DIRECT PROBING OF PEROXY RADICAL CHEMISTRY: CONSTRAINTS ON ACCRETION & AUTOXIDATION

Zhao, Thornton, & Pye, *PNAS* 2018
Pye, D'Ambro, Lee, Shilling, et al

ACM 2018

Joel Thornton, Atmospheric Sciences
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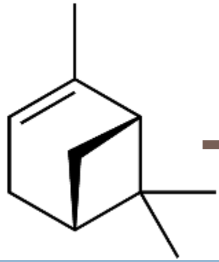
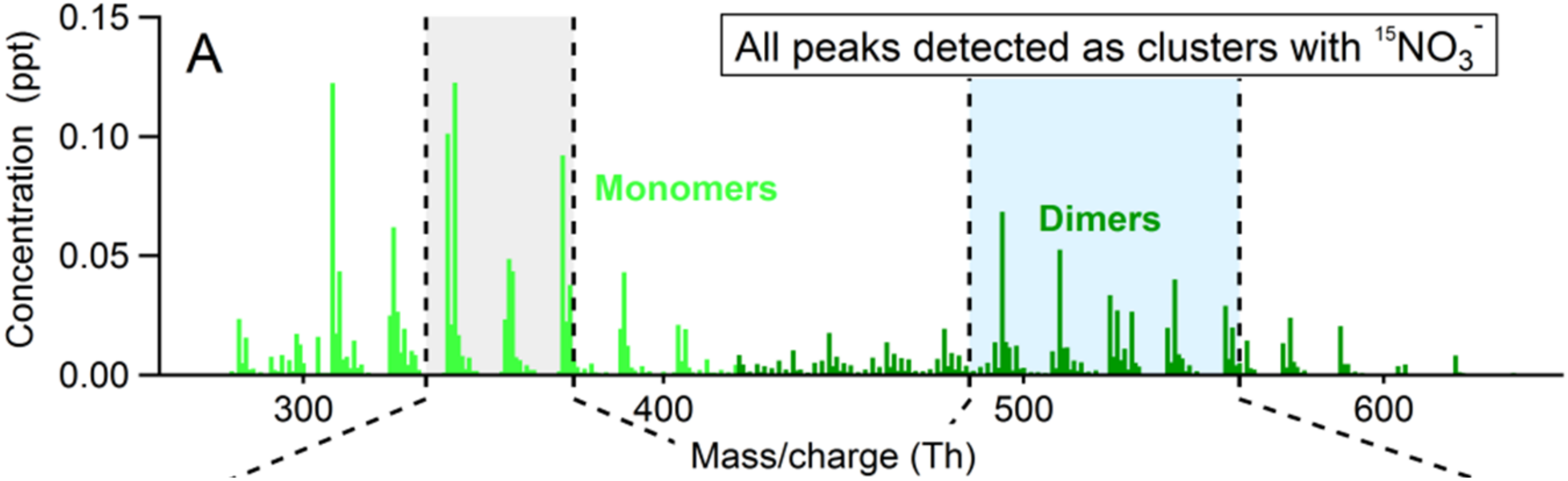
 + Ozone → Gas-phase Products

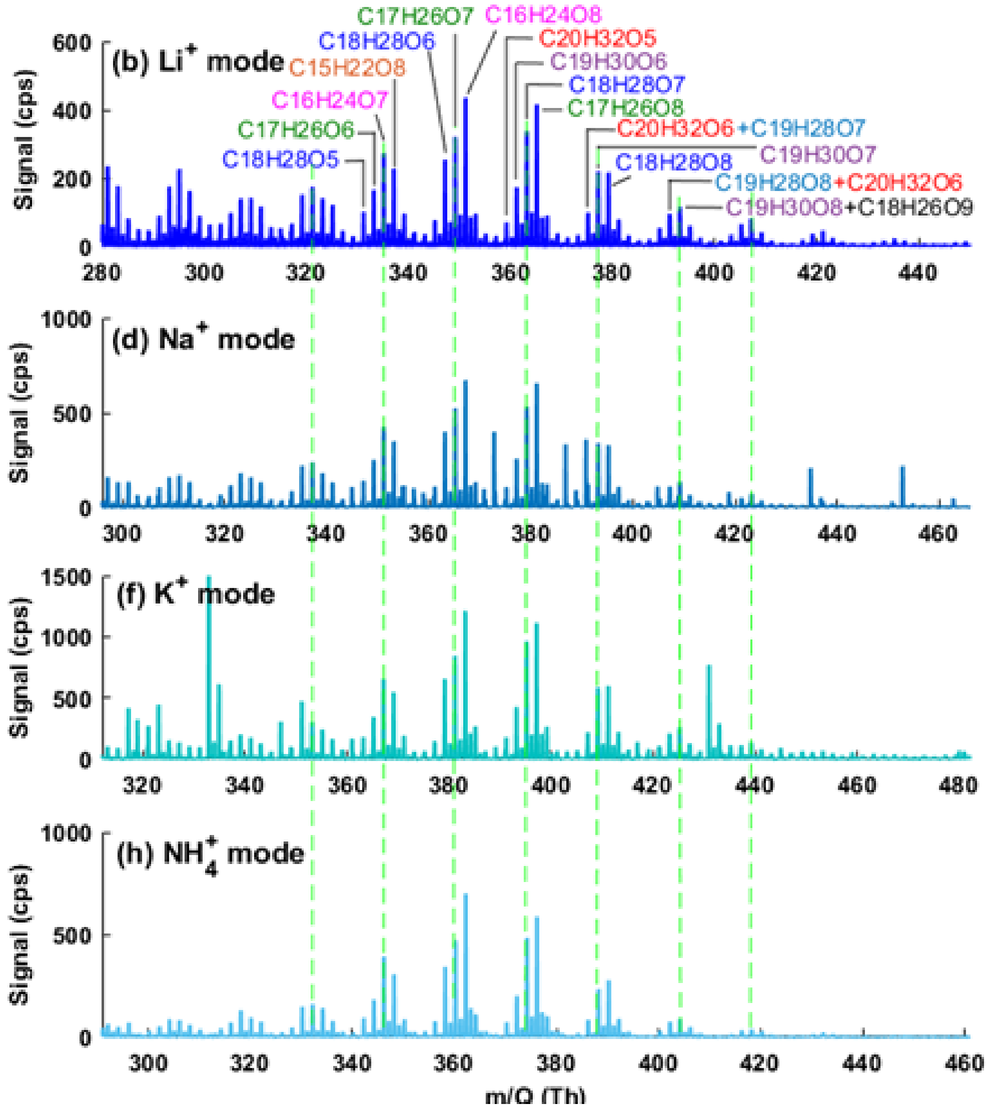


$C_{8-10}H_{14-16}O_{7-11}$	$C_{18-20}H_{28-32}O_{10-18}$

Ehn et al, Nature 2014

Berndt et al Nature Comm 2016

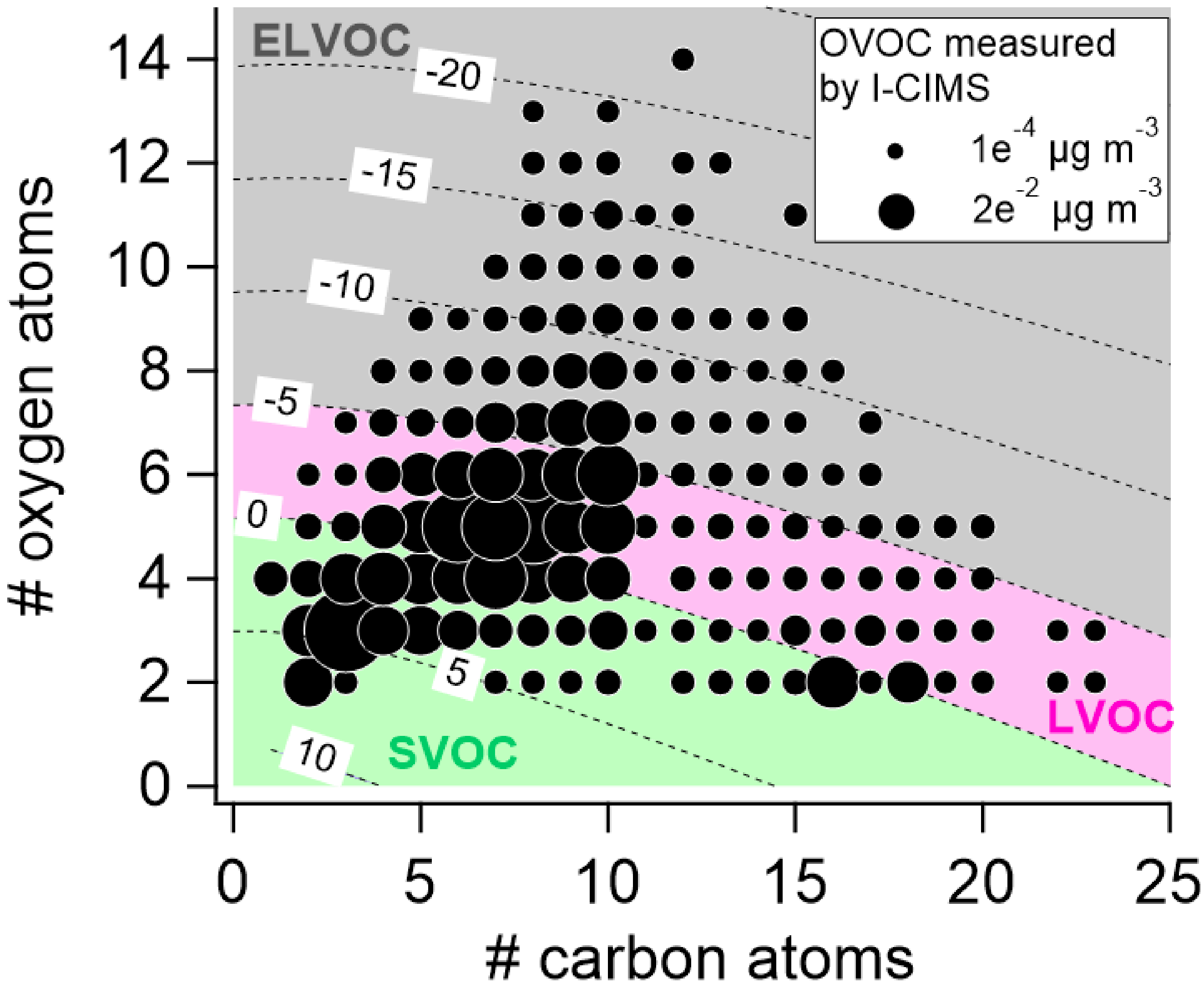
C_{16} - C_{20} vapors during a-pinene ozonolysis



