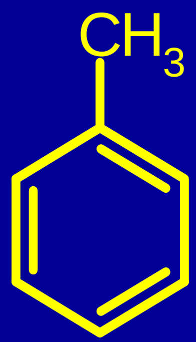
A Predictive Kinetic Model for Aerosol Formation from Toluene



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gas phase chemistry

↓

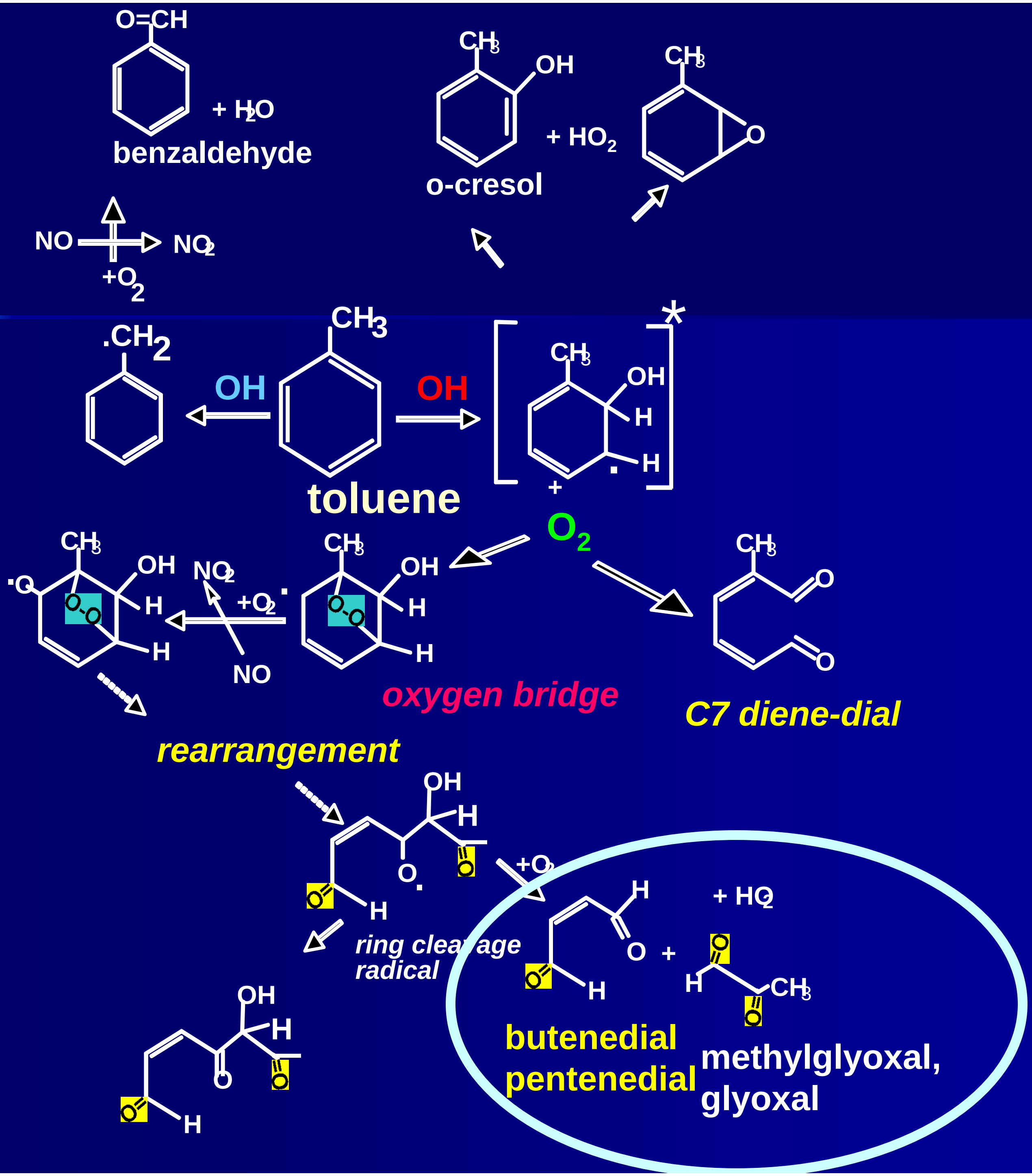
oxygenated products

⇅

partition to the particle phase

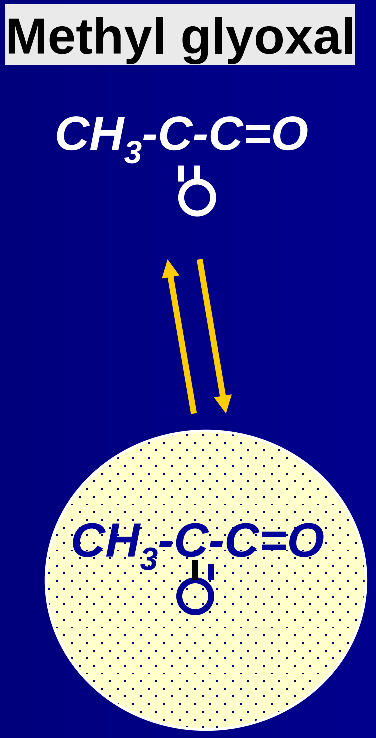
↓

particle phase reactions


O=CH
+ H2O
benzaldehyde
NO
NO2
+O2
CH3
OH
+ HO2
o-cresol
CH3
O
.CH2
OH
CH3
toluene
OH
CH3
OH
H
H
+
*
O2
CH3
OH
NO2
+O2
H
H
NO
·O
O-O
CH3
OH
H
H
O-O
oxygen bridge
CH3
O
O
C7 diene-dial
rearrangement
OH
H
O
O
O
H
ring cleavage radical
+O2
H
O
+
O
H
+ HO2
O
H
CH3
O
butenedial
pentenedial
methylglyoxal,
glyoxal
OH
H
O
O
O
H

Gas and particle phases are linked via G/P partitioning

Gas phase reactions →



Methyl glyoxal

$CH_3\text{-}\underset{\overset{\|}{O}}{C}\text{-}C=O$

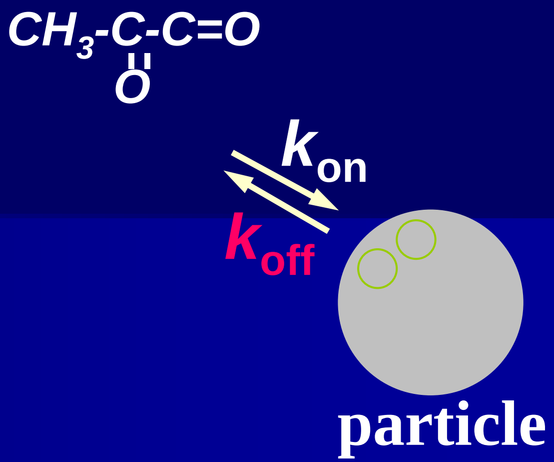
$CH_3\text{-}\underset{\overset{\|}{O}}{C}\text{-}C=O$

particle

$^{i}C_{gas} + \Sigma OM \rightleftarrows {}^{i}C_{part}$

$$\boxed{K_p = \frac{{}^{i}C_{part}}{{}^{i}C_{gas}\,\Sigma OM}}$$

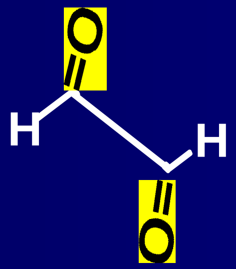
- $$K_p = \frac{760\,R\,T\,f_{om}}{\boxed{p_{iL}^{*}\ \gamma}\,Mw\,10^6}$$



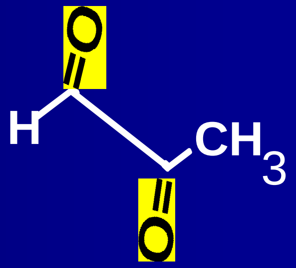
- $K_p = k_{on}/k_{off}$

- $$[\,{}^{i}\mathrm{gas}] + [{}^{i}\mathrm{om}] \underset{k_{off}}{\overset{k_{on}}{\rightleftharpoons}} [\,{}^{i}\mathrm{part}]$$

