Mechanisms and SOA Formation for the Atmospheric Degradation of Xylenes

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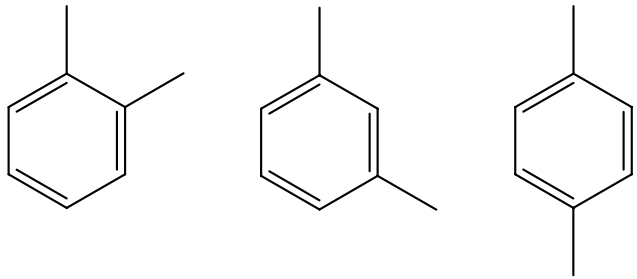
Sources Transformation Impacts



Sources

- Automobile fuels, solvents
- Aromatics typically contribute 20-25% to anthropogenic VOC emissions

Transformation

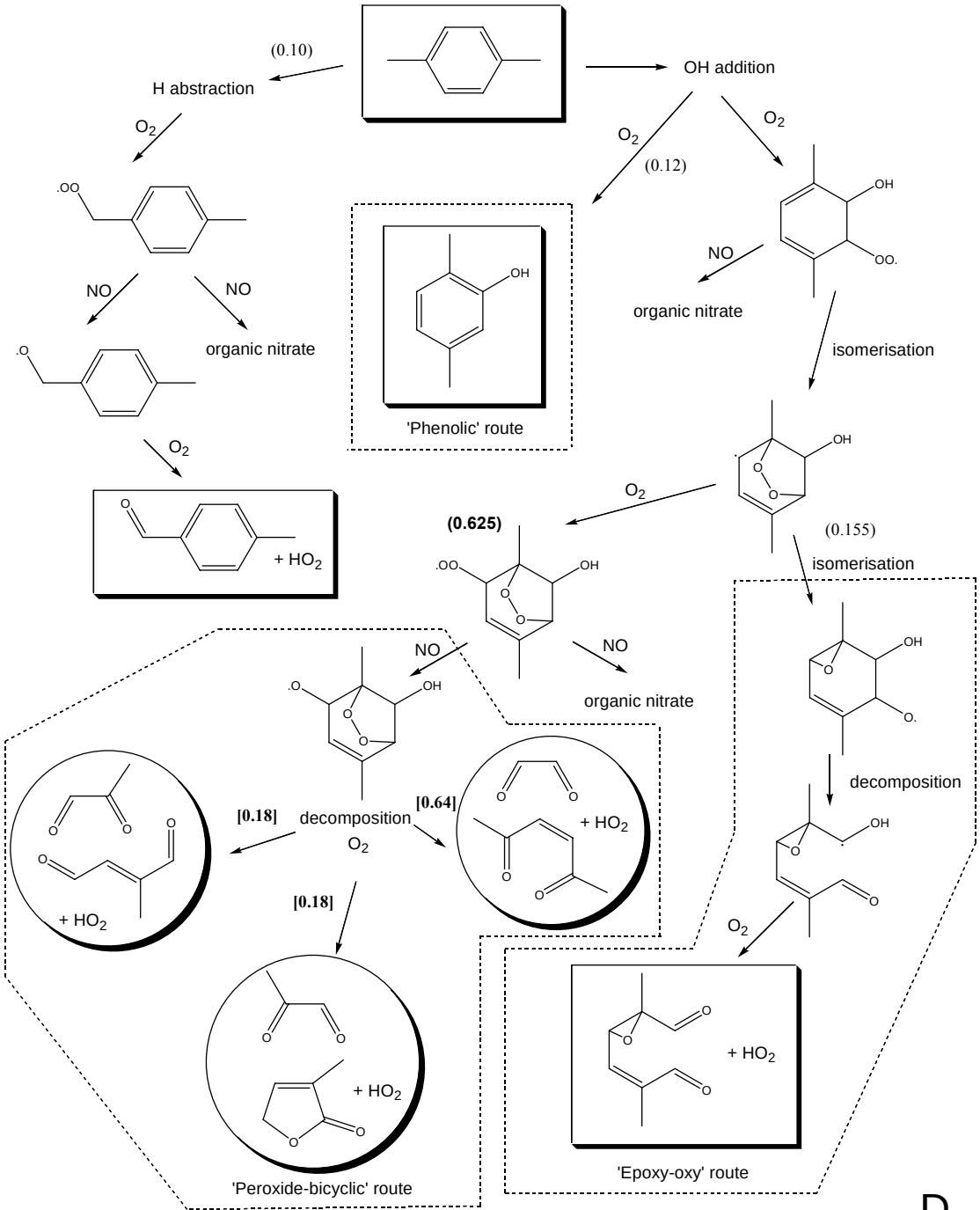
- Reaction with hydroxyl radical (OH) in troposphere
- Formation of ozone, nitrates, secondary organic aerosol (SOA)

Impacts

- Air pollution and Health effects in urban areas

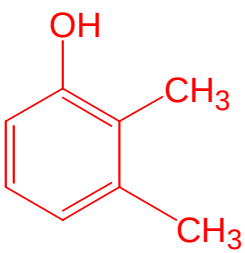
Information required

- Kinetics of reaction, identity & yields of oxidation products
- Reactivity of the oxidation products towards OH, NO_3, O_3, sunlight
- Produce a detailed atmospheric degradation mechanism for inclusion in models (e.g. MCM) used to predict pollution forming ability of VOCs

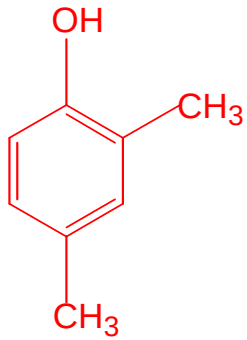


D. Johnson et al. Env. Chem, 2005

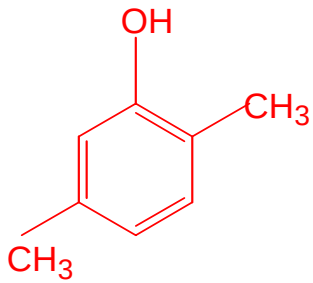
Dimethylphenols and Tolualdehydes



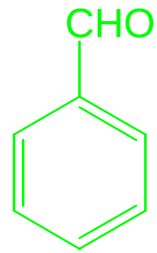
2,3-DMP



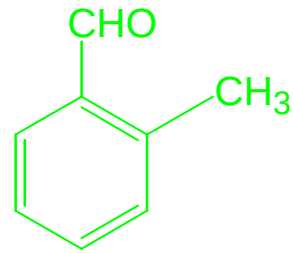
2,4-DMP



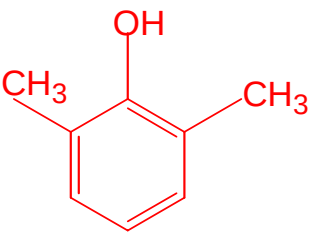
2,5-DMP



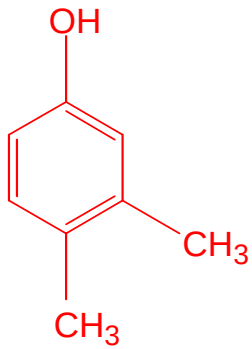
benzaldehyde



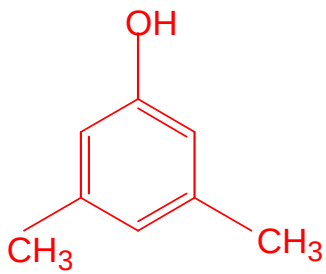
o-tolualdehyde



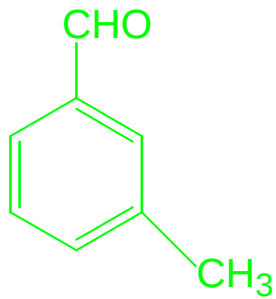
2,6-DMP



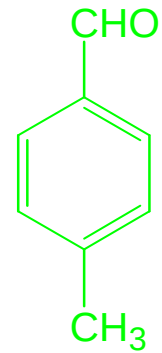
3,4-DMP



3,5-DMP

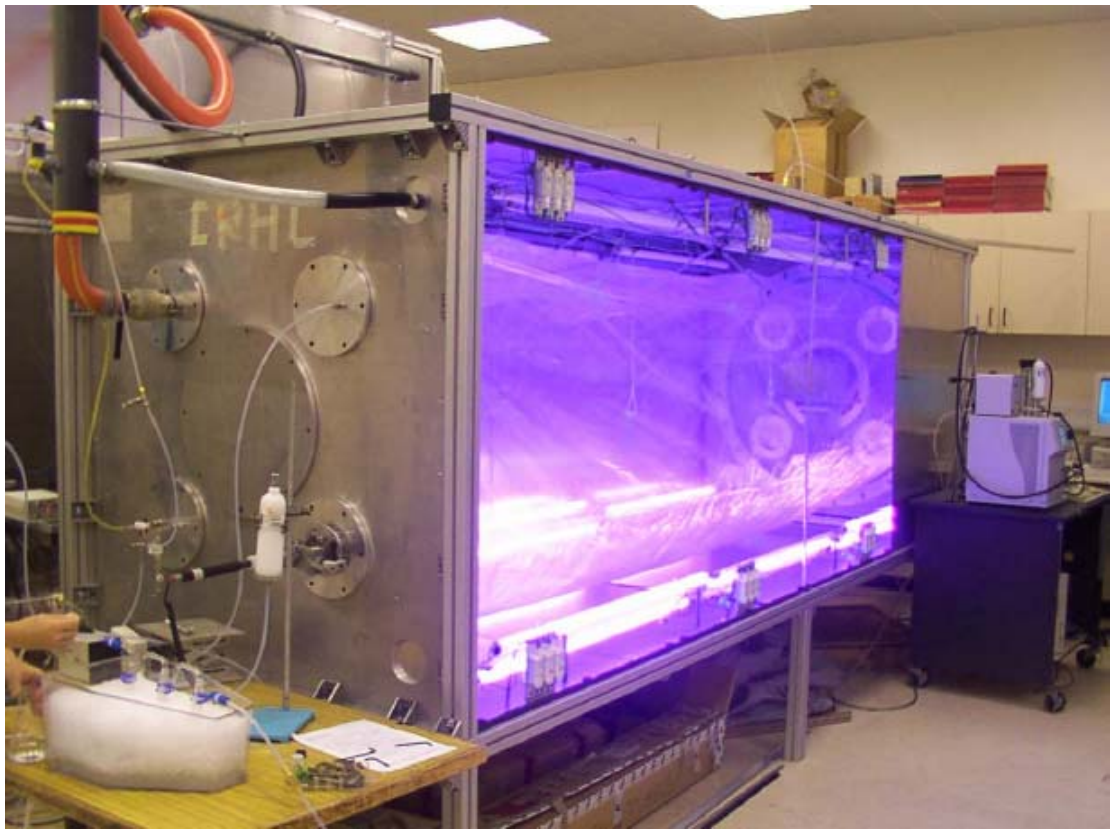


m-tolualdehyde



p-tolualdehyde

Atmospheric Simulation Chamber



- in situ FTIR spectroscopy
- NOx and O_3 analysers
- GC, GC-MS
- Particle Sizer and counter