Zhao et al AMT 2017

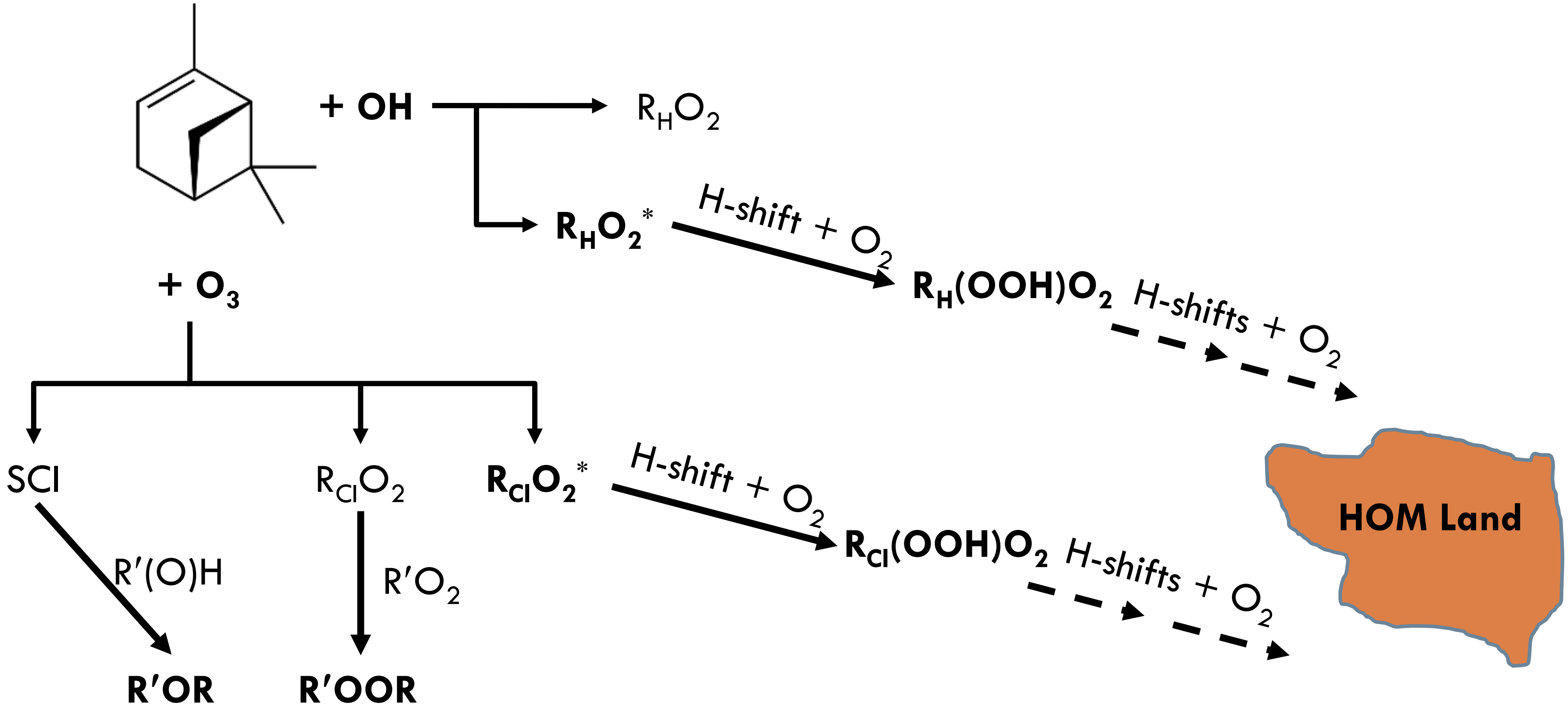
Mohr et al GRL 2017

Iodide adduct HRToF-CIMS Spectra (Hyytiälä)

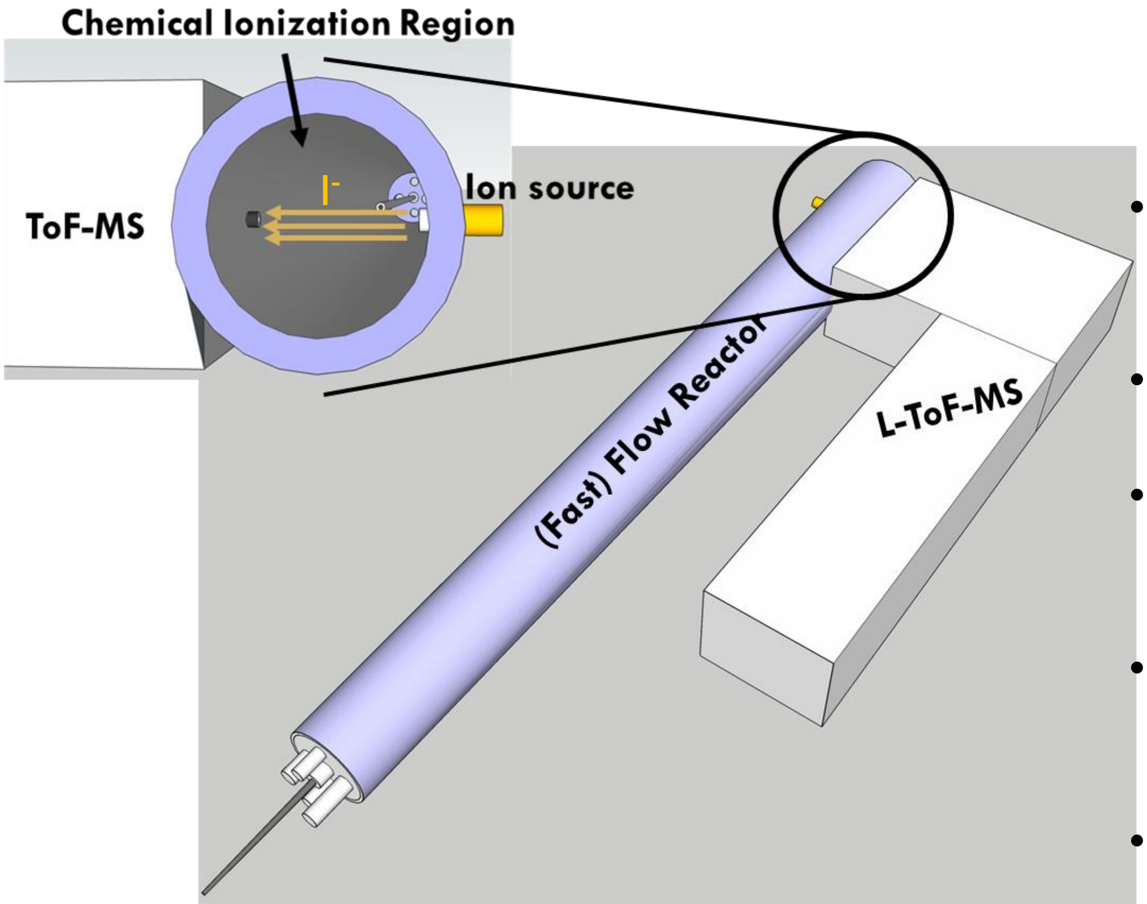


Mohr et al

Autoxidation and accretion in a-pinene oxidation



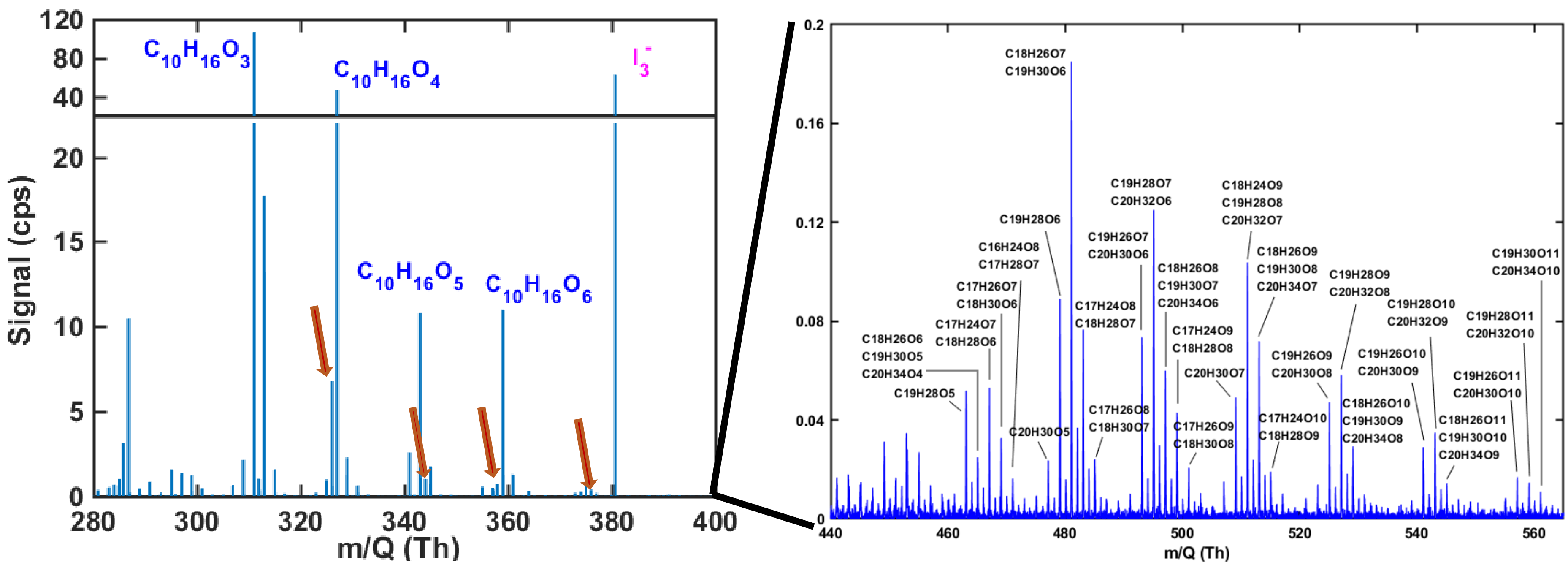
Flow reactor with In Situ Chemical Ionization