Glyoxal in the gas and particle phase



glyoxal



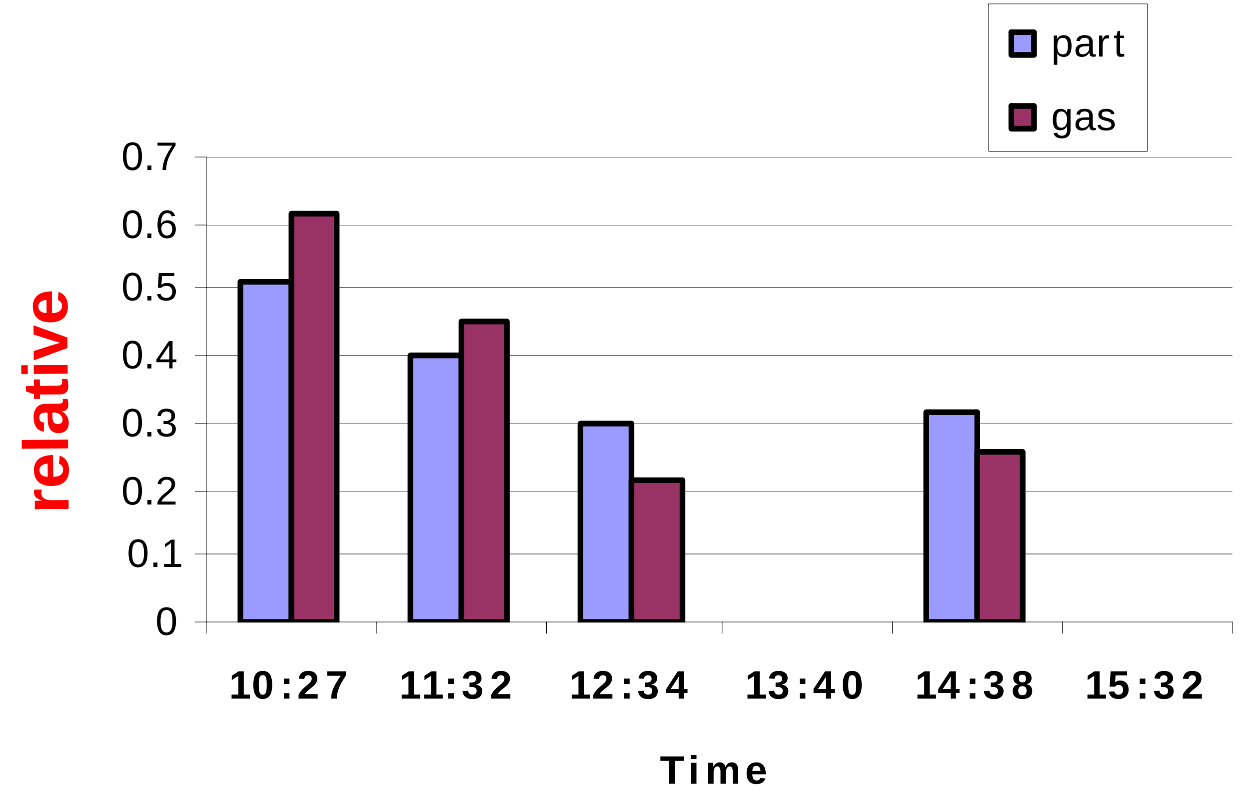
methylglyoxal

Vapor pressures ~ 40-50 torr

$$K_p = \frac{760\,R\,T\,f_{om}}{p^{*}_{iL}\;\gamma\;Mw10^{6}}$$

$$\mathbf{K_p = \frac{{}^{i}C_{part}}{{}^{i}C_{gas}\Sigma OM}}$$

Glyoxal in the gas and particle phase (PFBHA)



$$GLY_{gas} + \Sigma OM \rightarrow GLYpart$$

$500 \times k_{on}$

Glyoxal in water strongly favors hydration

The hydration equilibrium constant for

glyoxal $\leftrightarrows$ dihydrate; $K_h = 7 \times 10^4$

Glyoxal uptake coefficients

Liggio, Li, McLaren suggest uptake coefficients (γ_{accom}) of $8\ x10^{-4}$ to **$7.3x10^{-3}$**

$$k_{on} = \frac{6.0\times10^{-10}\,\gamma_{accom} < c > \Sigma OM}{4\rho_p D_p}$$

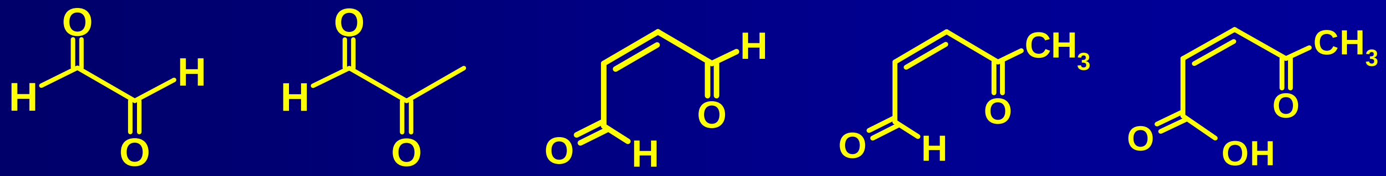
Particle Off-gassing Experiments

$$ln\left(\frac{C^{i}_{out}}{C^{i}_{in}}\right) = -k^{i}_{off} \times t^{i}_{off}$$

$$k^{i}_{off} = \frac{k_b T}{h} exp\left(-\frac{\Delta\phi_a}{k_b T}\right)$$

$$k_{off}^{i} = \frac{k_b T}{h} exp(-\frac{\Delta\phi_a}{k_b T})$$

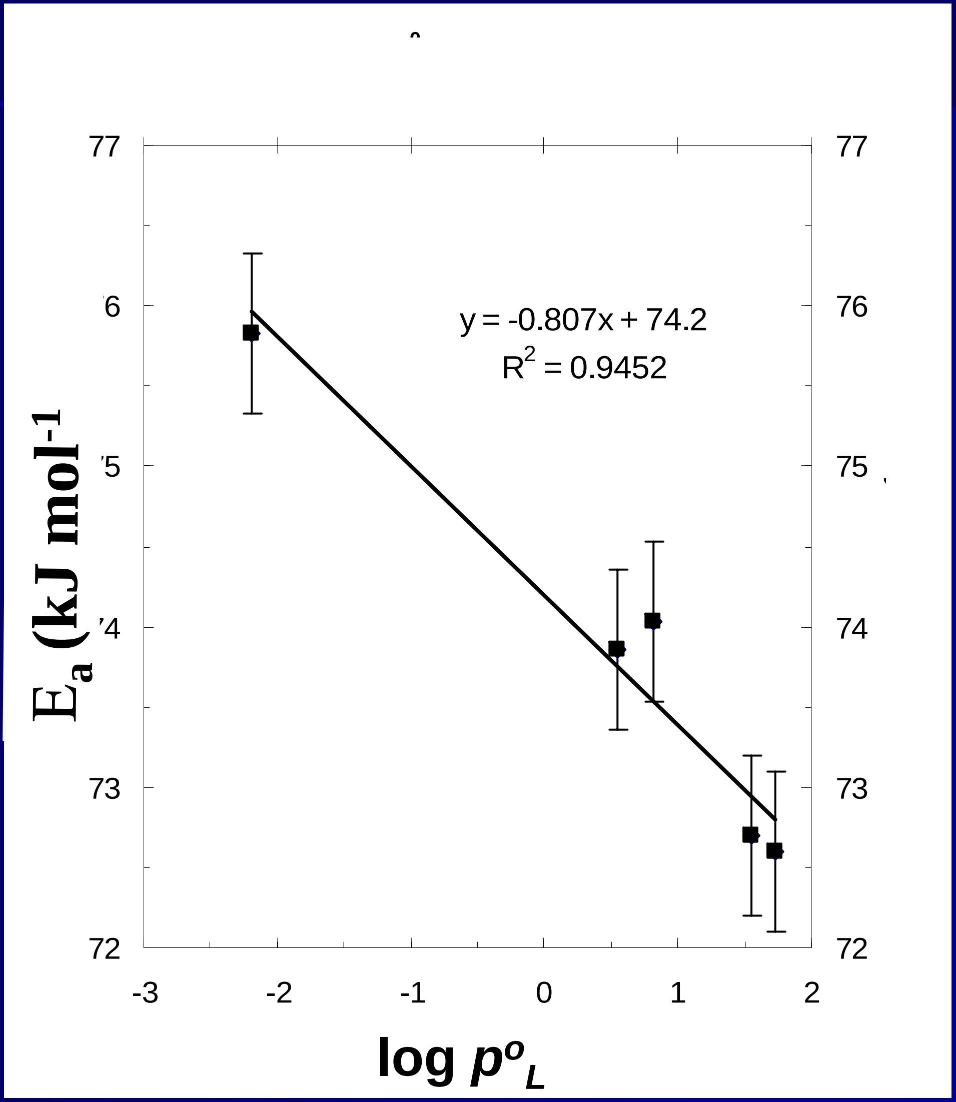
$$ln(\frac{C_{out}^{i}}{C_{in}^{i}}) = -k_{off}^{i} \times t_{off}^{i}$$