- FEP foil (3910 litres)
- Dry purified air
- Atmospheric P and T
- Humidity control

Kinetic Studies

Relative rate method

(1) OH + aromatic $\xrightarrow{k_1}$ Products

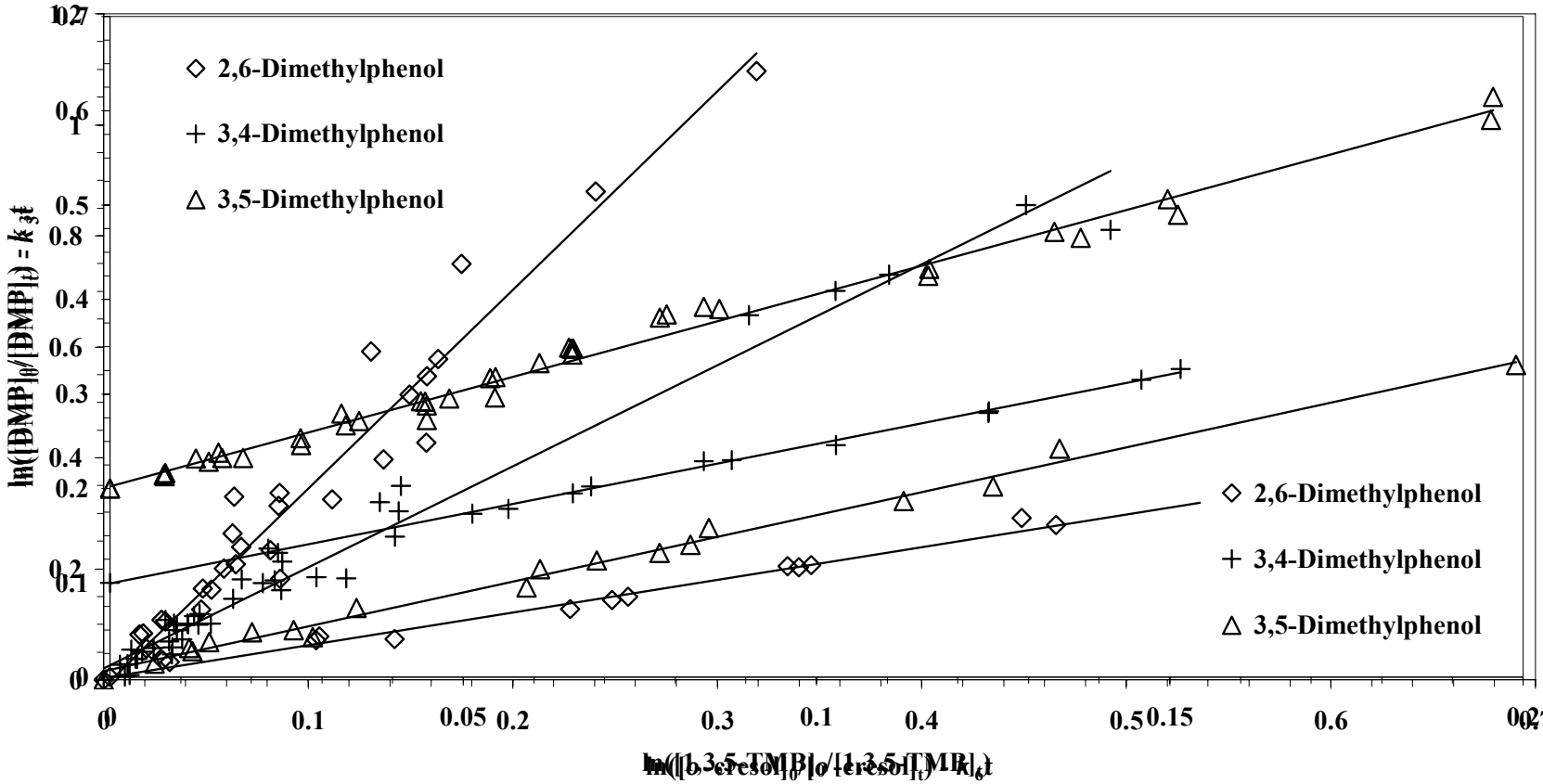
(2) OH + reference $\xrightarrow{k_2}$ Products

$$-\frac{d\ln[\text{aromatic}]}{dt} = k_1[OH] \qquad -\frac{d\ln[\text{reference}]}{dt} = k_2[OH]$$

$$\ln\frac{[\text{aromatic}]_0}{[\text{aromatic}]_t} = \frac{k_1}{k_2}\ln\frac{[\text{reference}]_0}{[\text{reference}]_t}$$

	OH reactions	**NO_3 reactions**
Radical Source	$CH_3ONO + h\nu \rightarrow CH_3O + NO$ $CH_3O + O_2 \rightarrow CH_2O + HO_2$ $HO_2 + NO \rightarrow OH + NO_2$	$NO_2 + O_3 \rightarrow NO_3 + O_2$ $NO_3 + NO_2 \leftrightarrow N_2O_5$
Reference Compound	1,3,5-trimethylbenzene for DMPs 1,2,4-trimethylbenzene for aldehydes	o-cresol for DMPs n-propyl ether for aldehydes

Kinetics data for dimethylphenols



Kinetics results for dimethylphenols

Compound	k_{OH}[a]		k_{NO3}[a]	τ_{OH}[b] (s)	τ_{NO3}[c](s)
	This work	Literature			
2,3-Dimethylphenol	8.3 ± 1.1	8.0 ± 2.0	2.9 ± 0.3	7502	69
2,4-Dimethylphenol	7.4 ± 0.8	7.2 ± 1.8	3.1 ± 0.3	8468	65
2,5-Dimethylphenol	8.8 ± 1.2	8.0 ± 2.3	3.0 ± 0.4	7078	67
2,6-Dimethylphenol	6.7 ± 0.9	6.6 ± 1.7	4.9 ± 0.5	8635	41
3,4-Dimethylphenol	8.3 ± 0.9	8.1 ± 2.1	2.5 ± 0.2	7558	80
3,5-Dimethylphenol	11.4 ± 1.4	11.3 ± 3.0	1.1 ± 0.1	5482	180

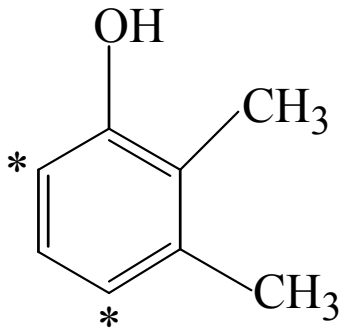
[a] In units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

[b] $\tau_{OH} = 1/k_{OH}[OH]$, where 12 hour daily average [OH] = 1.6×10^6 molecule cm^{-3}

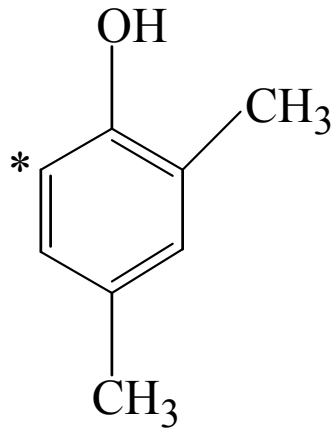
[c] $\tau_{NO3} = 1/k_{NO3}[NO_3]$, where 12 hour daily average $[NO_3] = 5 \times 10^8$ molecule cm^{-3}

- Both OH and NO_3 reactions important
- Opposite trends in reactivity for OH and NO_3
- Different reaction mechanisms