- 12 s reaction time: 1 – 30 ppb of α-Pinene with ozone (ppb to ppm)
- 1 atm and 290 K
- SCI and OH scavengers as needed (acetone, deuterated cyclohexane)
- *In situ* chemical ionization of reaction mixture (I^-) L-ToF-MS (R~11,000).
- O_3 detection by UV abs and CIMS

Berndt et al Nature Comm 2016
Hanson and Eisele

Example MS of 12 s a-pinene ozonolysis mixture



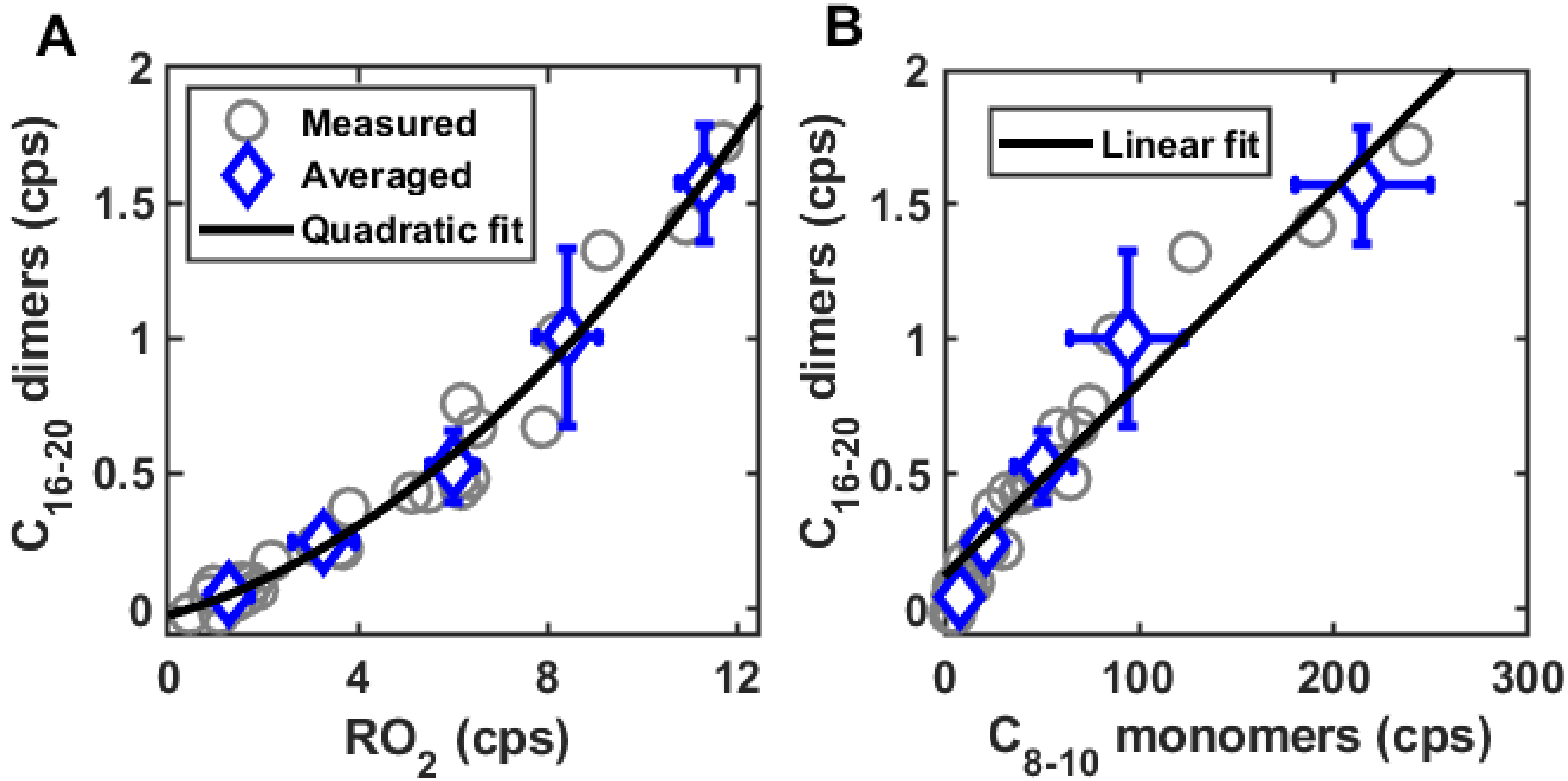
Major products identified:

$C_{8-10}H_{12-18}O_{2-13}$

$C_{16-20}H_{24-32}O_{4-13}$

RO_2 radicals: e.g., $C_{10}H_{15}O_{4-11}$ and $C_{10}H_{17}O_{5-11}$

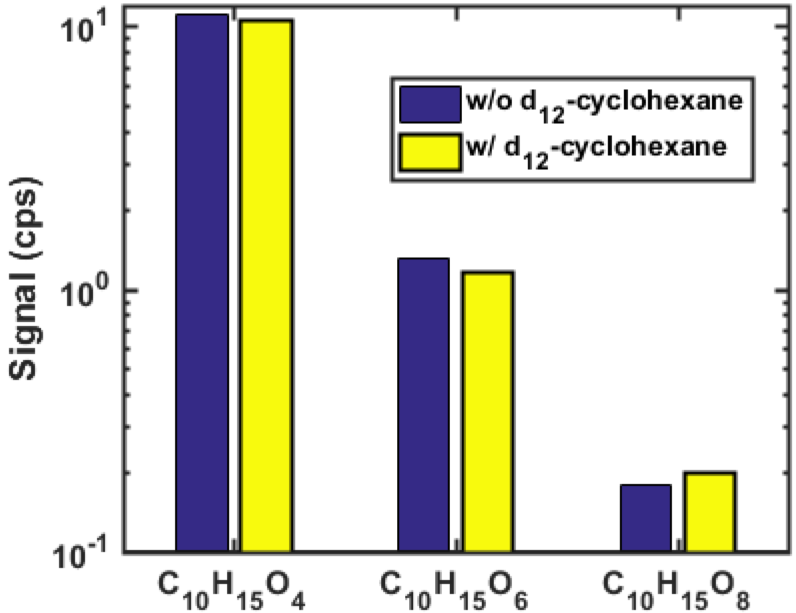
C_{16} - C_{20} vapors consistent w/RO_2 + $R'O_2$ source



$$[C_{16\text{-}20}]_{ss} \sim \tau \cdot \delta \cdot k^{II}[RO_2]^2$$

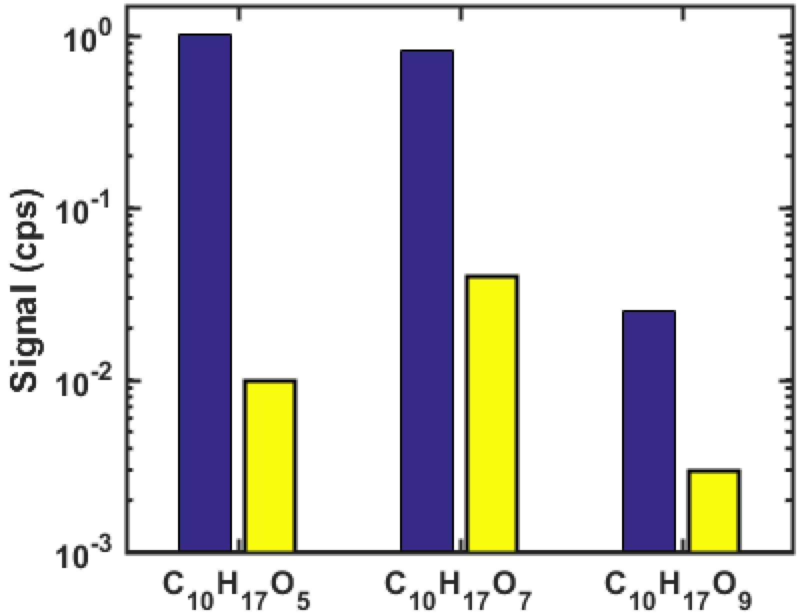
Effects of OH scavenger on RO_2 radicals

$C_{10}H_{15}O_{4,6,8}$



- No effects on $C_{10}H_{15}O_{4,6,8}$ (ozonolysis + autoxidation)