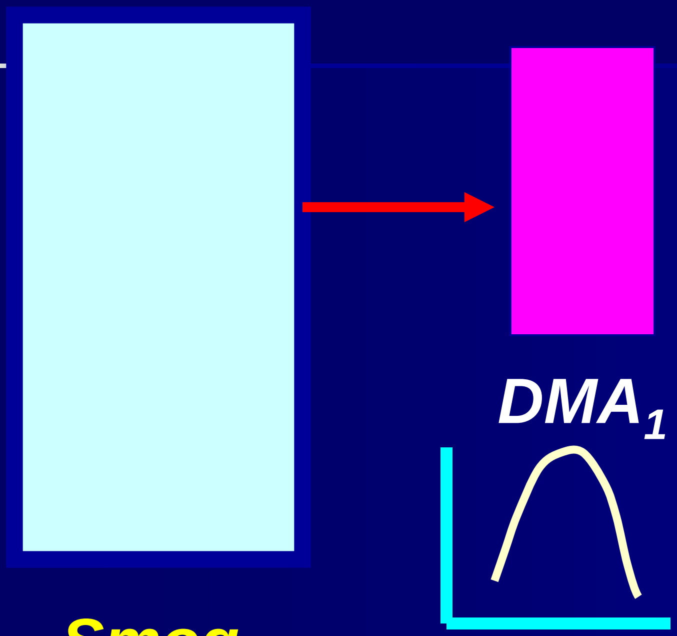
$p_{L,298K}^{0}(torr)$	50	36	6.5	3.6	0.006

$$E_a(kJmol^{-1}) = -3.7 \times \log({}^{i}p_{l,298K}^{0} / torr) + 64.8$$

Evaporation energy barriers and vapor pressures



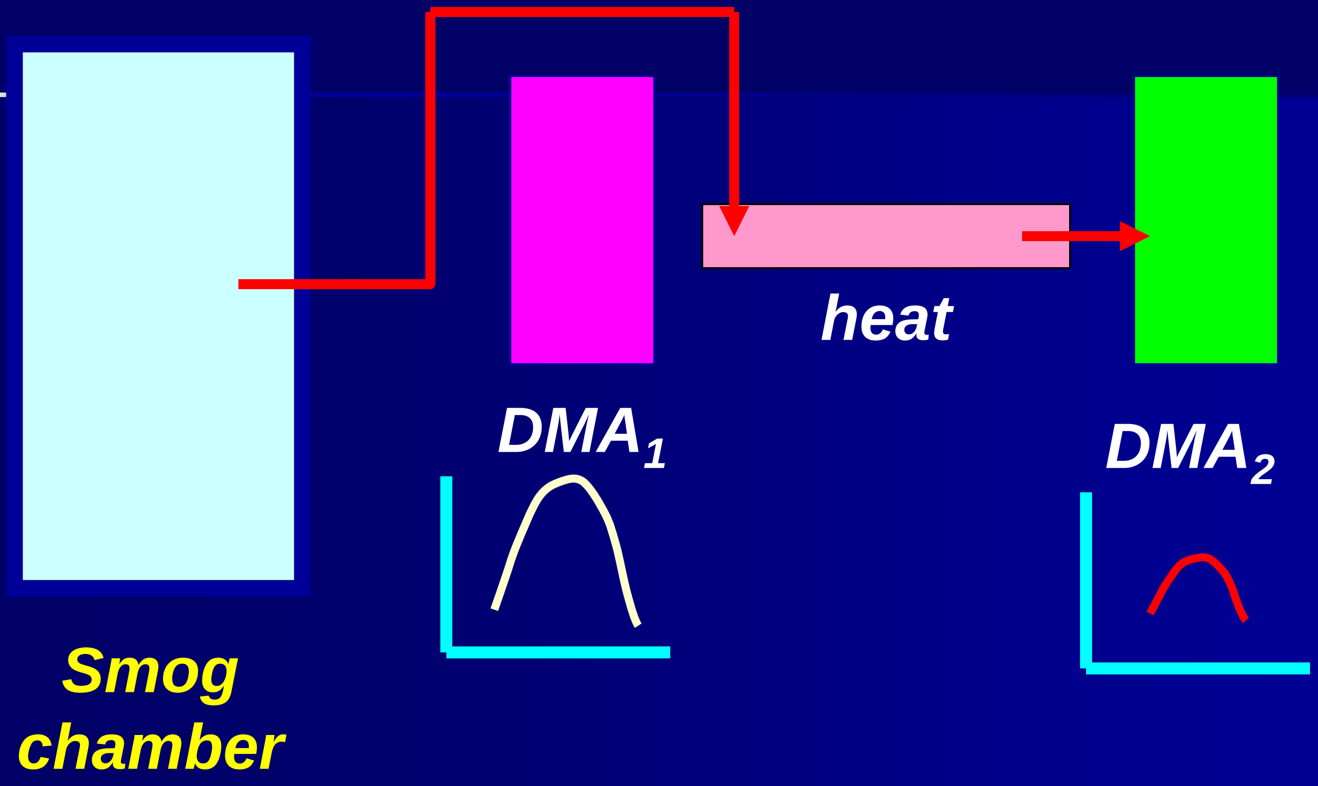
Volatile “Hot” DMA system **Kalberer, et al, Offenberg et al.**



DMA_1

Smog chamber

Volatile “Hot” DMA system



Current Mechanism has:

98 gas phase reactions
67 gas to particle phase species
16 “particle phase” reactions