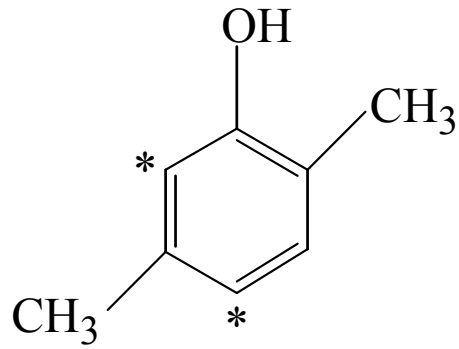
Sites activated for OH addition



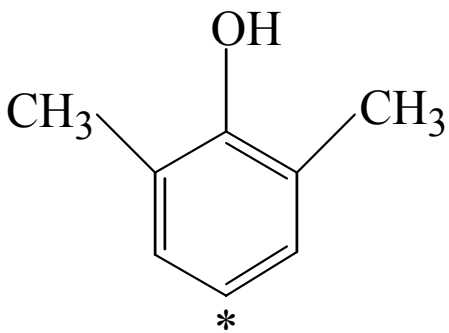
2,3-dimethylphenol



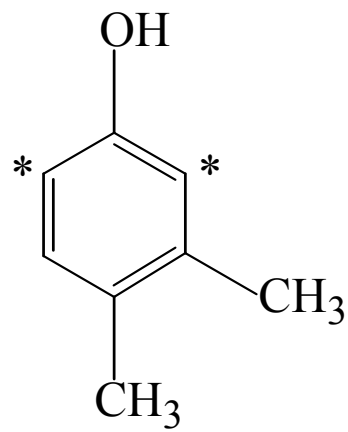
2,4-dimethylphenol



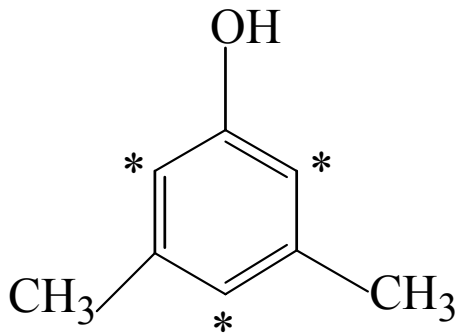
2,5-dimethylphenol



2,6-dimethylphenol

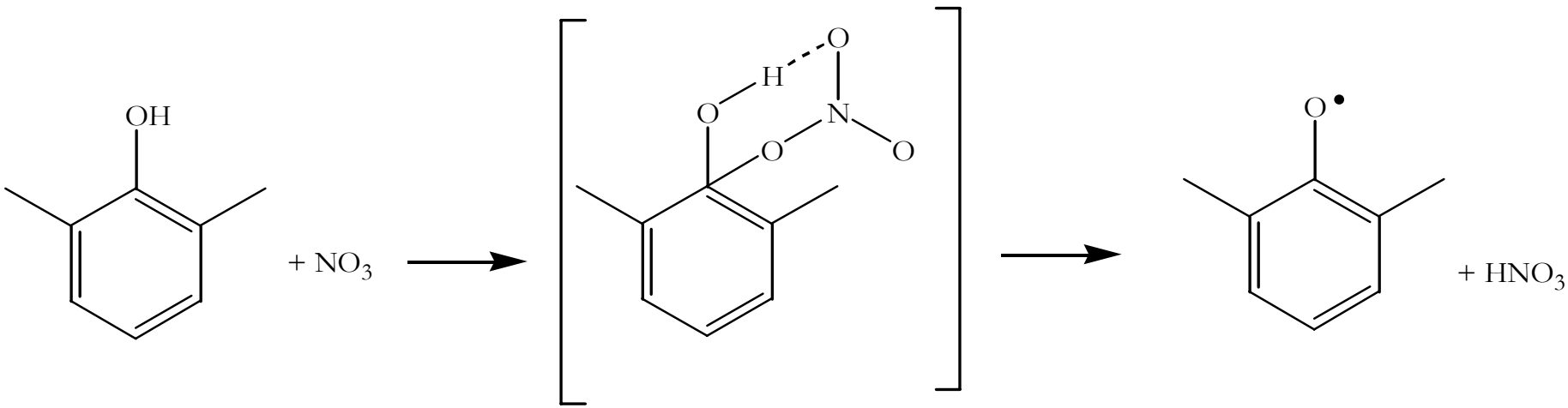


3,4-dimethylphenol

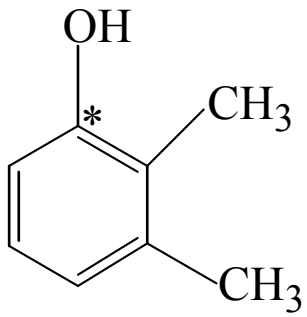


3,5-dimethylphenol

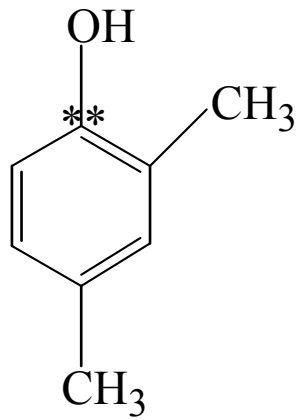
Mode of NO_3 attack



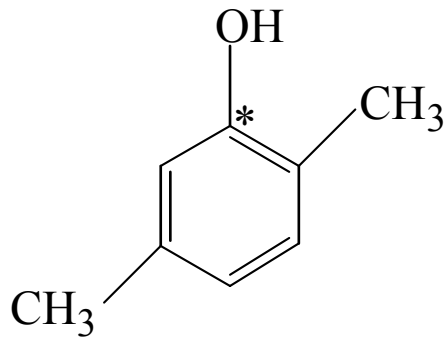
Sites activated for NO_3 addition



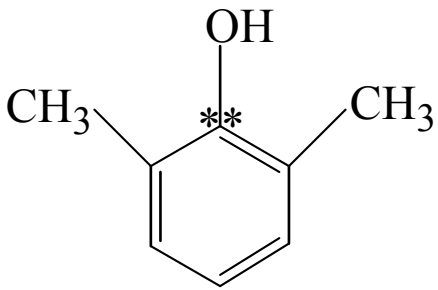
2,3-dimethylphenol



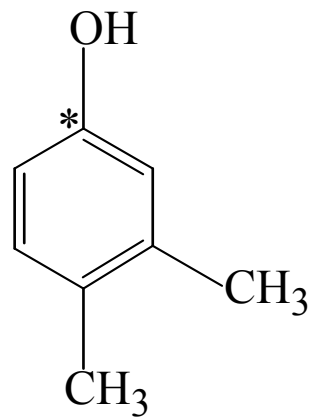
2,4-dimethylphenol



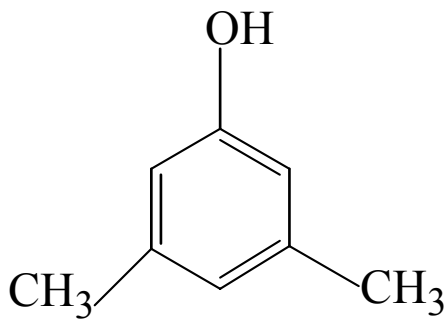
2,5-dimethylphenol



2,6-dimethylphenol



3,4-dimethylphenol



3,5-dimethylphenol

Kinetics results for tolualdehydes

Compound	k_{OH}[a]		k_{NO3}[b]	τ_{OH}[c] (hr)	τ_{NO3}[d](hr)
	This work	Literature			
benzaldehyde	1.4 ± 0.1	1.2 ± 0.2	4.3 ± 1.3	19.8	128.0
o-tolualdehyde	2.1 ± 0.2	1.8 ± 0.2	9.8 ± 2.6	13.6	56.7
m-tolualdehyde	2.1 ± 0.2	1.7 ± 0.2	9.5 ± 2.6	13.4	58.7
p-tolualdehyde	2.1 ± 0.2	1.3 ± 0.2	9.5 ± 3.0	13.6	58.7

[a] In units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

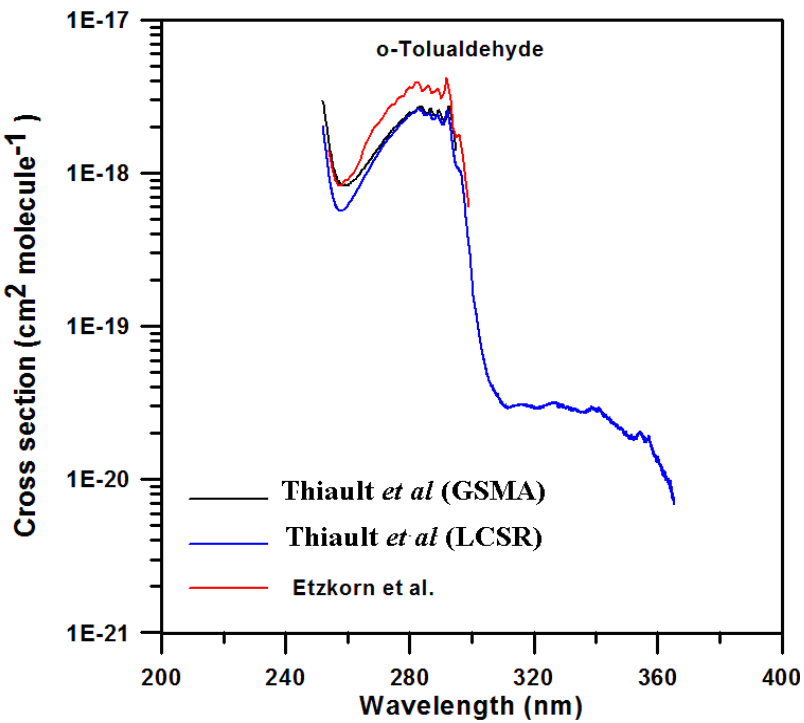
[b] In units of 10^{-15} cm^3 $molecule^{-1}$ s^{-1}

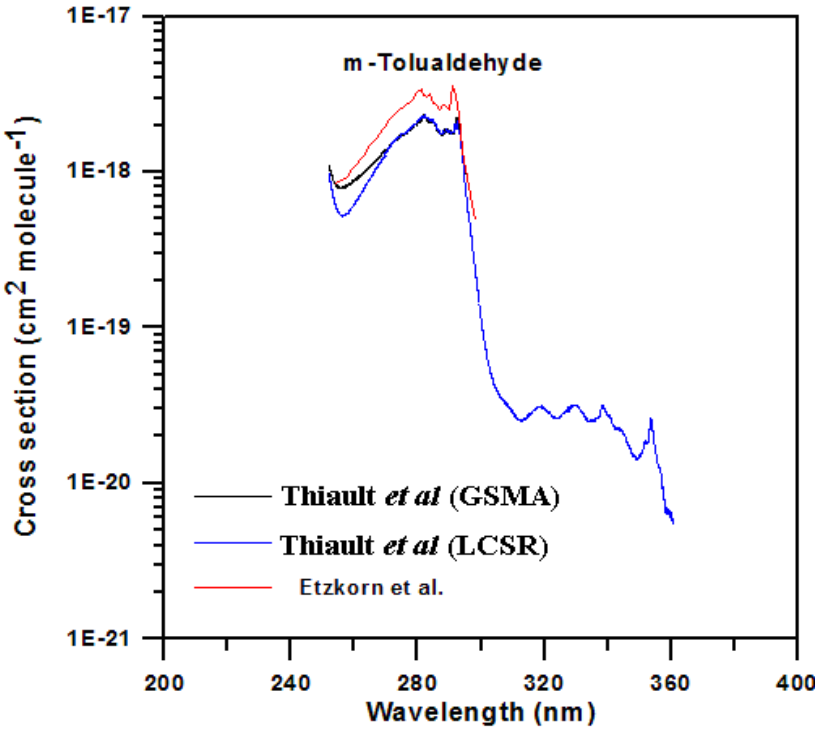
[c] $\tau_{OH} = 1/k_{OH}[OH]$, where 12 hour daily average $[OH] = 1.6 \times 10^6$ molecule cm^{-3}

[d] $\tau_{NO3} = 1/k_{NO3}[NO_3]$, where 12 hour daily average $[NO_3] = 5 \times 10^8$ molecule cm^{-3}

- Only OH reaction is important
- Tolualdehyde isomers have the same reactivity
- Similar trend in reactivity for OH and NO_3