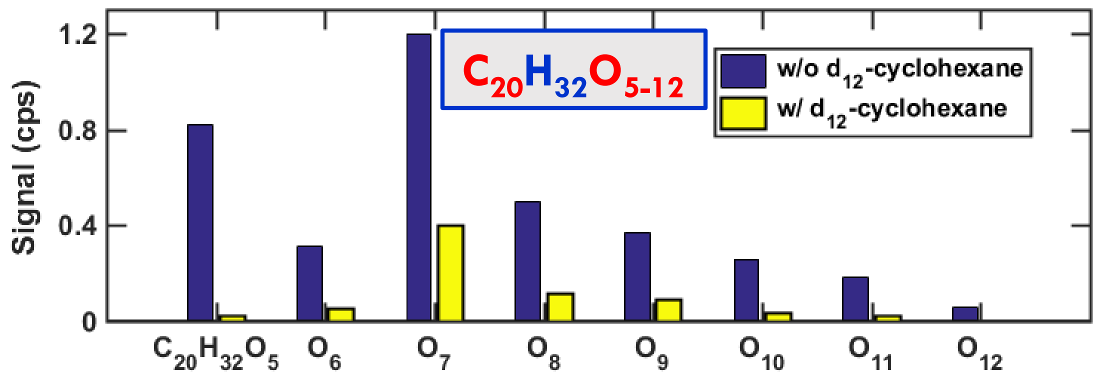
$C_{10}H_{17}O_{5,7,9}$



- Strong effects on $C_{10}H_{17}O_{5,7,9}$ (OH + α-Pinene + autoxidation)

Ehn et al., Nature, 2014; Rissanen et al., JPCA, 2015; Berndt et al., Nature Commun. 2016

Effects of OH scavenger on C_{16-20} products



Strongly affected

$C_{20}H_{32}O_{5-12}$;

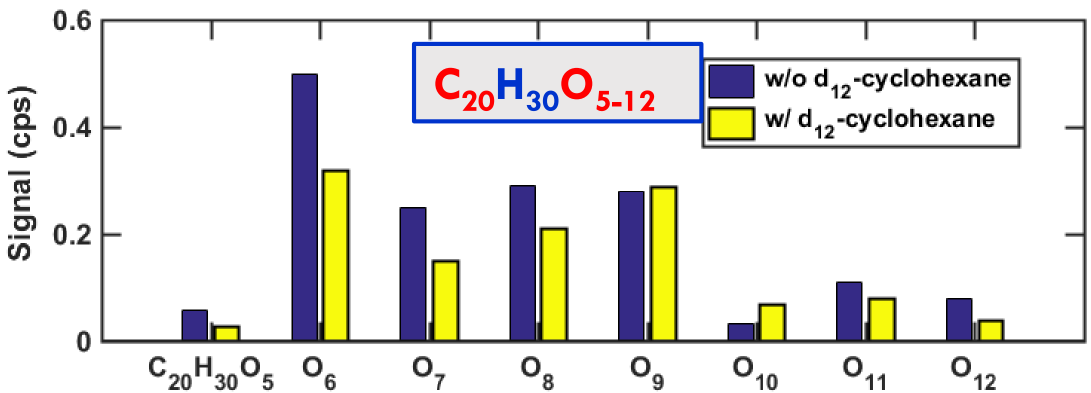
$C_{19}H_{30}O_{4-13}$; $C_{19}H_{28}O_6$

$C_{18}H_{28}O_{6-7}$; $C_{18}H_{28}O_{7-9}$

$C_{17}H_{28}O_{8,\ 10}$

$C_{16}H_{24}O_{7-8}$;

Formation pathways: e.g., $C_{10}H_{15}O_x + C_{10}H_{17}O_y \rightarrow C_{20}H_{32}O_z + O_2$



Less affected

$C_{20}H_{30}O_{5-12}$; $C_{20}H_{28}O_{5-12}$

$C_{19}H_{28}O_{5,\ 7-13}$

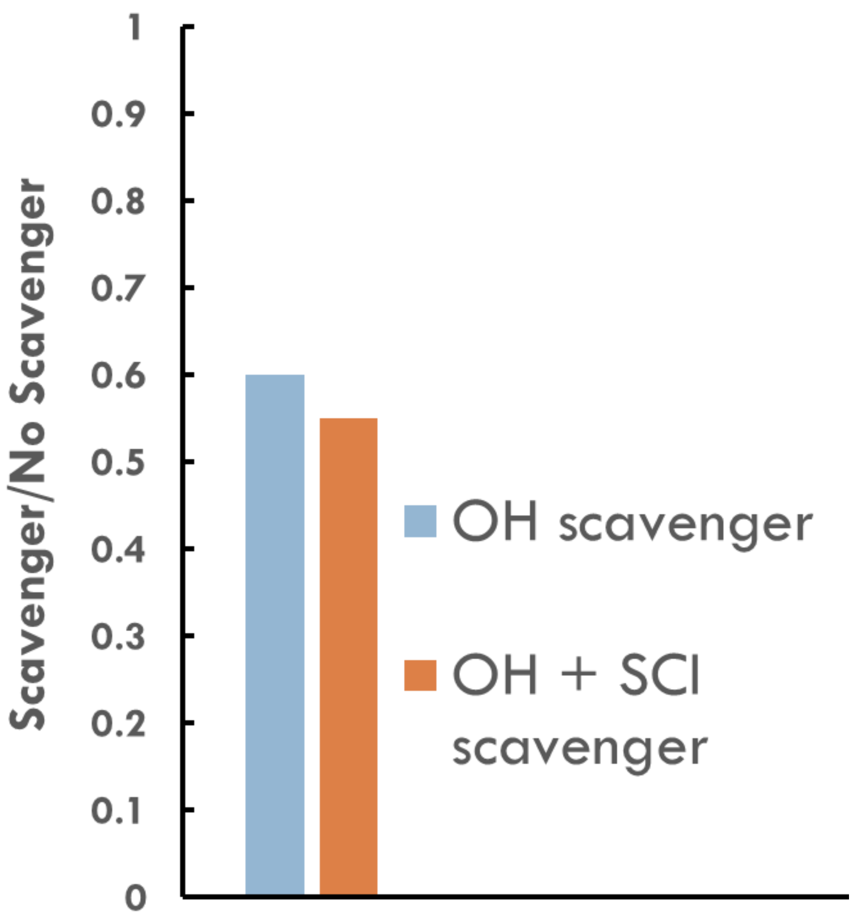
$C_{18}H_{28}O_{8-12}$; $C_{18}H_{28}O_{5-6,\ 10}$

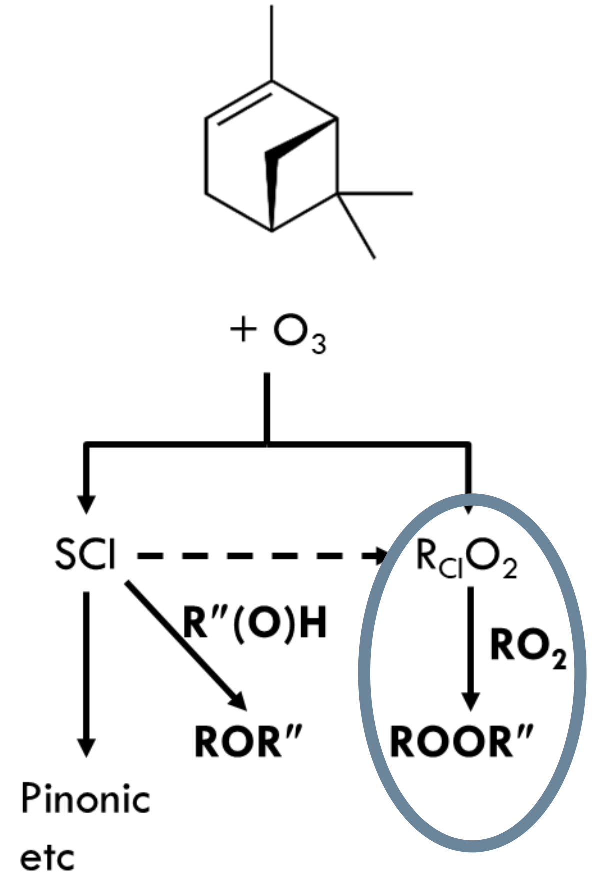
$C_{17}H_{26}O_{7-9}$; $C_{17}H_{28}O_{6-7}$

$C_{16}H_{24}O_{9-11}$;