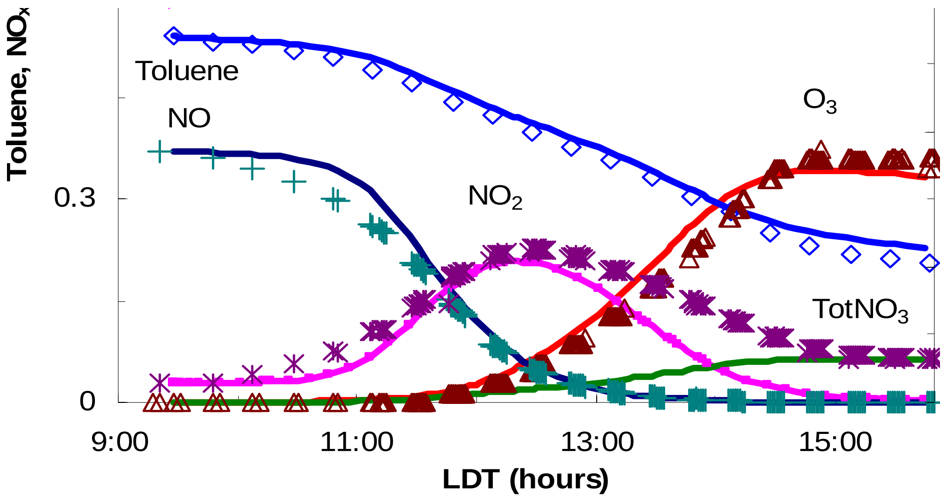
CB4 (2002) chemistry

Model Simulations of UNC outdoor Toluene/NOx Experiments

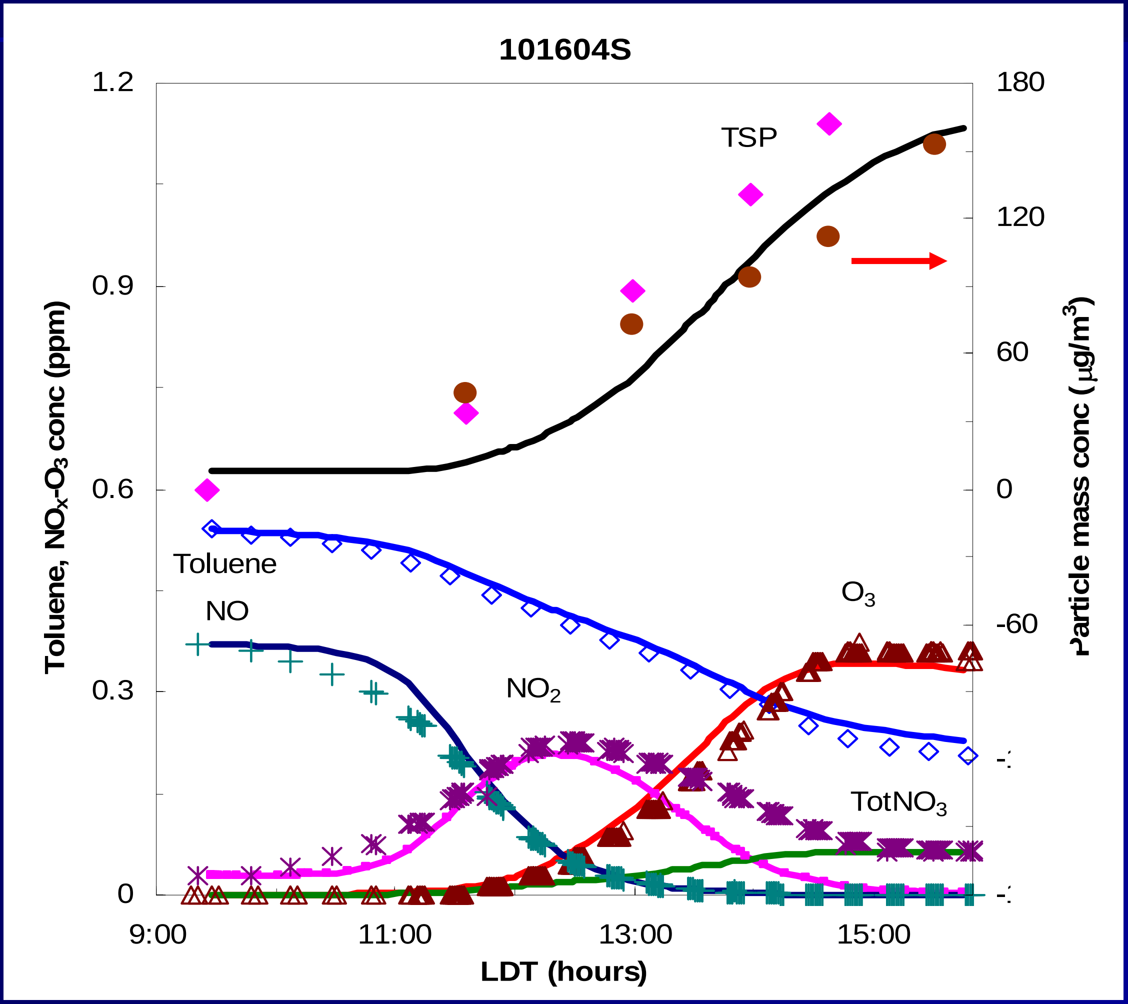
Products

	250μg/m^3	13 μg/m^3
GLYPOLY	60	17
MGLYPOLY	5	1
SEED1	10	20
Organic nitrates	7	26
CH3N02phenols	11	13
organic peroxides	4	5
C6OHNO2ACID	1	13
others	2	5