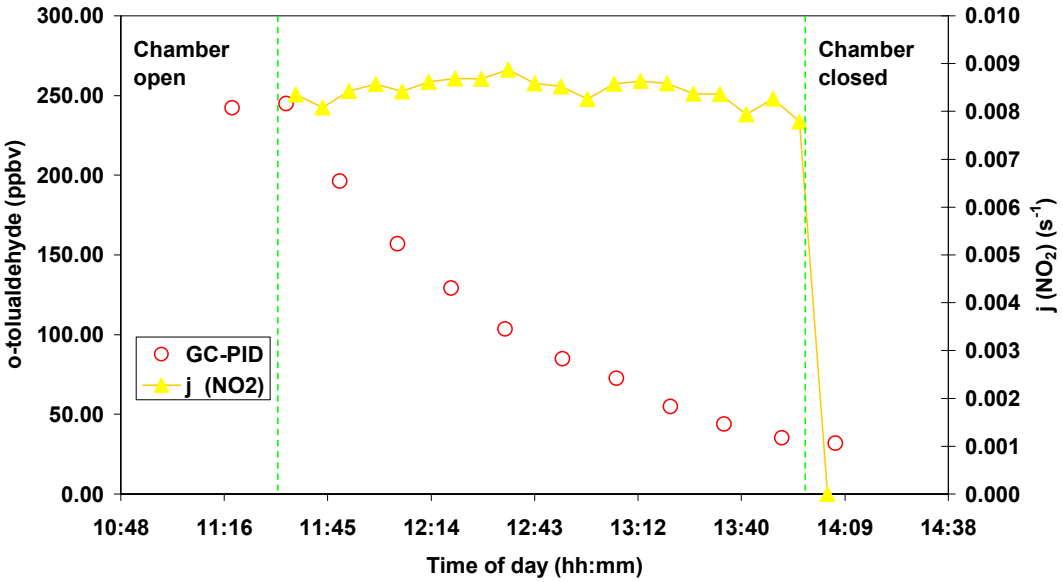
UV Absorption Spectra of Tolualdehydes





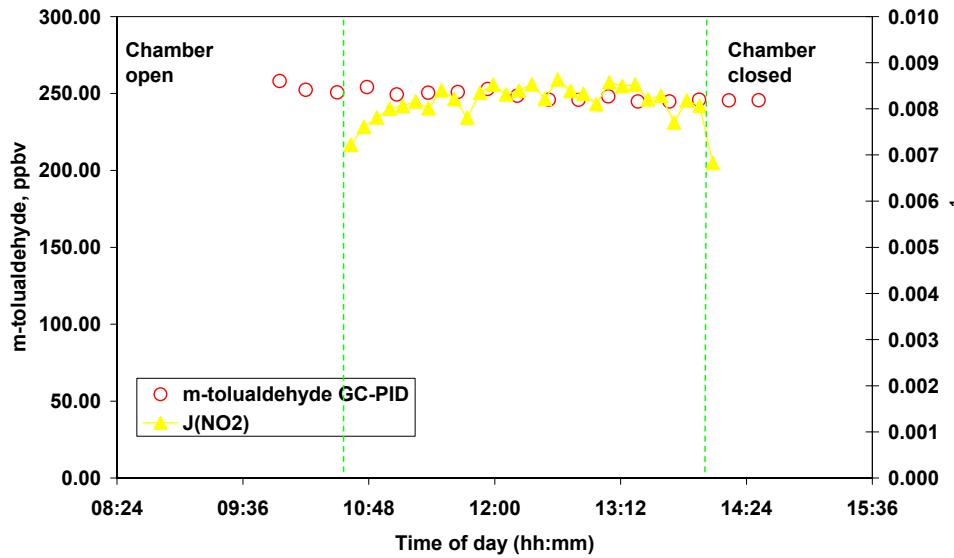
Sunlight Photolysis of Tolualdehydes

Sunlight Photolysis of Tolualdehydes

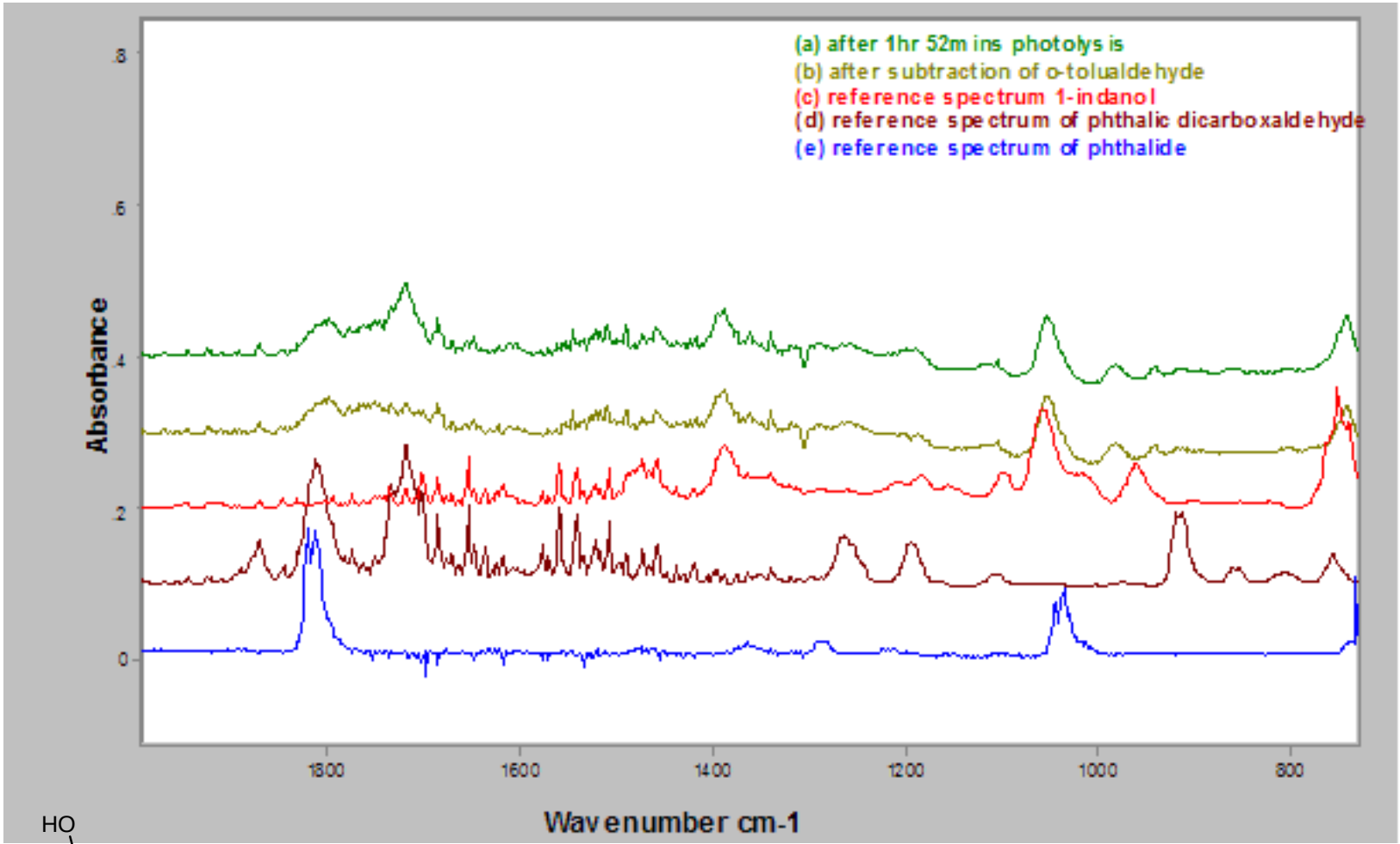


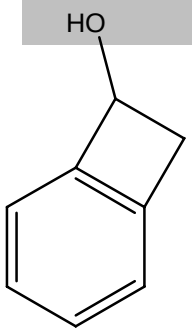
- photolysis lifetime for o-tolualdehyde = 1-2 hr

