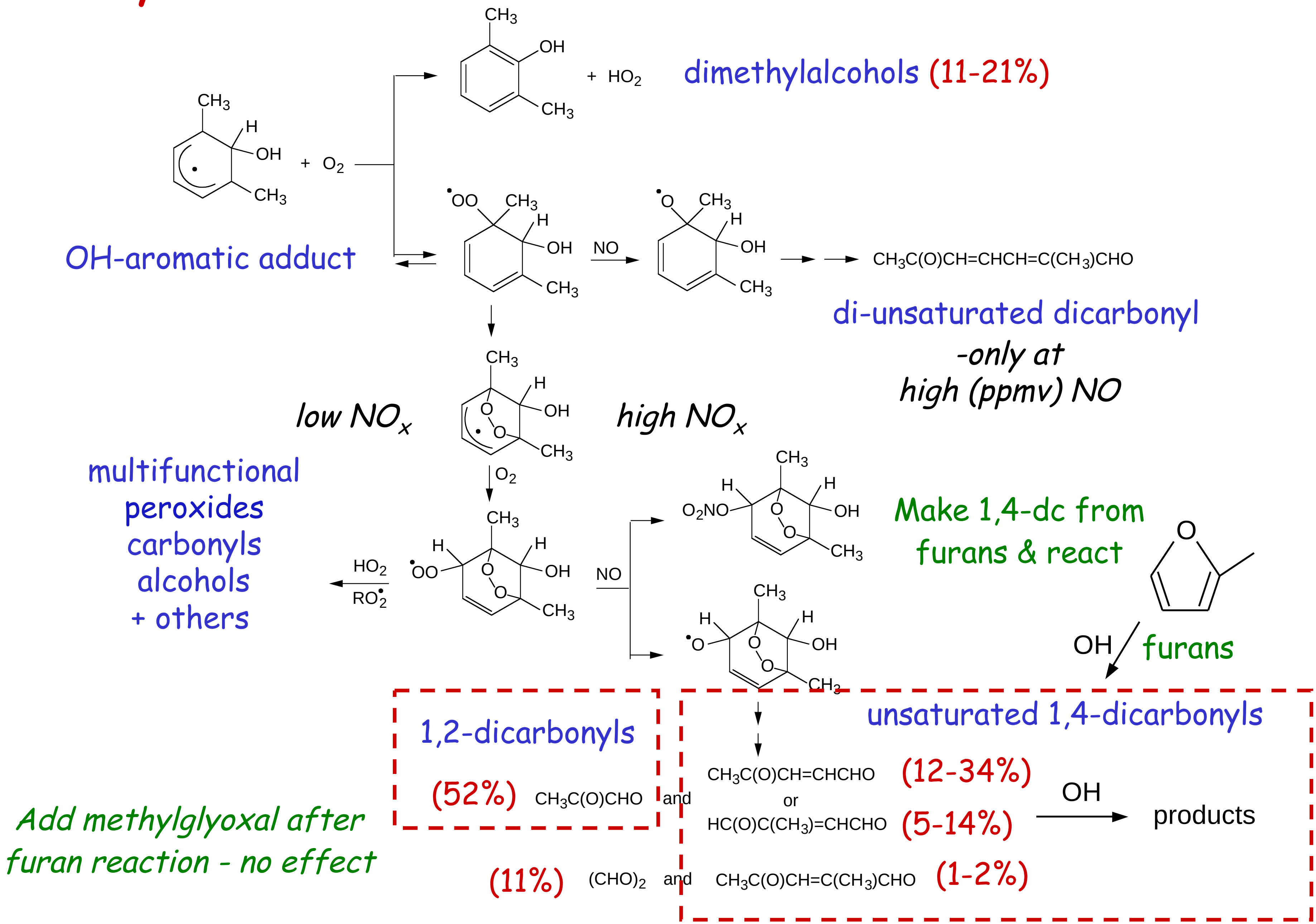
High desorption temperatures:
oligomers

m-Xylene + OH



OH-aromatic adduct
+ O2
+ HO2
dimethylalcohols (11-21%)
Add dimethylalcohols after furan reaction - no effect
NO
CH3C(O)CH=CHCH=C(CH3)CHO
di-unsaturated dicarbonyl
-only at high (ppmv) NO
low NOx
high NOx
O2
multifunctional peroxides carbonyls alcohols + others
HO2
RO2
NO
Make 1,4-dc from furans & react
OH
furans
unsaturated 1,4-dicarbonyls
1,2-dicarbonyls
(52%) CH3C(O)CHO and
CH3C(O)CH=CHCHO (12-34%)
or
HC(O)C(CH3)=CHCHO (5-14%)
OH
products
(11%) (CHO)2 and CH3C(O)CH=C(CH3)CHO (1-2%)

m-Xylene + OH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-only at
high (ppmv) NO
low NOx
high NOx
CH3
H
O
O
OH
CH3
O2
multifunctional
peroxides
carbonyls
alcohols
+ others
HO2
RO2•
•OO
H
CH3
H
O
O
OH
CH3
NO
O2NO
H
CH3
H
O
O
OH
CH3
•O
H
CH3
H
O
O
OH
CH3
Make 1,4-dc from
furans & react
O
OH
furans
1,2-dicarbonyls
(52%)
CH3C(O)CHO
and
unsaturated 1,4-dicarbonyls
CH3C(O)CH=CHCHO
(12-34%)
or
HC(O)C(CH3)=CHCHO
(5-14%)
OH
products
Add methylglyoxal after
furan reaction - no effect
(11%)
(CHO)2
and
CH3C(O)CH=C(CH3)CHO
(1-2%)

m-Xylene + OH + NO_x

SOA Analysis

functional group		mole fraction
carbonyl	C=O	0.048
hydroxyl	CHOH	0.039
nitrate	$CHONO_3$	0.103
carboxyl	C(O)OH	0.013
ester	C(O)OR	0.060
peroxide	CHOOH	0.001
methylene	CH_2	0.735

	functional group	elemental analysis
O/C	0.48	0.94
N/C	0.09	0.10
H/C	1.63	1.43

$\sim[CHOH]_{0.4}[CO]_{0.2}$
$[CHONO_2]_{0.1}[CH_2]_{0.3}$

Future Plans

- Improved quantification of yields of unsaturated 1,4-dicarbonyls from OH + aromatic and furan reactions
- OH kinetics, products, and photolysis of unsaturated 1,4-dicarbonyls formed in situ from OH reactions of furans
- SOA formation & products from reactions of various recipes of aromatics & aromatic + OH products
- Effects of RH, particle acidity, & NH_3
- SOA mass spectral, functional group, and elemental analysis
- Joint experiments with real-time gas and SOA analysis