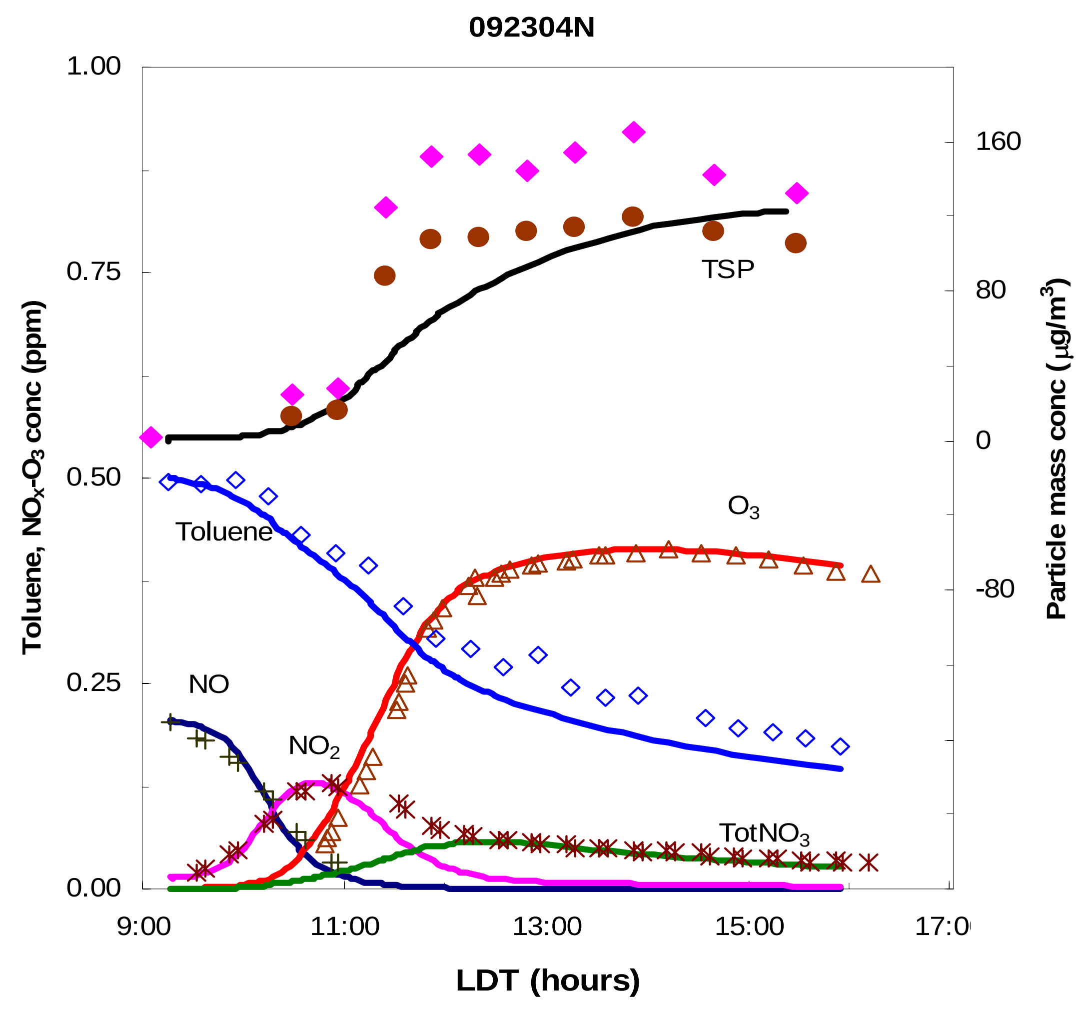
0.54 ppmV TOL + 0.37 ppm NOx



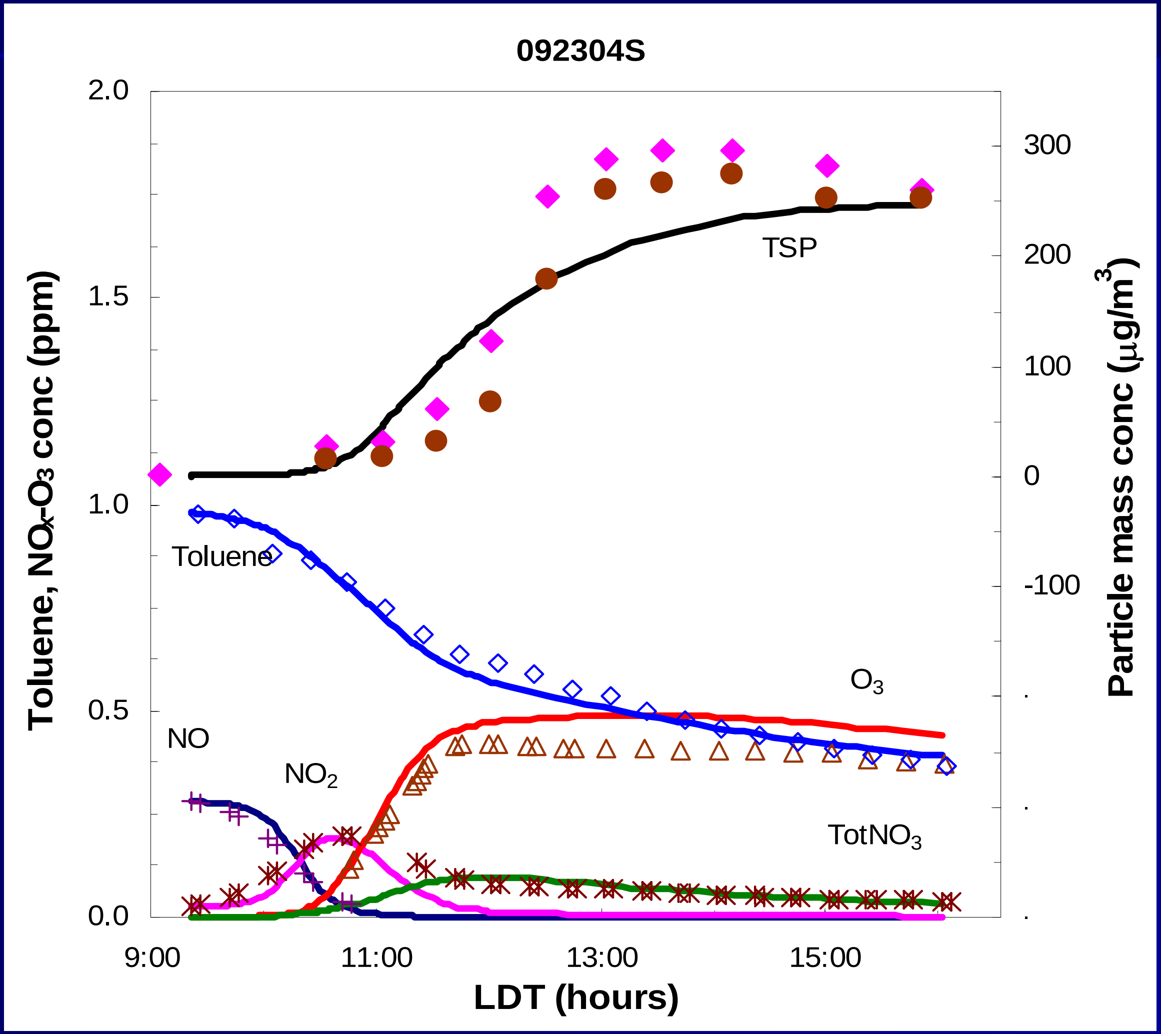
0.54 ppmV TOL + 0.37 ppm NOx



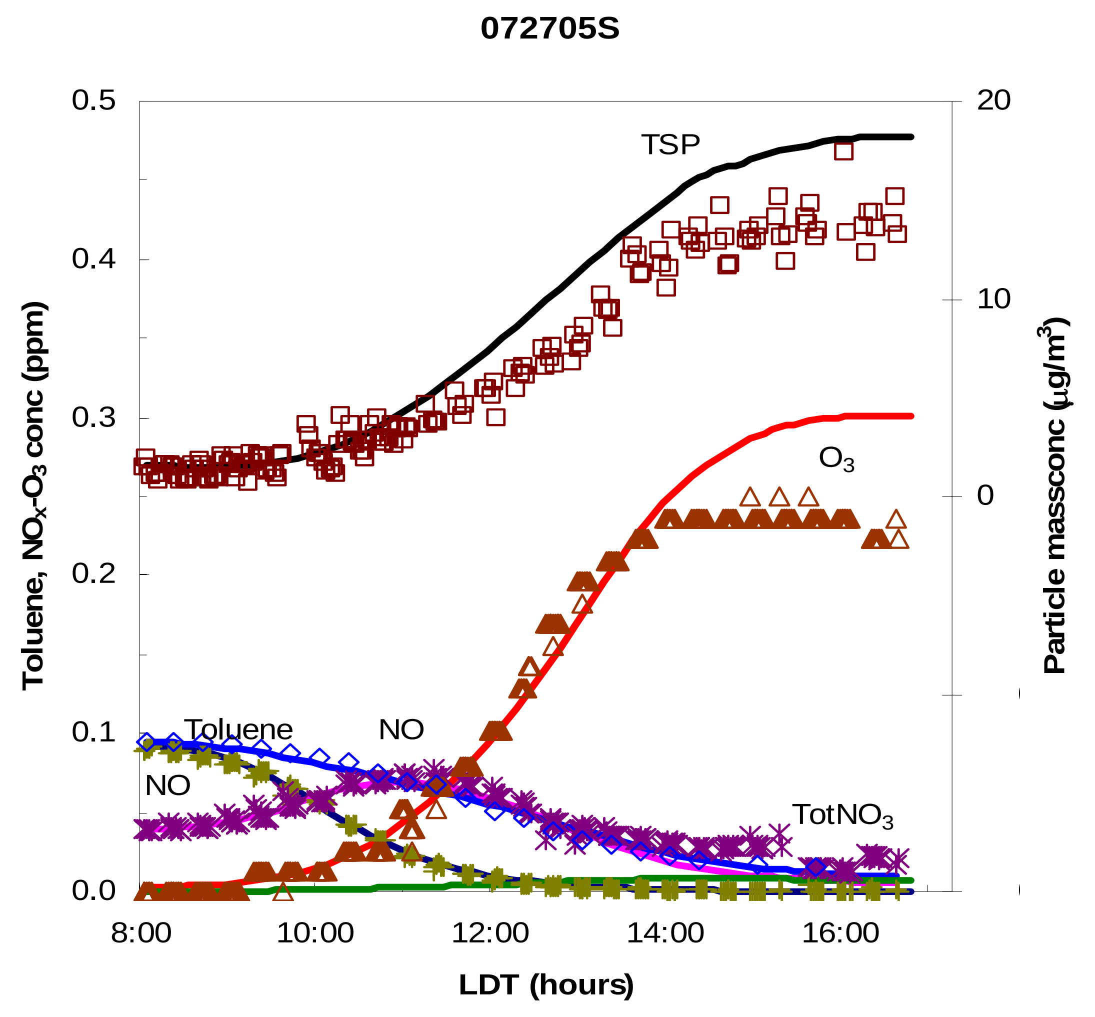
0.5 ppmV TOL + 0.2 ppm NOx



1 ppmV TOL + 0.3 ppm NOx