- m- and p-tolualdehyde are not photolysed

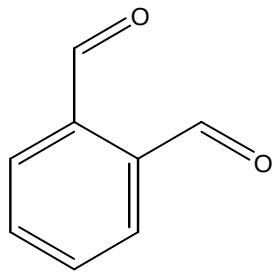


FTIR Spectra of Products



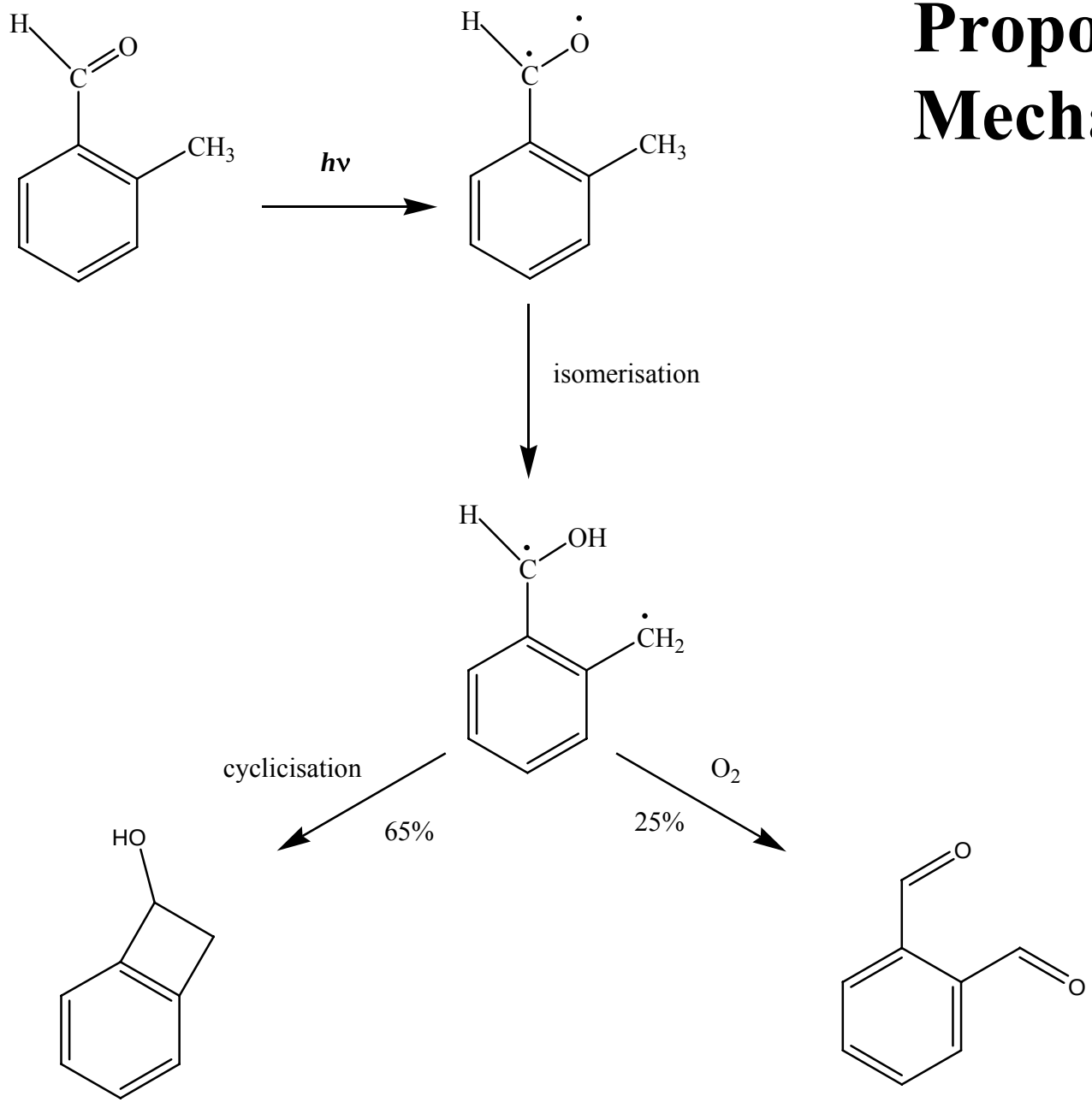


Aromatic cyclic alcohol
~ 65% yield

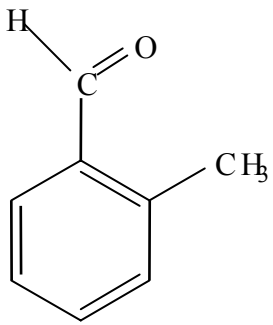


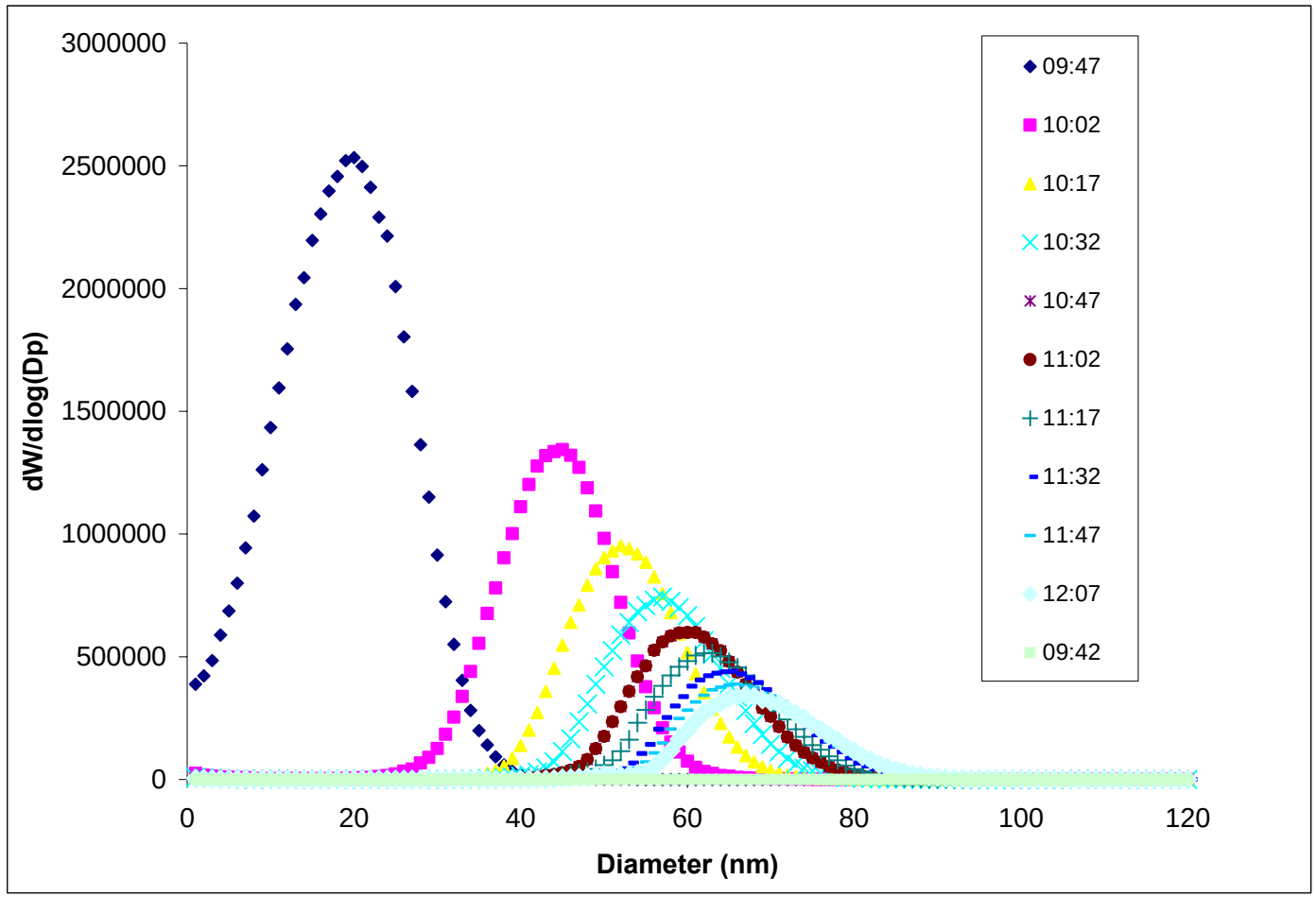
1,2-benzenedicarboxaldehyde
~ 25% yield

Proposed Mechanism

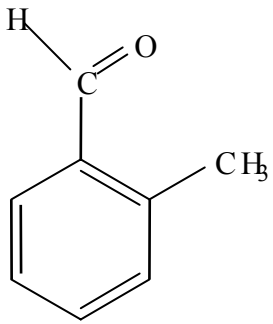


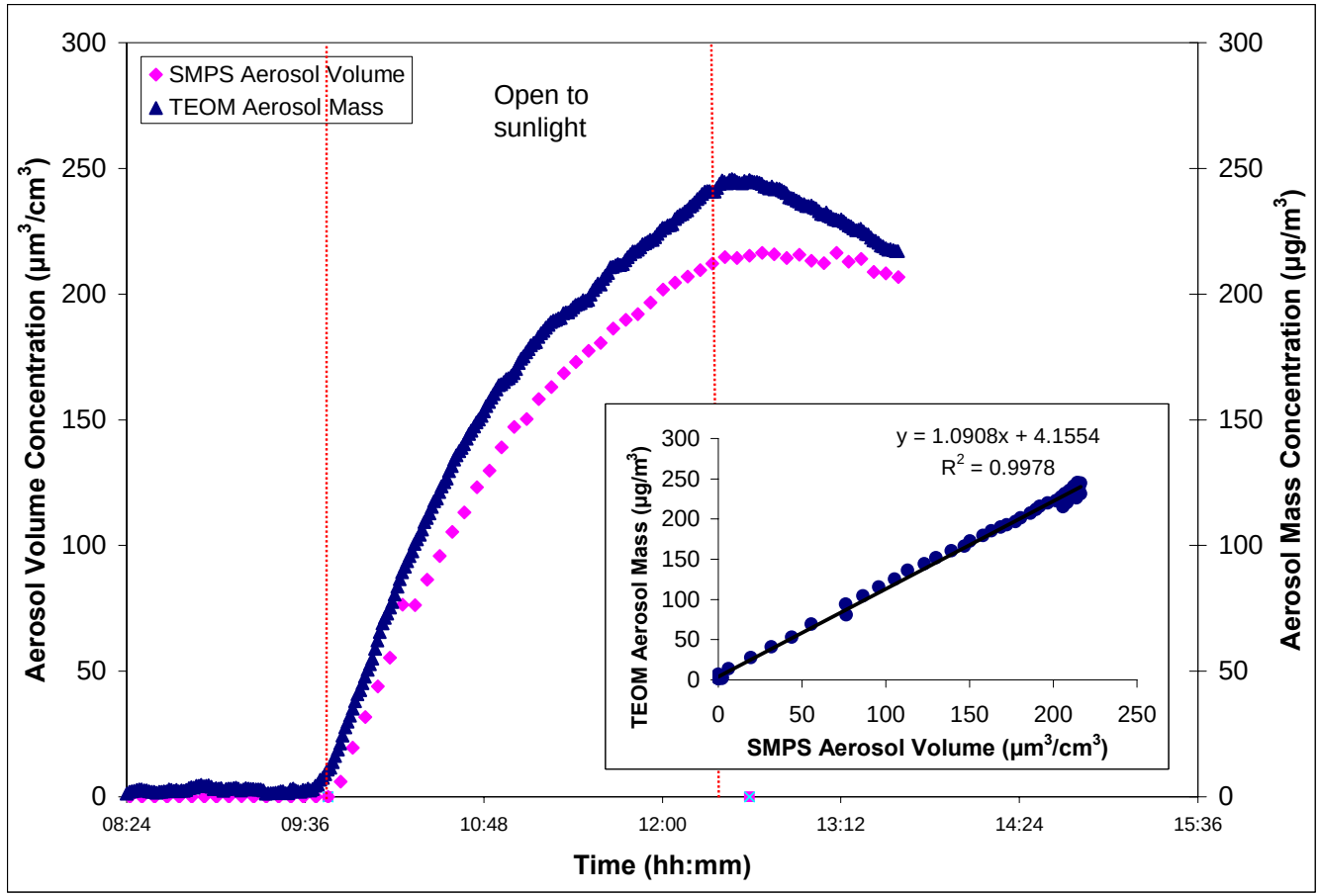
Secondary Organic Aerosol Formation





Secondary Organic Aerosol Formation

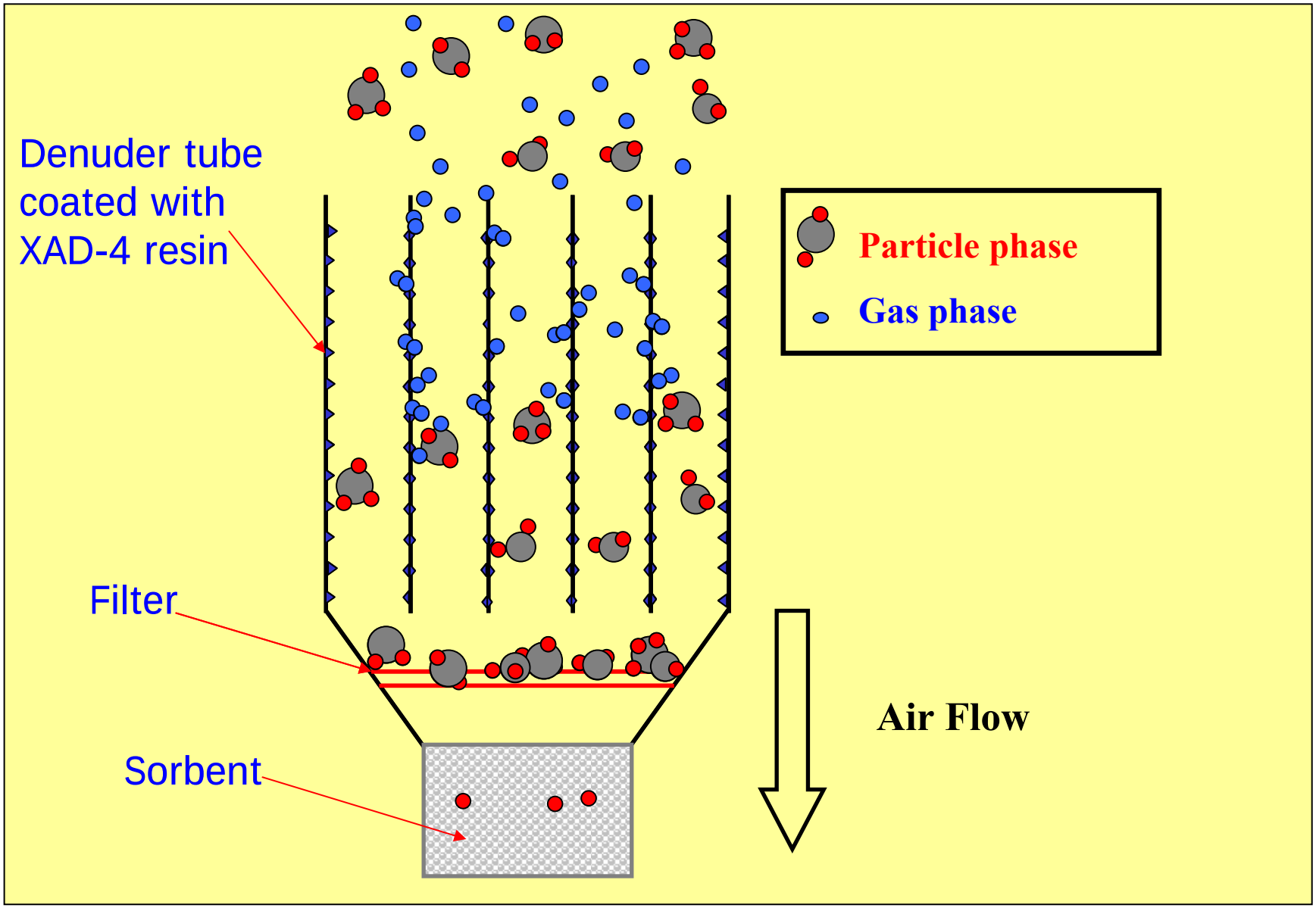




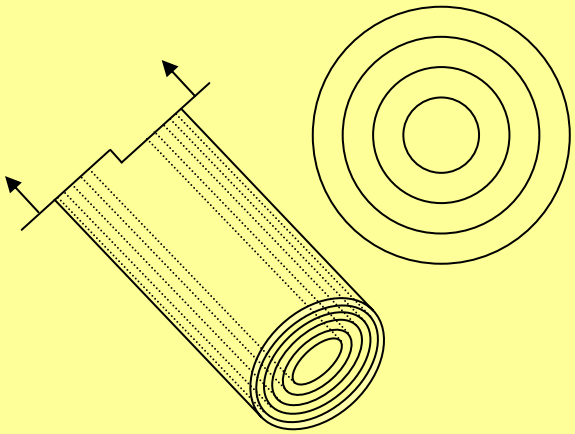