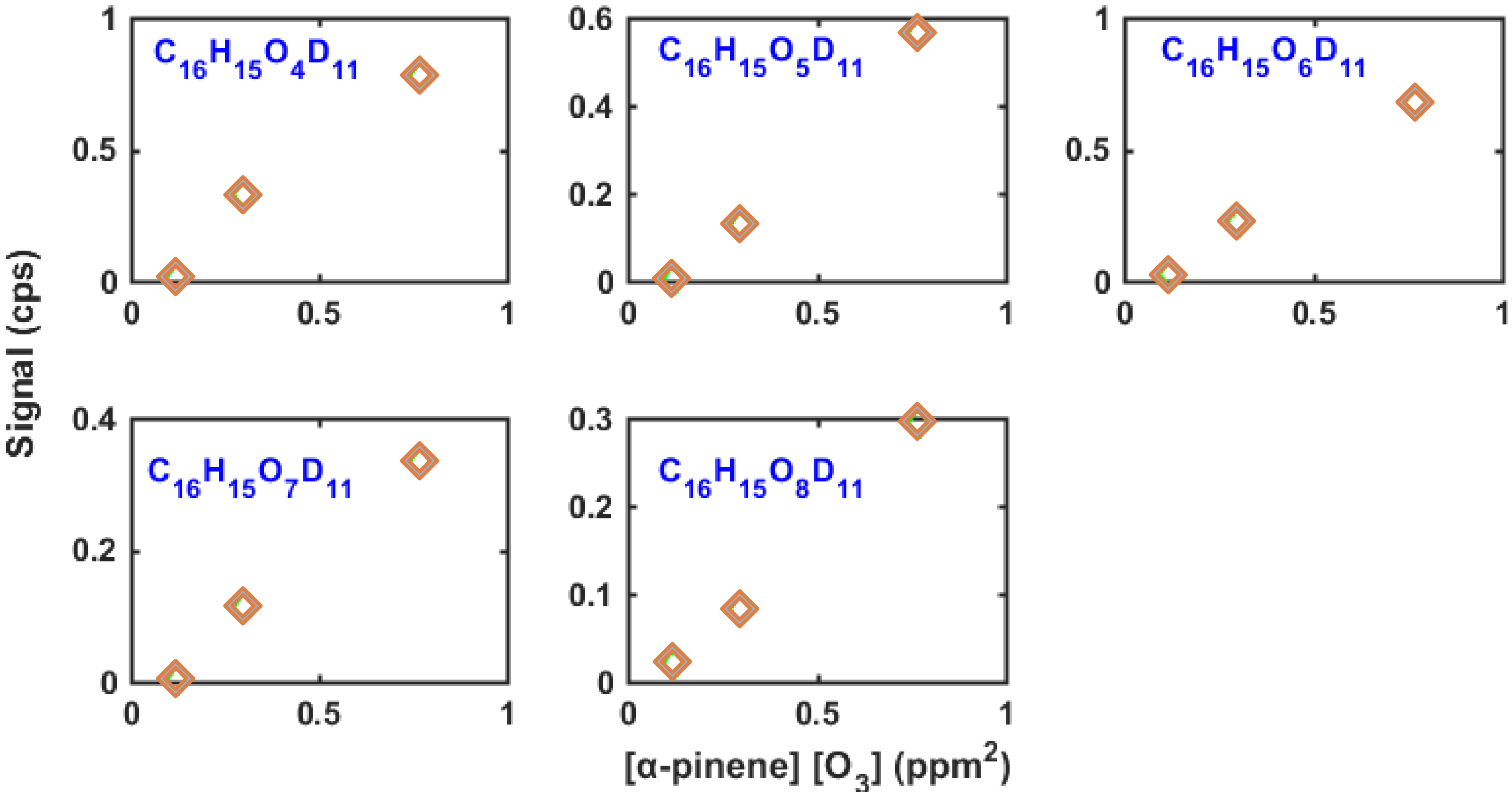
Formation pathways : e.g., $C_{10}H_{15}O_x + C_{10}H_{15}O_y \rightarrow C_{20}H_{30}O_z + O_2$

C_{16}-C_{20} ~ 40% from OH-derived RO_2



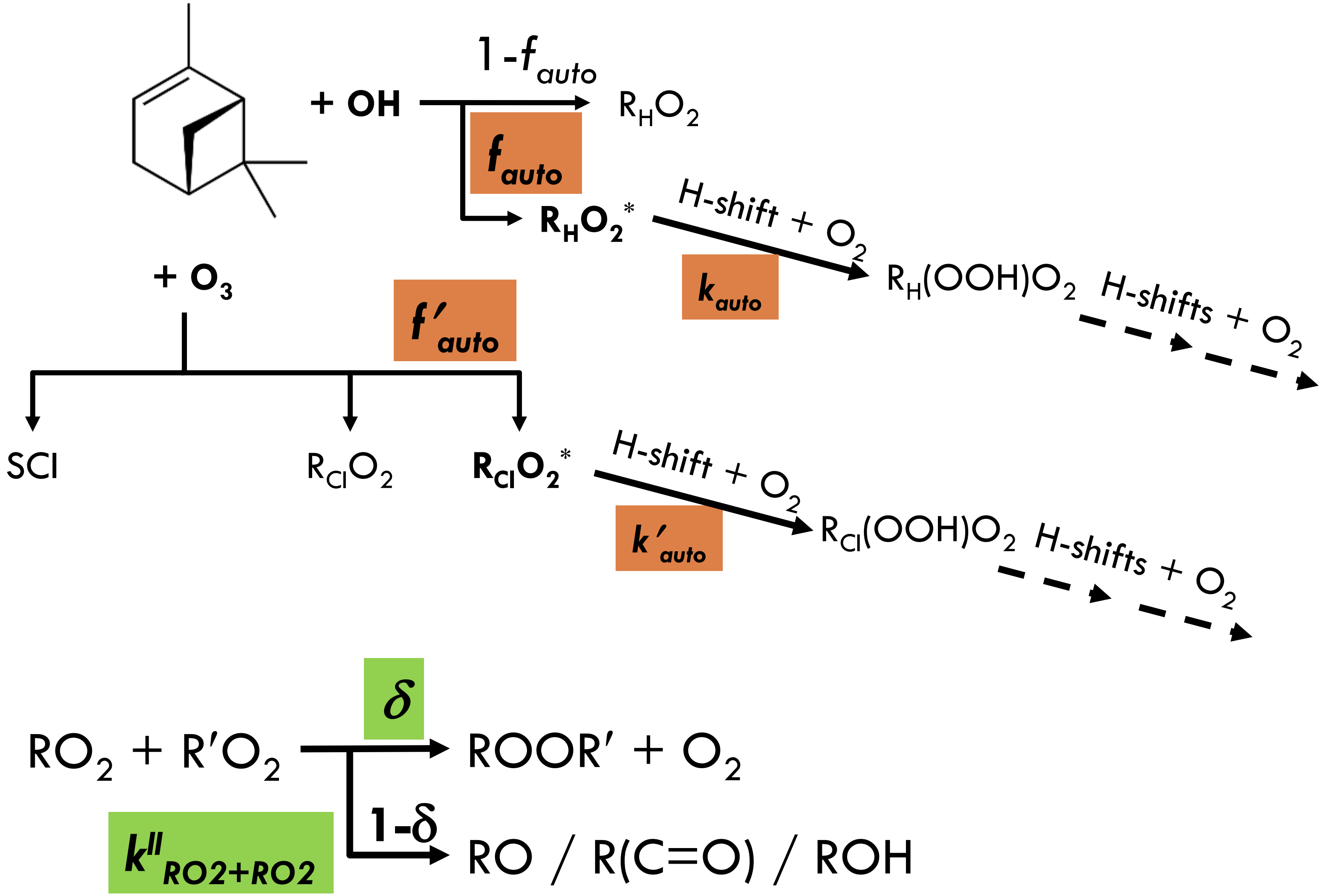


Deuterated dimers from D_{11}-cyclohexyl-O_2

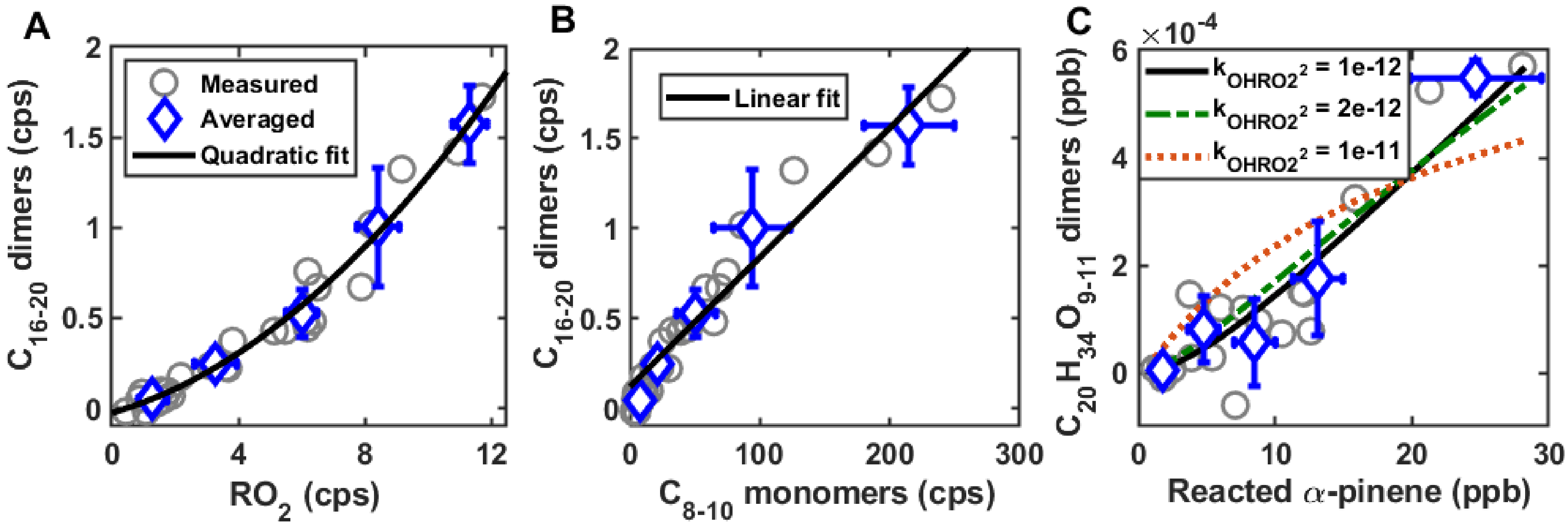


$$C_{10}H_{15}O_{(4\text{-}8)} + C_6D_{11}O_2 \rightarrow C_{16}H_{15}O_{(4\text{-}8)}D_{11} + O_2$$

Constraints on RO_2 fates: F0AM (MCM 3.3.1)