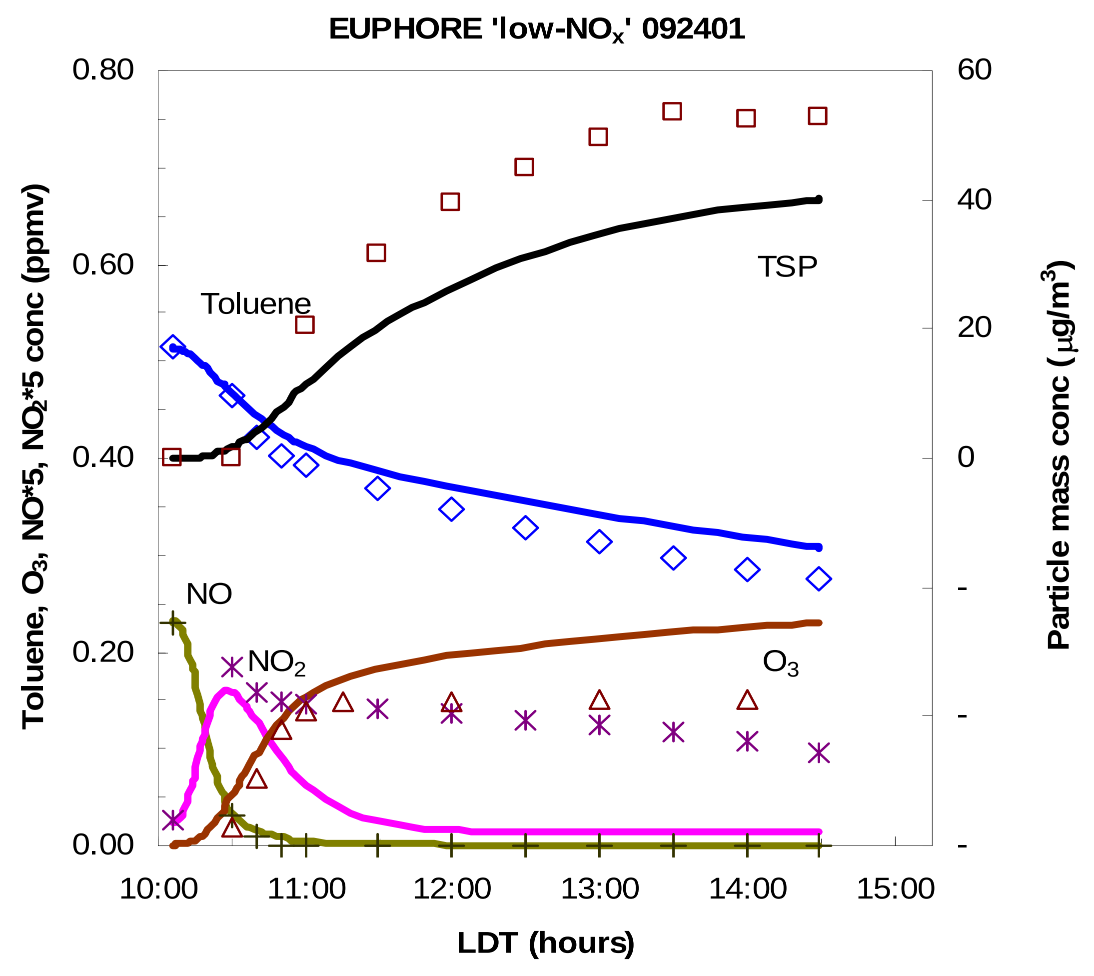


0.1 ppmV TOL + 0.13 ppm NOx

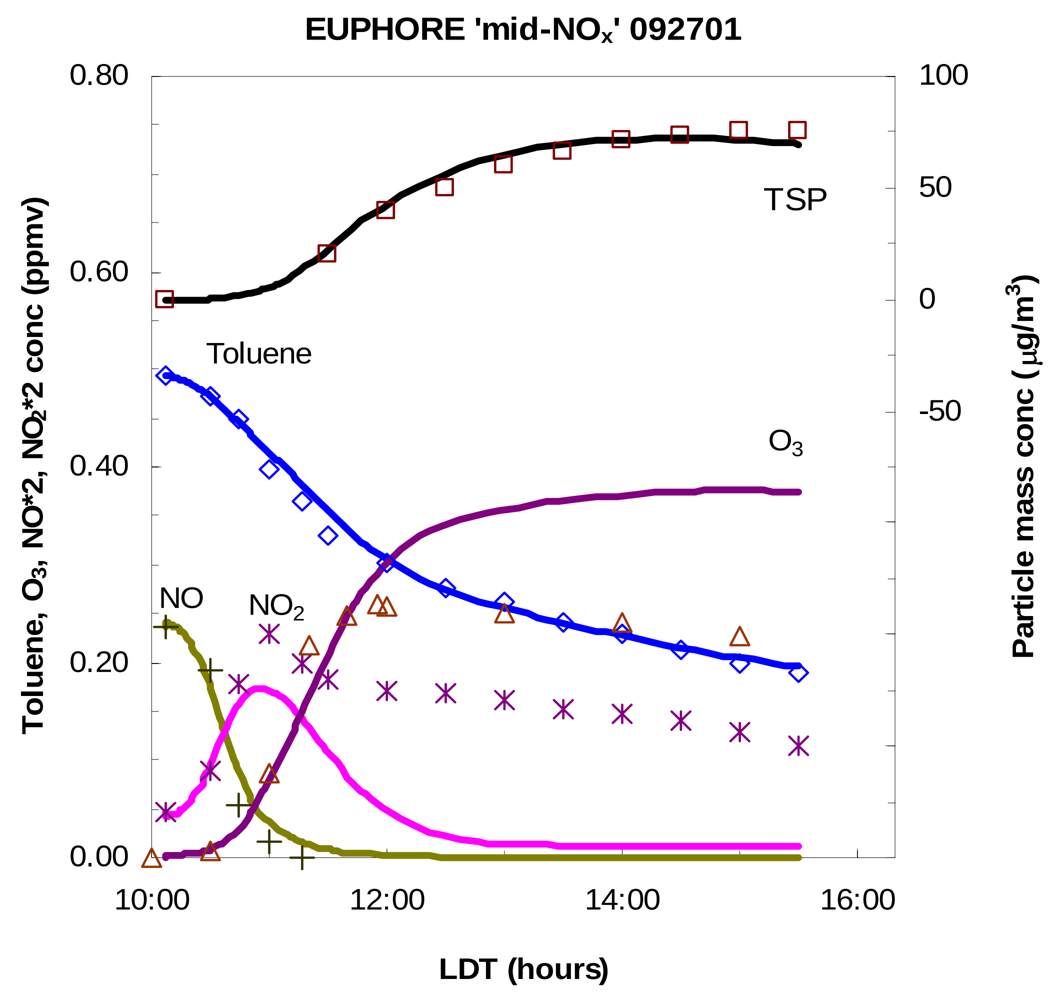


Model Simulations of the EUPHORE Chamber Data

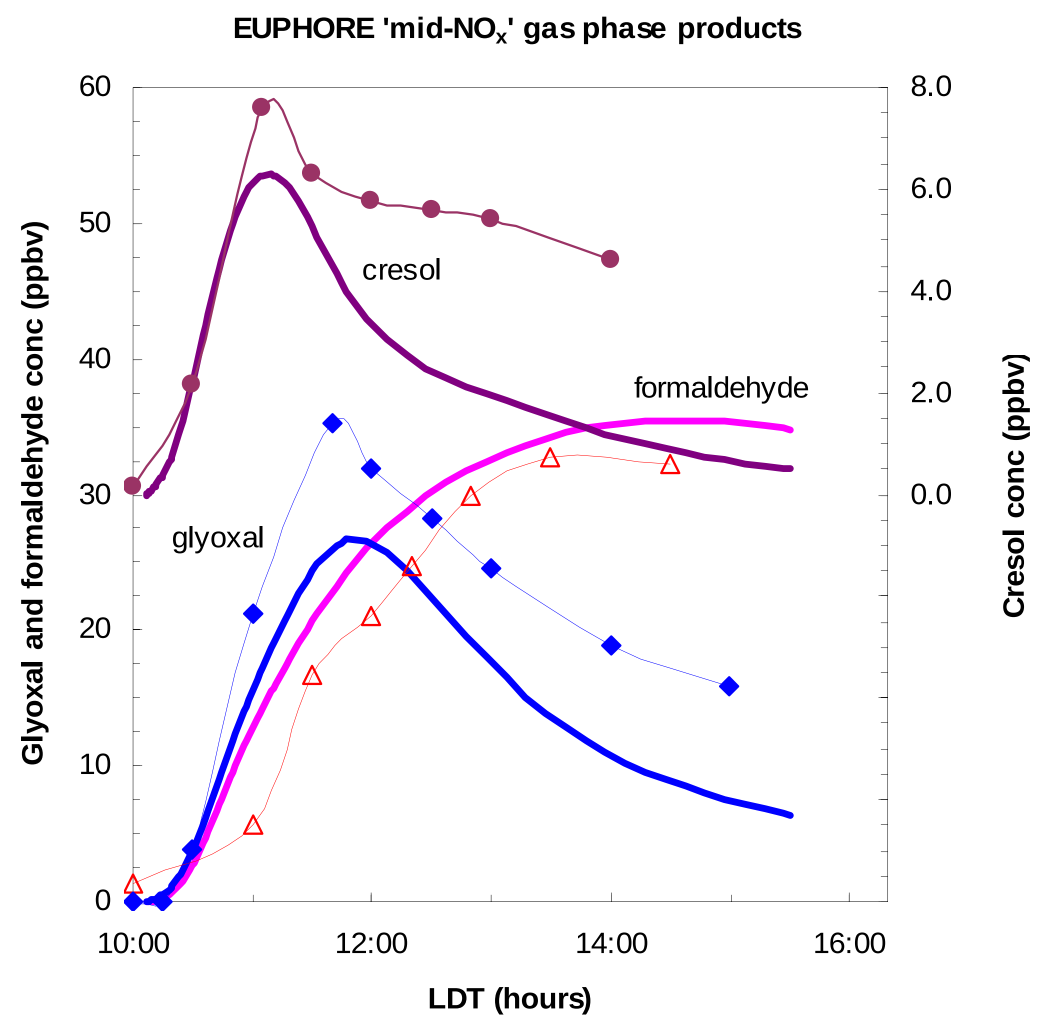
0.5ppmv TOL + 0.05 ppm NOx