Secondary Organic Aerosol

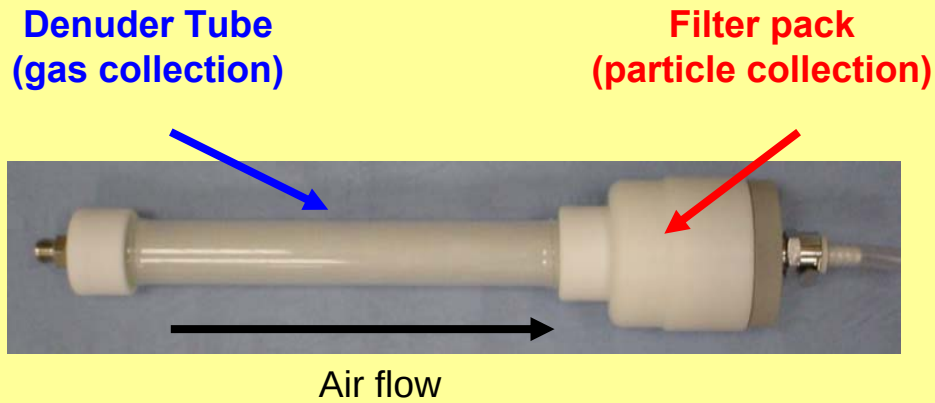
- Not just formed in laboratory studies!!
- Secondary organic fraction represents up to 70% of the organic mass of fine aerosols (PM2.5)
- Composition of SOA ?
- Formation mechanisms ?
- Main species contributing to SOA ?

Denuder-Filter Sampling



Denuder-Filter Sampling at UCC





- 5-channel glass denuder
- Coated with XAD-4 resin
- Doped with pentafluorobenzyl hydroxyl amine (PFBHA)

Derivatization of oxygenated organics

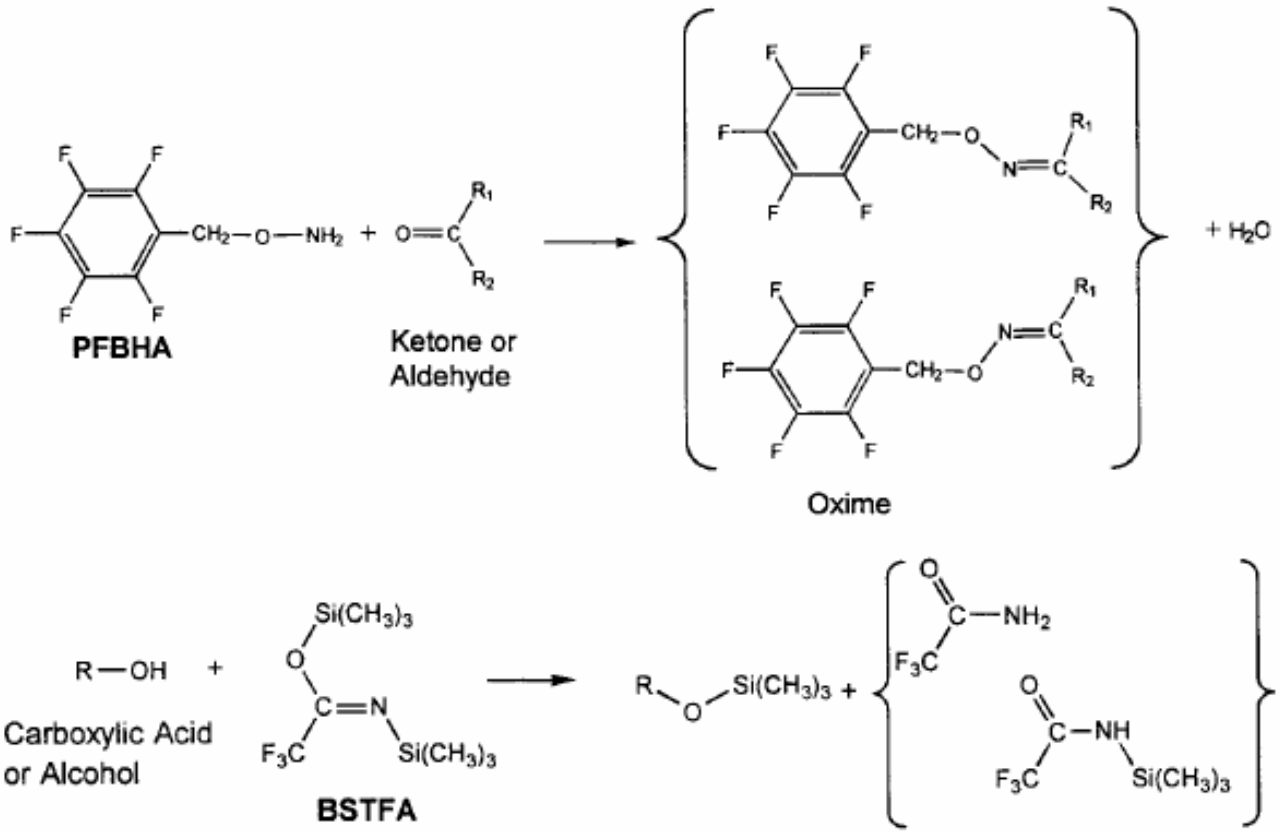
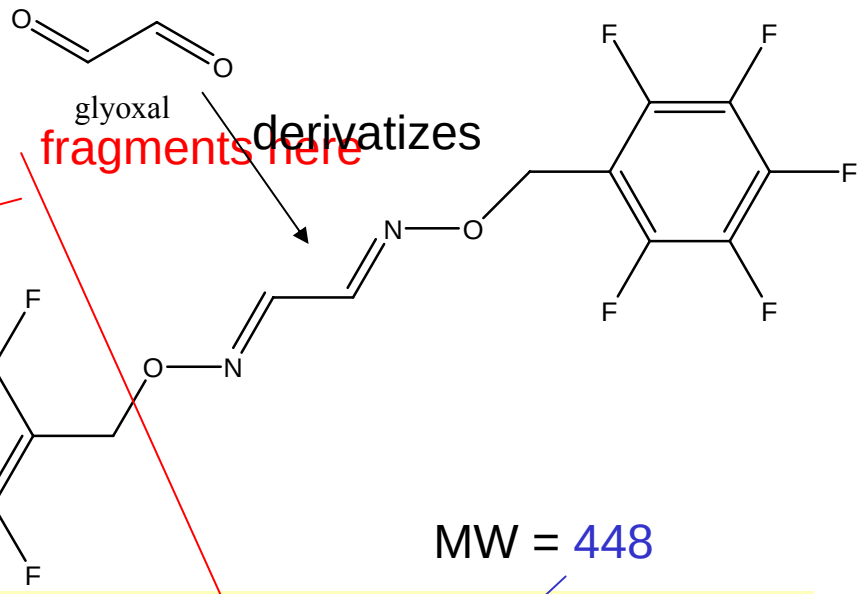