$RO_2 + R'O_2$



δ **~ 0.04**

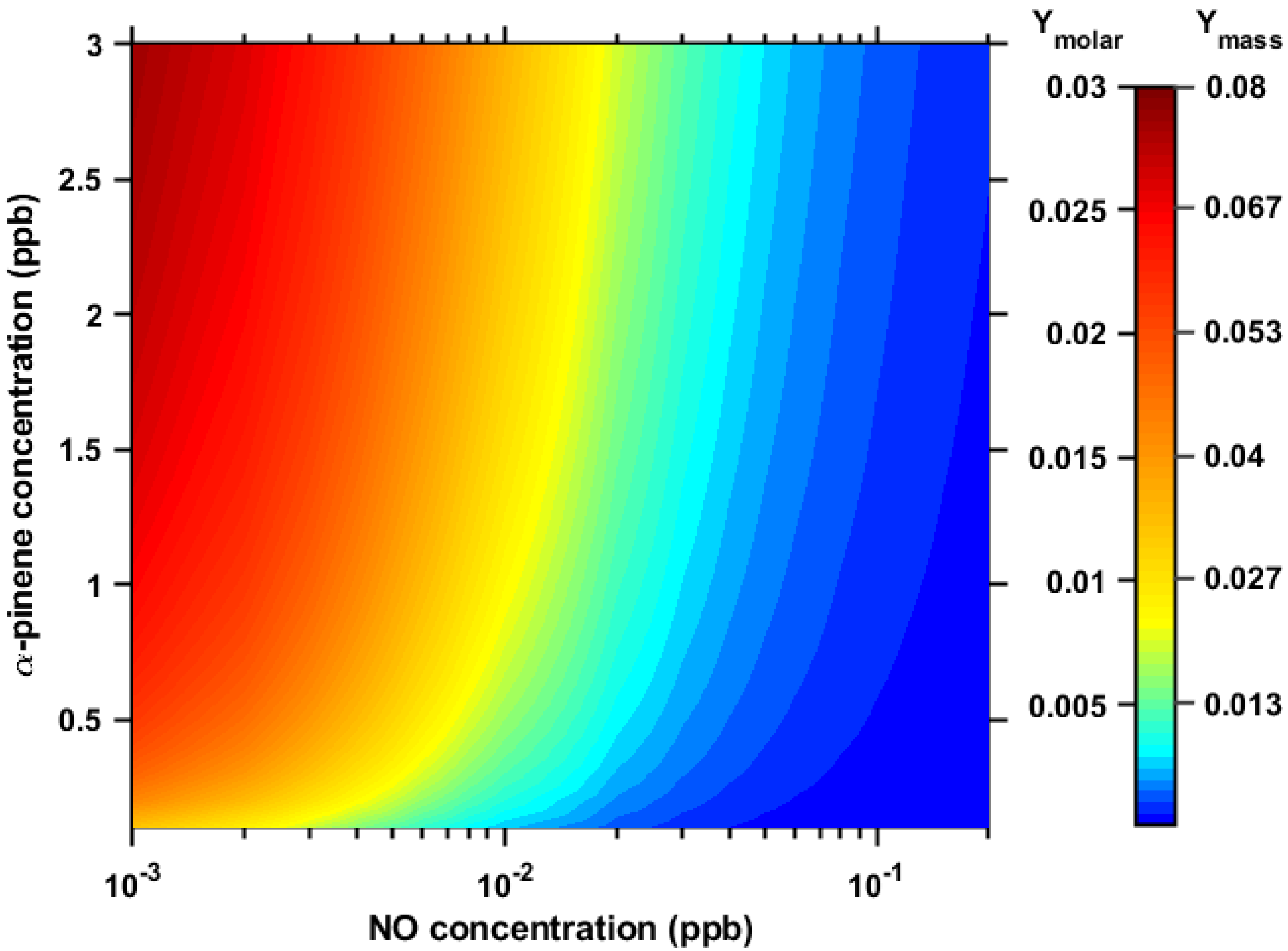
$RO_2 + R'O_2 \rightarrow ROOR' + O_2$ (δ)

$\rightarrow$ RO / R(C=O) / ROH ($1-\delta$)

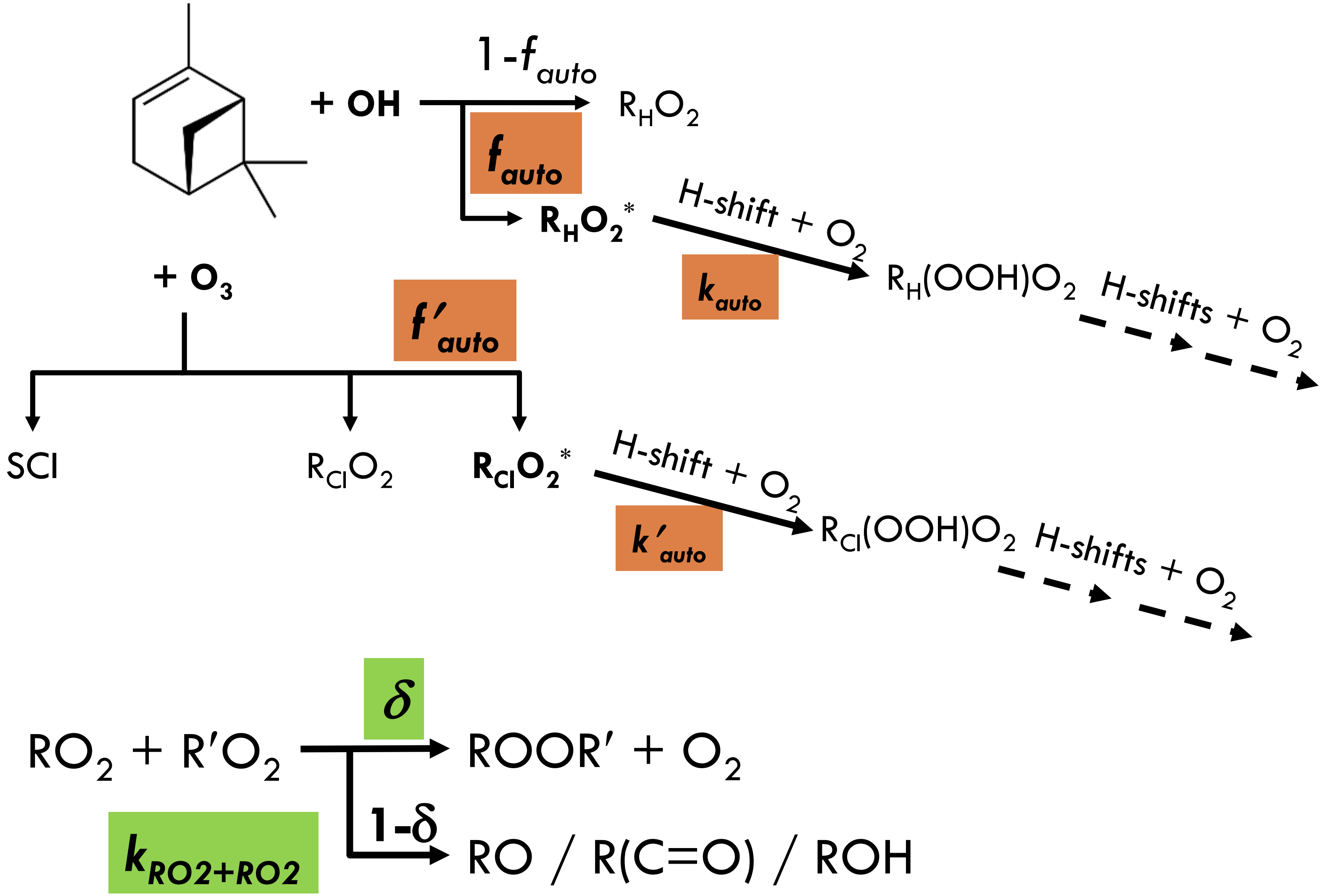
$k^{II}_{RO2+RO2}$

~2x10^{-12} cm^3 molec^{-1} s^{-1}

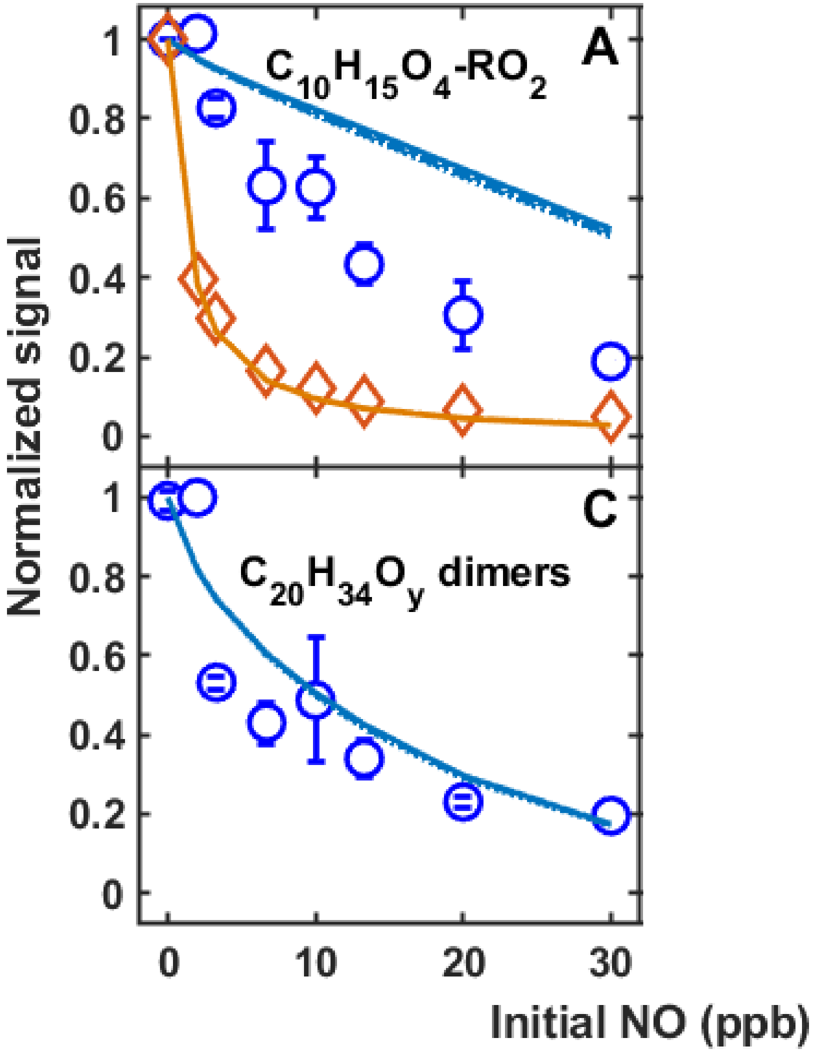
$RO_2 + RO_2$ as LVOC source in chambers and field