0.5 ppmV TOL + 0.13 ppm NOx

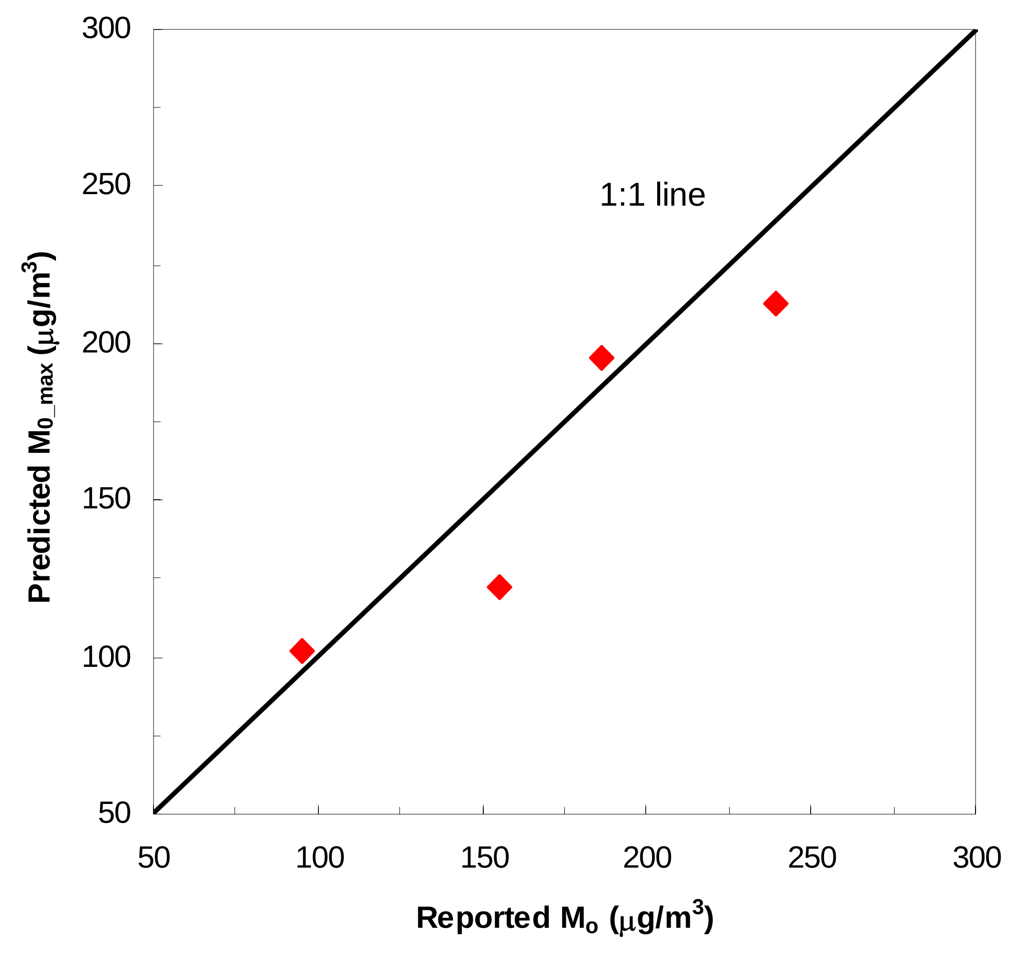


0.5 ppmv TOL + 0.13ppmv NOx



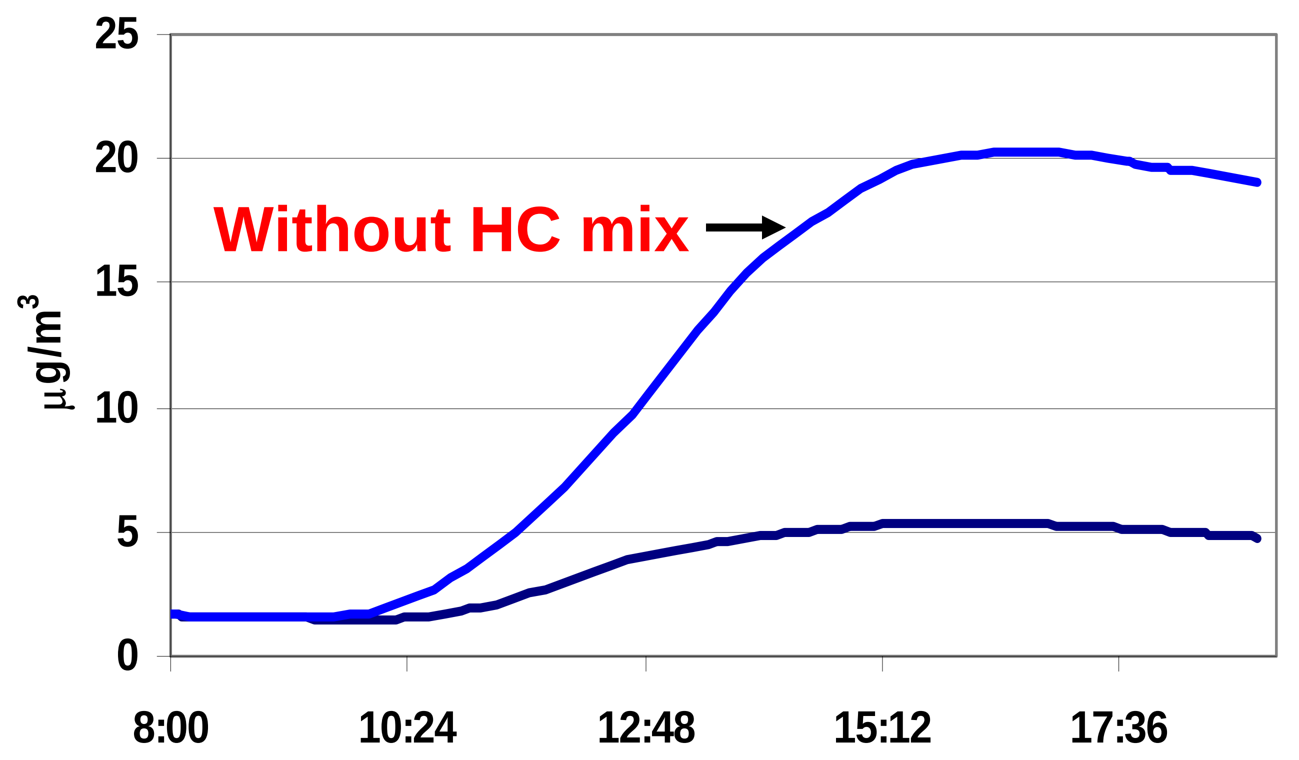
Model Simulations of the Caltech Chamber Data

Predicted aerosol mass conc. vs. Caltech reported mass conc.