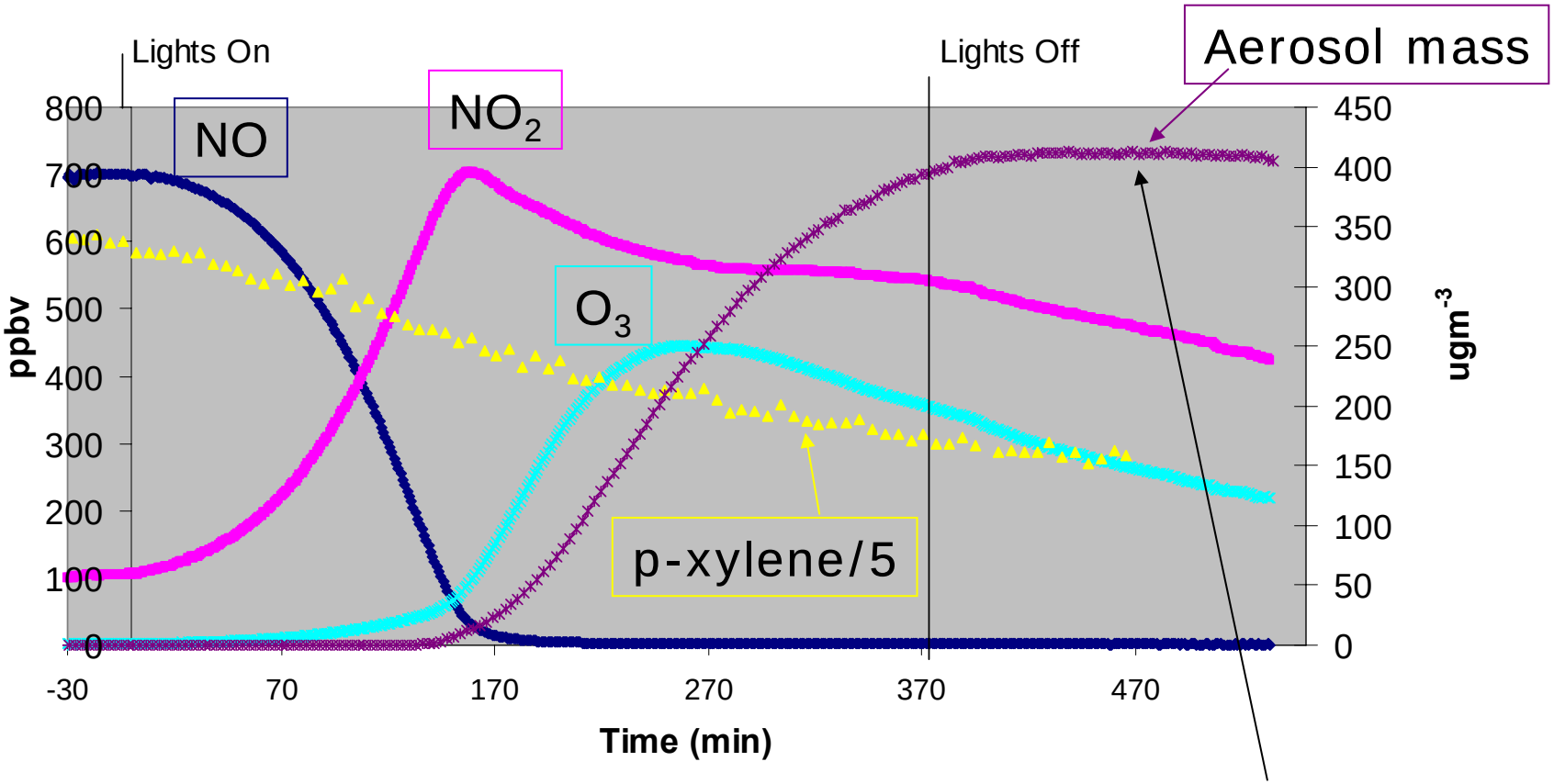
FIGURE 1. Derivatization reactions. (Top) PFBHA derivatizes a carbonyl group. (Bottom) BSTFA derivatizes an —OH group in acids and alcohols.