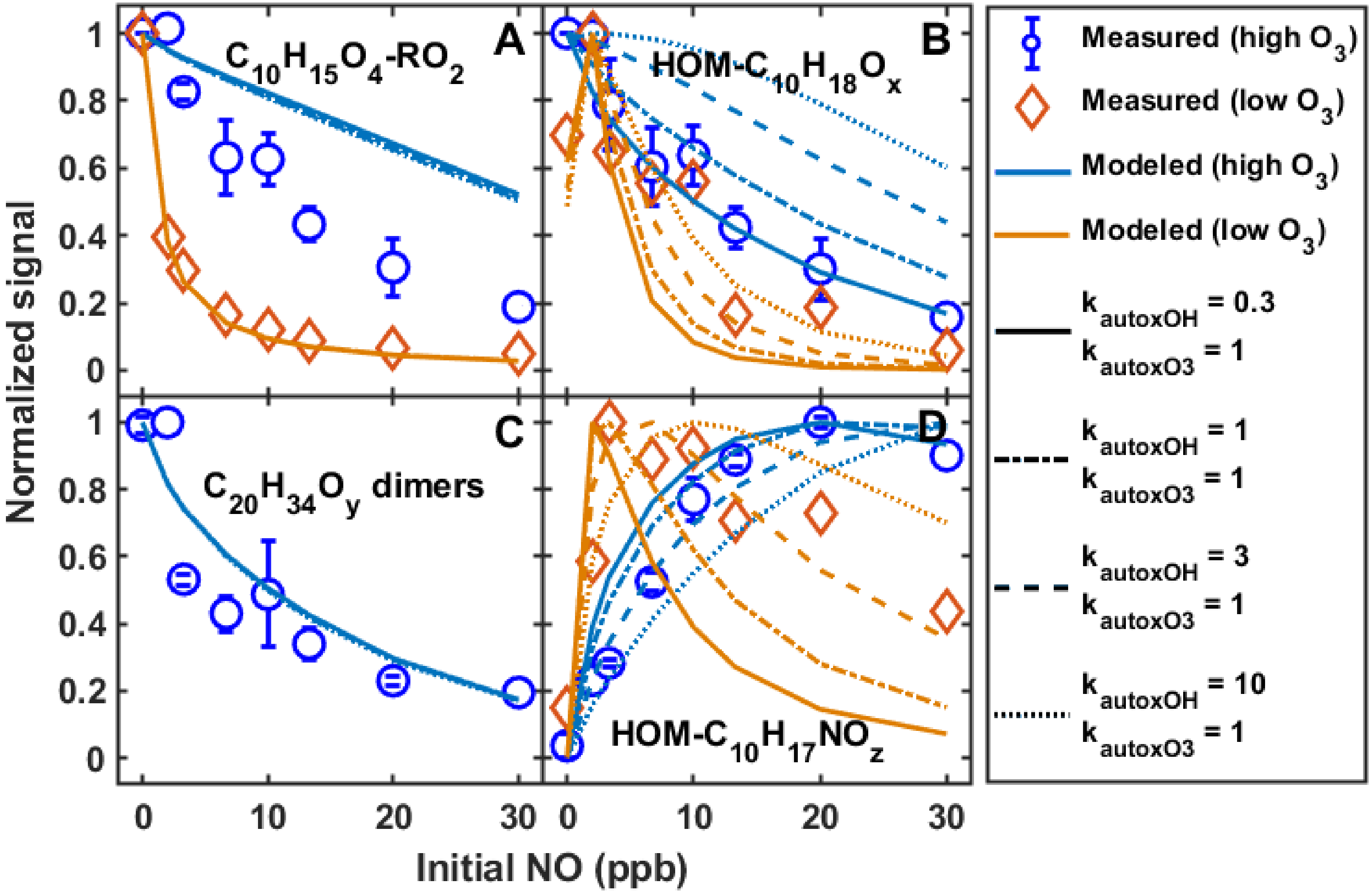
Constraints on RO_2 fates



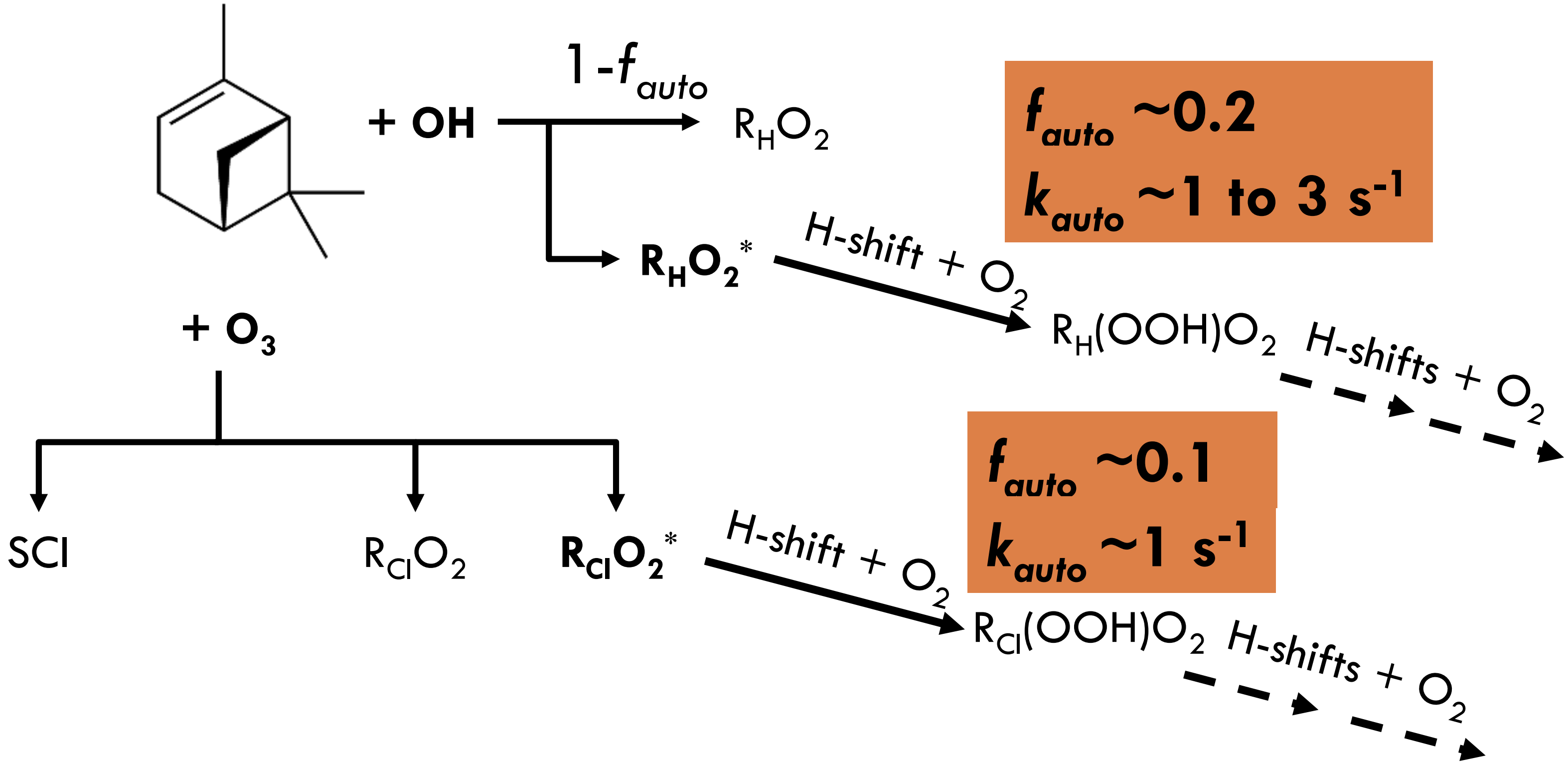
Autoxidation constraint: competition with NO