Toluene SOA behavior with in an atmospheric HC mixture

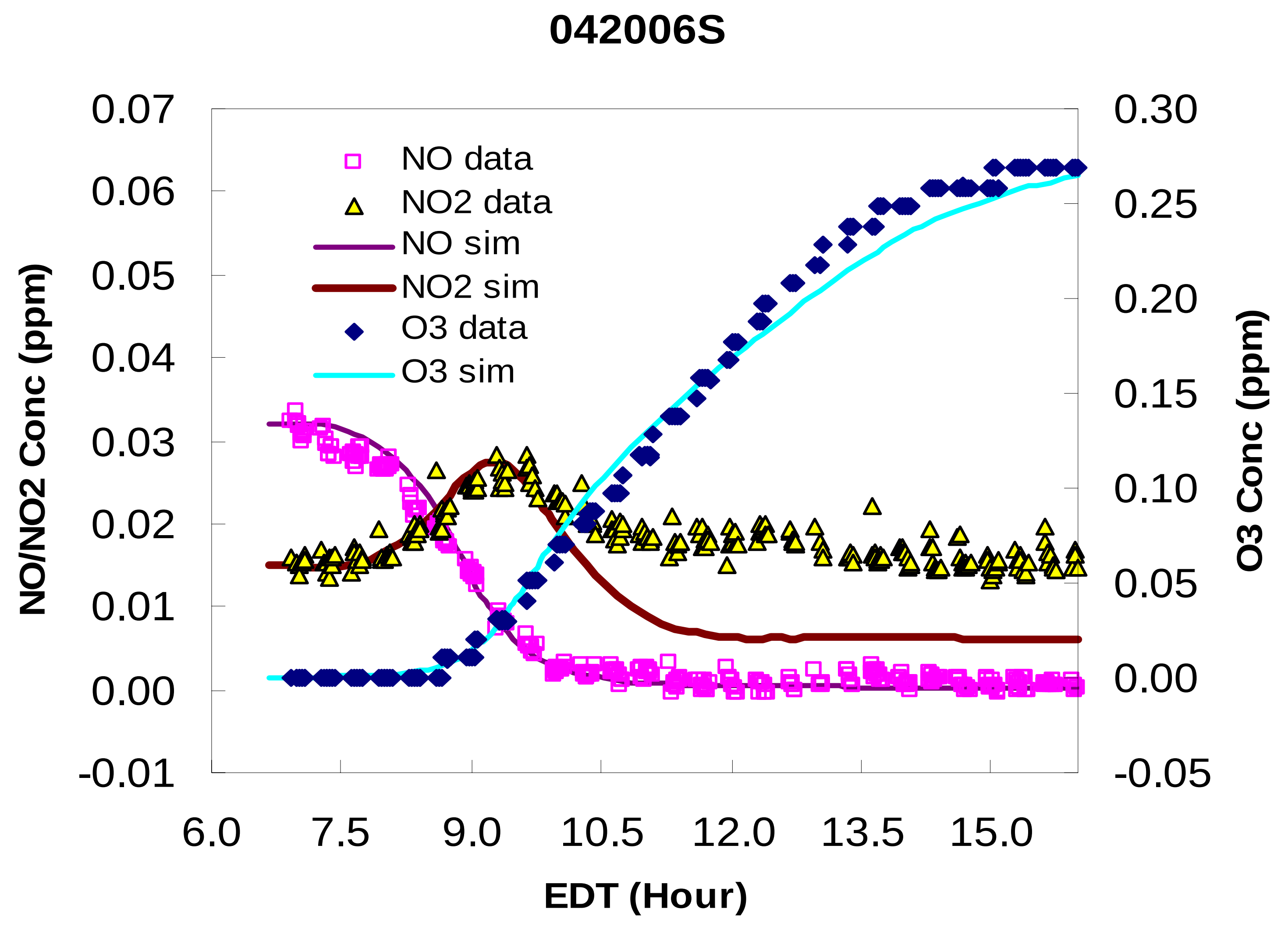
SOA from 0.1 ppmV toluene+0.1ppm NOx w/wo 3ppmC HC mixture



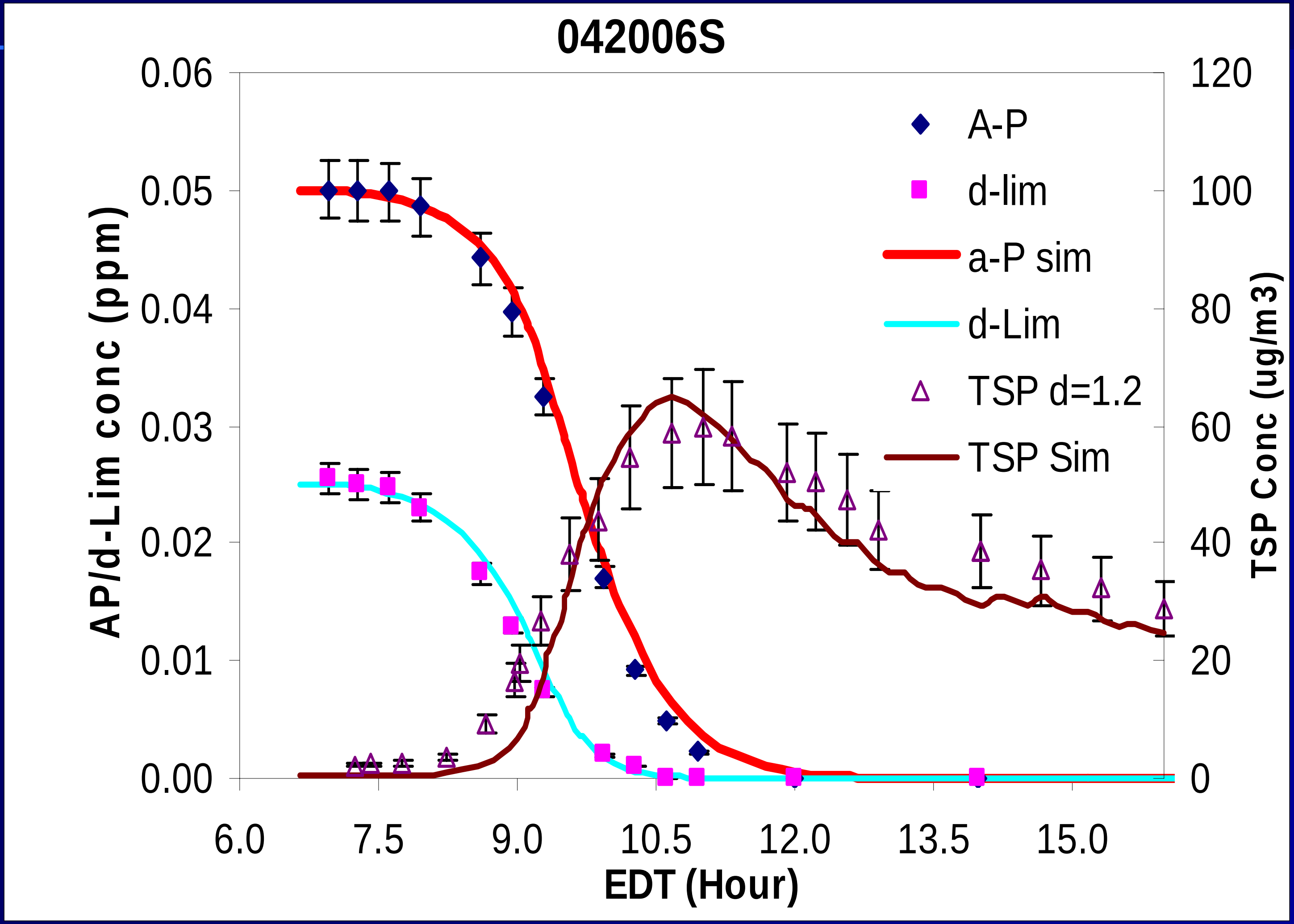
SOA from terpene mixtures

0.05 ppmV α-pinene
0.02 ppmV d-limonene
0.05 ppm NO_X

SOA from terpene mixtures



SOA from terpene mixtures



Summary statements

- Did not used any acidity reactions
- tends to simulate toluene
- many products
- concentration levels
- Nucleation
- Thanks to the EPA STAR program
- And to Harvey Jeffries for providing the Morpho kinetics solver