Yu et al. ES&T 1998, 32, 2357-2370

Glyoxal derivatized

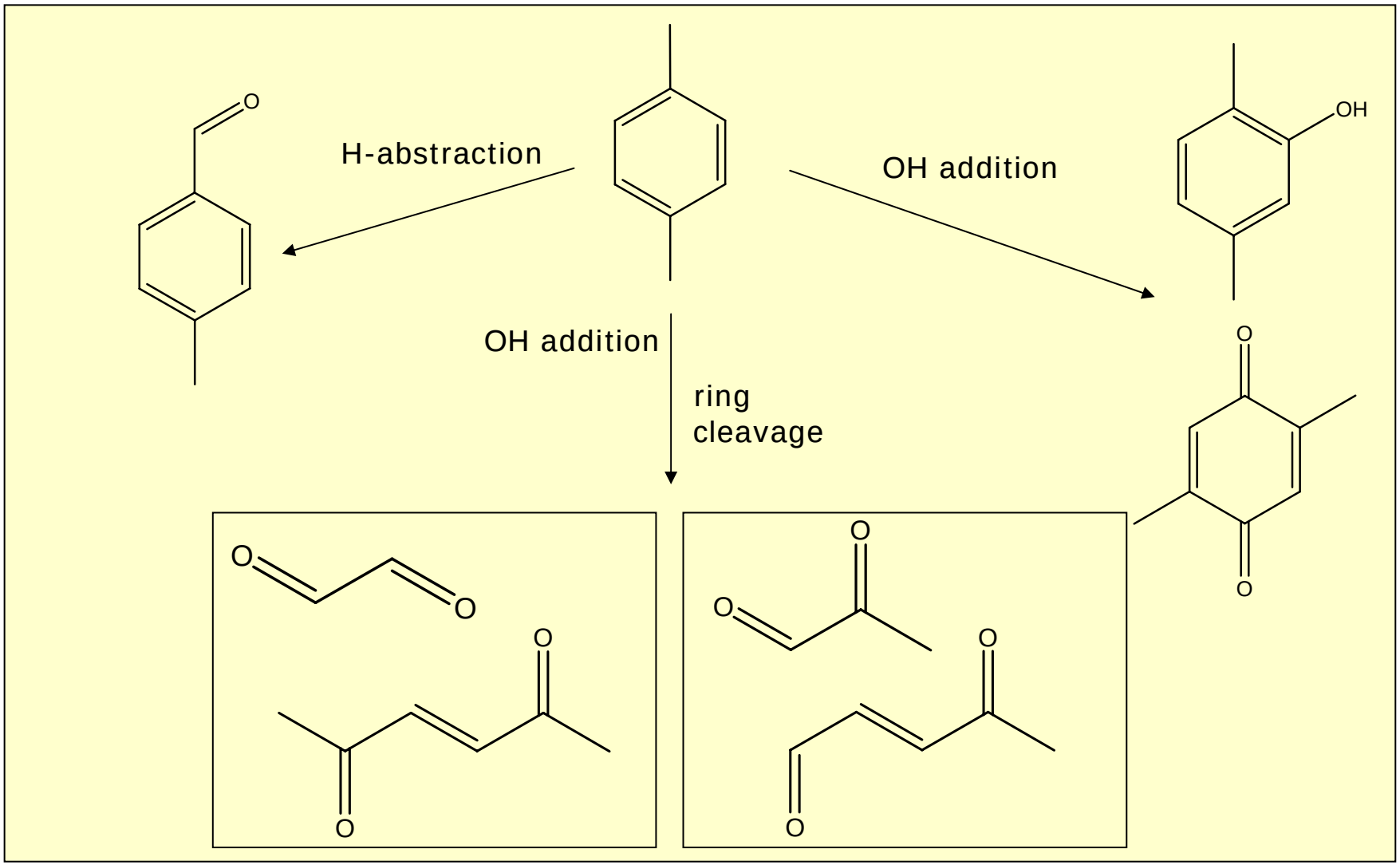


p-xylene photo-oxidation experiment

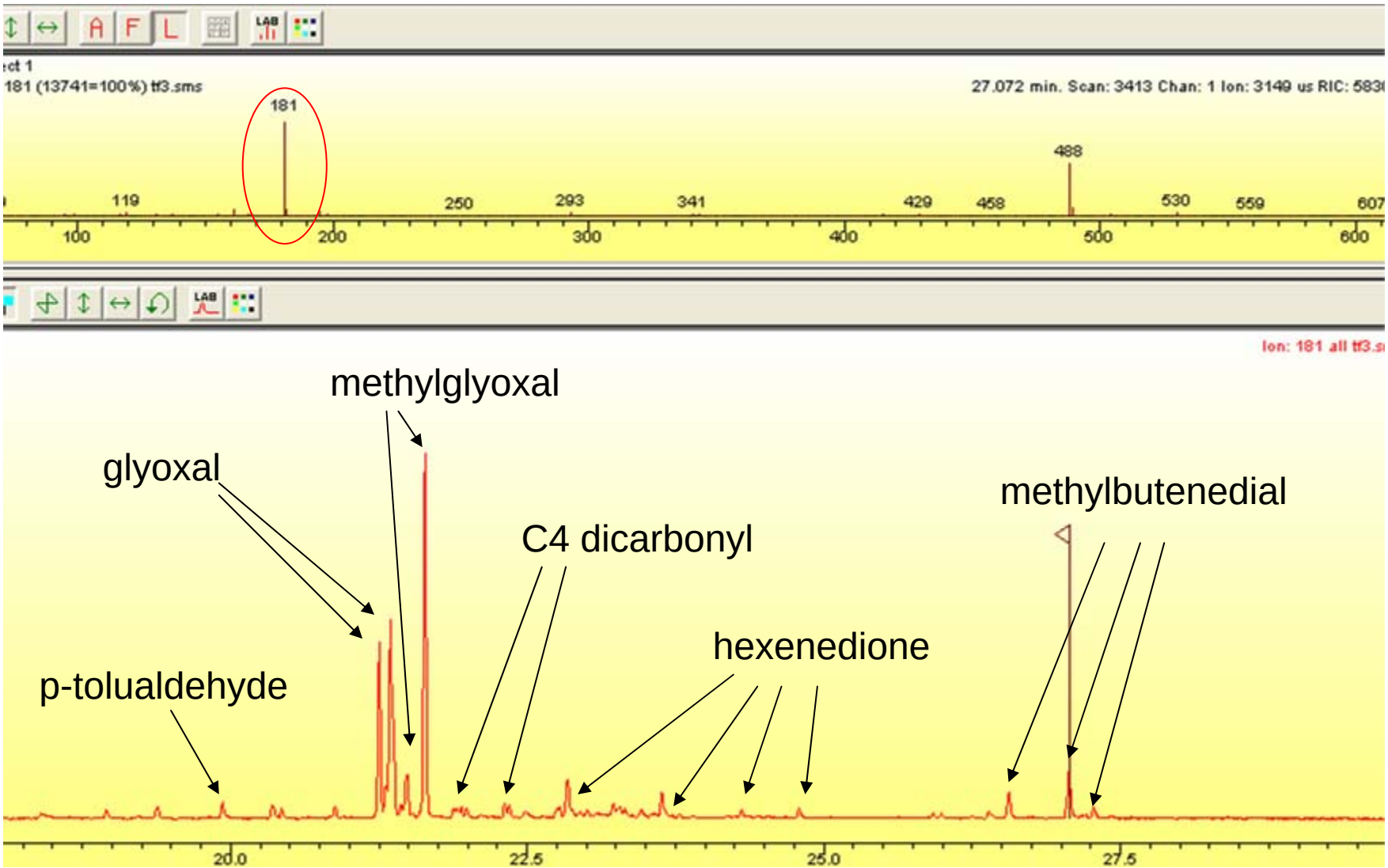


- Aerosol mass yield=3.84%

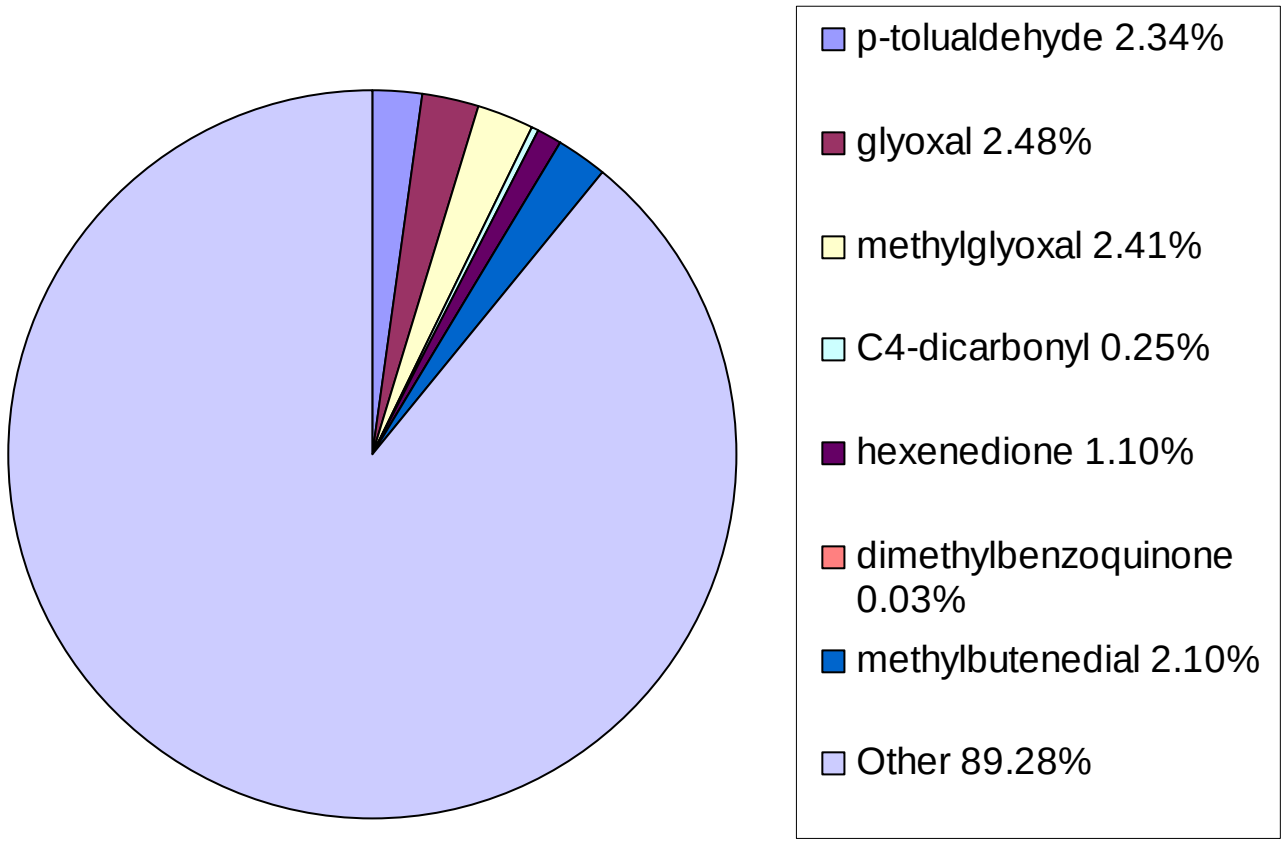
p-xylene photo-oxidation



GC-MS Analysis of p-xylene extracts (filter)

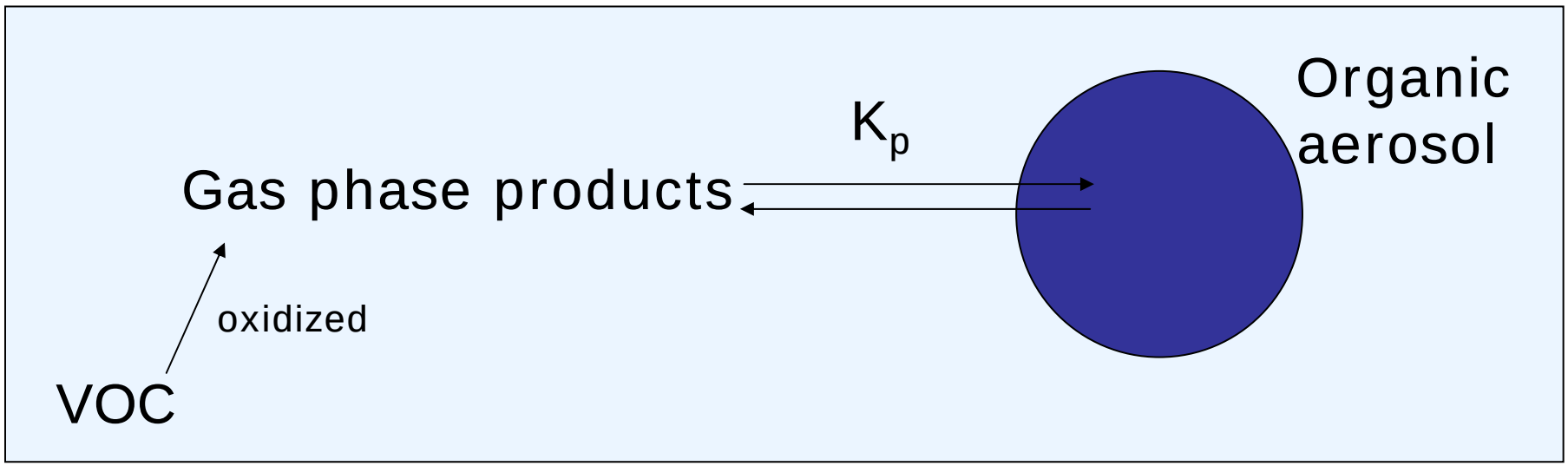


GC-MS Analysis of p-xylene extracts (filter)



Gas/Particle Partitioning

- Many organic compounds partition between gas and particle phase



Gas/Particle Partitioning Values

- Kp calculated both theoretically:

$$Kp_{theoretical} = \frac{f_{om} \times 760 \times R \times T}{MW_{om} \times \gamma_{om} \times P^{\circ}_{L} \times 10^{6}}$$

- and experimentally:

$$Kp_{\exp} = \frac{C_{particle}}{C_{gas} \times [aerosol]}$$

(Pankow)

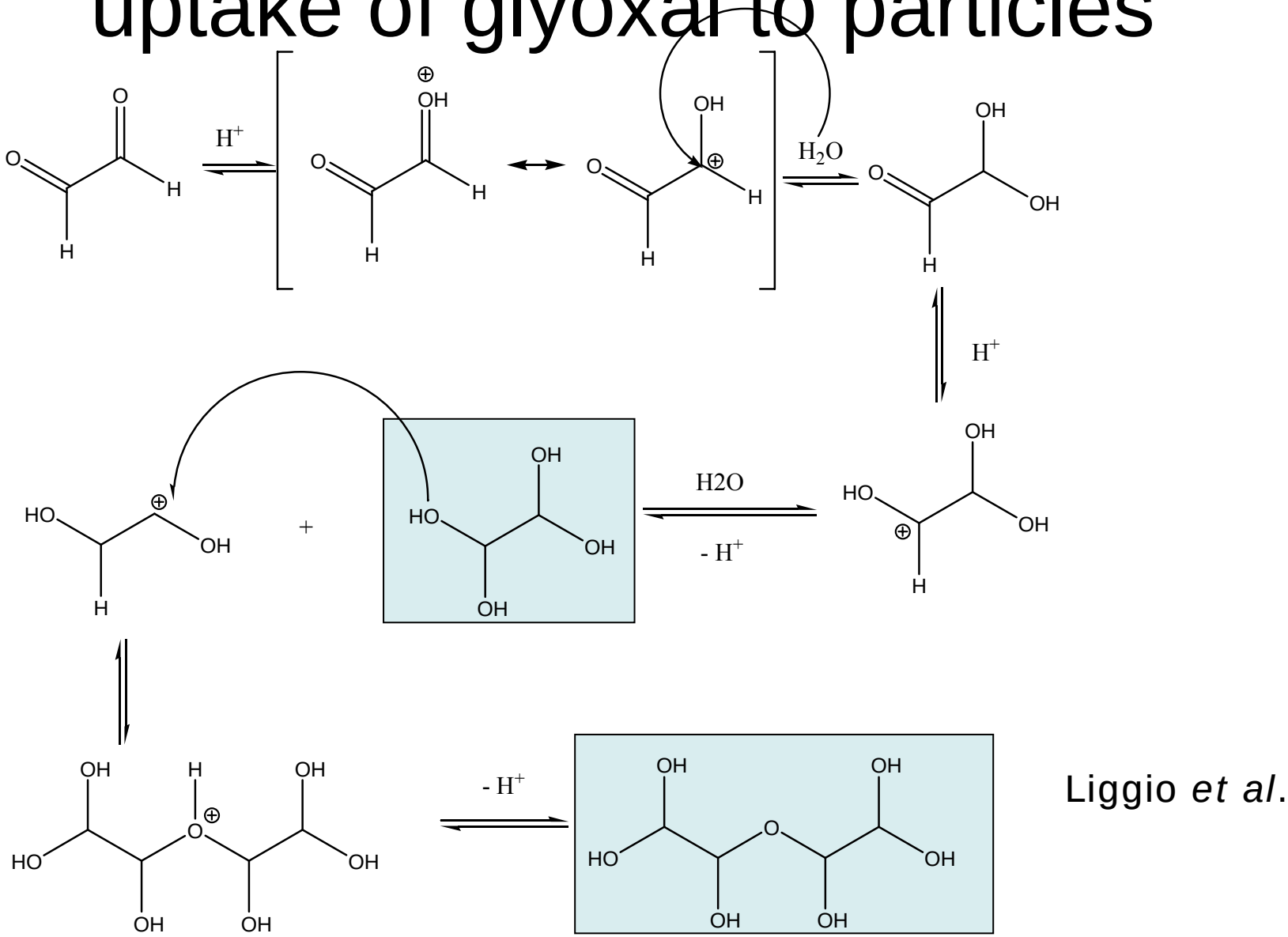
Gas/Particle Partitioning Values

Product	p-tolualdehyde	Hexenedione	Glyoxal	Methylglyoxal
$Kp_{theoretical}$	3.93×10^{-07}	2.04×10^{-06}	1.73×10^{-09}	3.69×10^{-09}
$Kp_{experimental}$	8.84×10^{-06}	4.58×10^{-06}	5.57×10^{-05}	3.28×10^{-05}

- Glyoxal and methylglyoxal K_p several orders of magnitude higher than expected

(vapor pressures from SPARC on line calculator- University of Georgia)

Acid-catalyzed Polymerization-uptake of glyoxal to particles



Liggio *et al*.

Conclusions

- Advances in knowledge of the reactivity of xylene oxidation products – improved mechanisms

- Small dicarbonyl compounds partition to the particle phase much more than expected from vapor pressure calculations

- Suggests further processes occuring on/in particles (oligomerization)
  -eg. *Kalberer et al. Science 2004*

Future Directions

- On-tube derivatization of acids/phenols
- Further chamber experiments on aromatic aldehydes and phenols
- Mass balance for xylene photo-oxidation systems still poor (at best 45%). New experimental approaches using state-of-the-art analytical techniques are needed.

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