Autoxidation constraint: competition with NO



Constraints on RO_2 fates

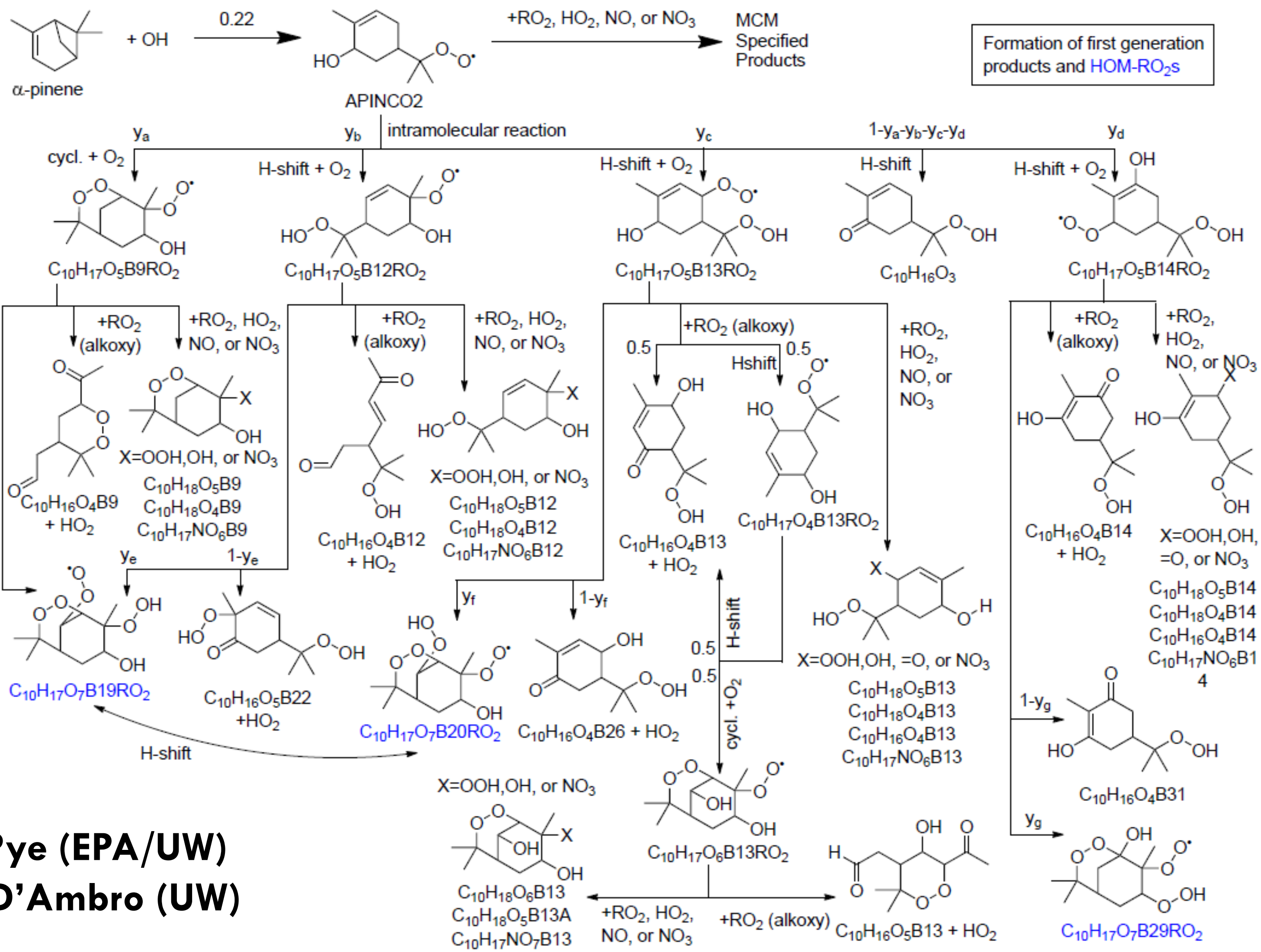


"Reasonable Agreement" with

Ehn et al Nature 2014

Berndt et al Nature Comm 2016

F0AM (MCM-based) Updates



Havla Pye (EPA/UW)
Emma D'Ambro (UW)

Representing autoxidation improves predictions of OH + a-pinene chamber SOA

	HOM Yield % by mole	SOA Yield % by mass	O/C $mol\ mol^{-1}$	C* of SOA $\mu g\ m^{-3}$
Base MCM v3.3.1	0	<1	0.59	104
CMAQ v5.2 (empirical)	0	7	0.52	55
Updated Mechanism	**>3.3**	**17**	**0.64**	**1.3**
Observed	**≥2.4**	**12 ± 4.6**	**0.68**	**0.08**

Berndt et al Nature Comm 2016 flow tube conditions

UW/PNNL multi-hour SOA experiment

Updated mechanism predicts SOA using an internally consistent representation of composition & volatility.

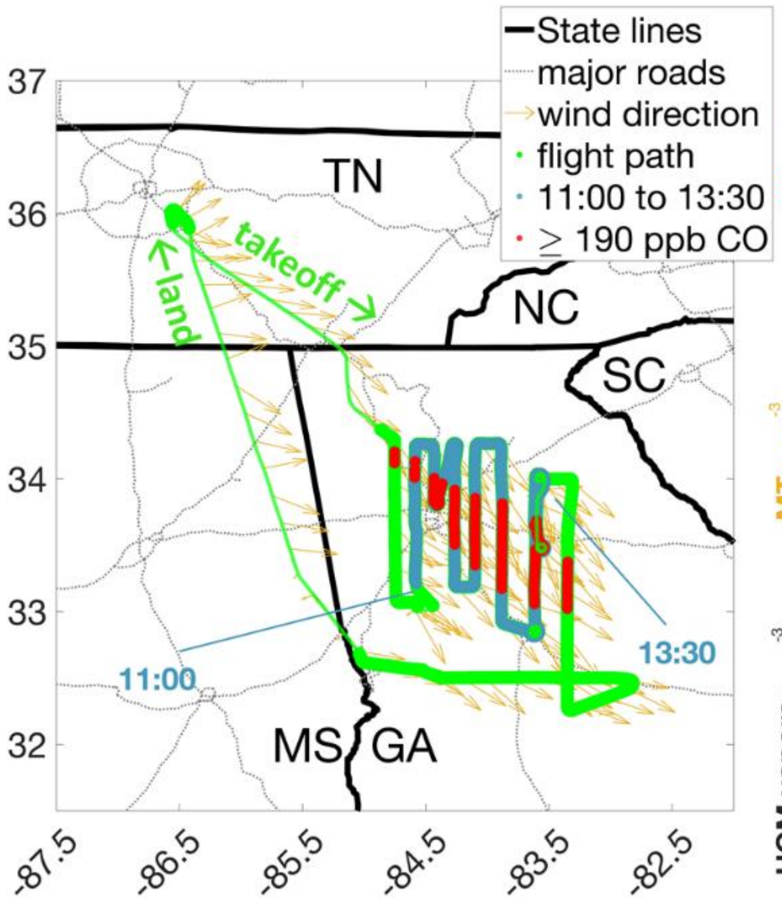
Summary

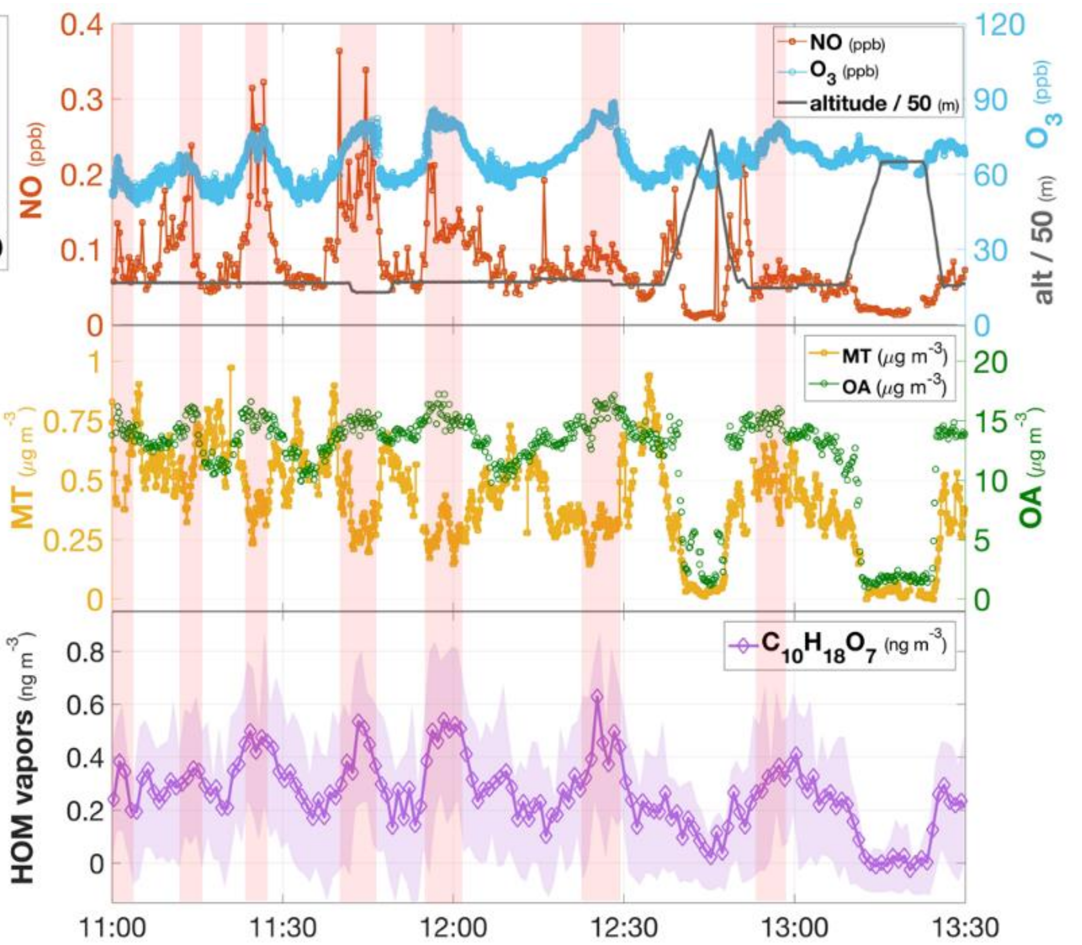
- $RO_2 + RO_2 \rightarrow$ accretion products is a fairly general, albeit low-level branching in a-pinene oxidation
  - 4% average branching; $k^{II} \sim 2\times10^{-12}\ cm^3\ s^{-1}$

- Autoxidation rate constants for a significant fraction of a-pinene derived RO_2 are fast (10 – 20% at 1 to 3 s^{-1})
  - 1 ppb NO $\rightarrow \sim 0.3\ s^{-1}$

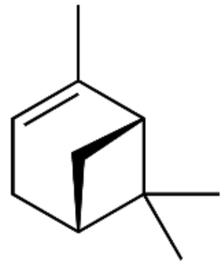
- Combined, these are prompt & sizable sources of low-volatility products w/a complex dependence on NOx

HOM enhanced in Atlanta urban plume





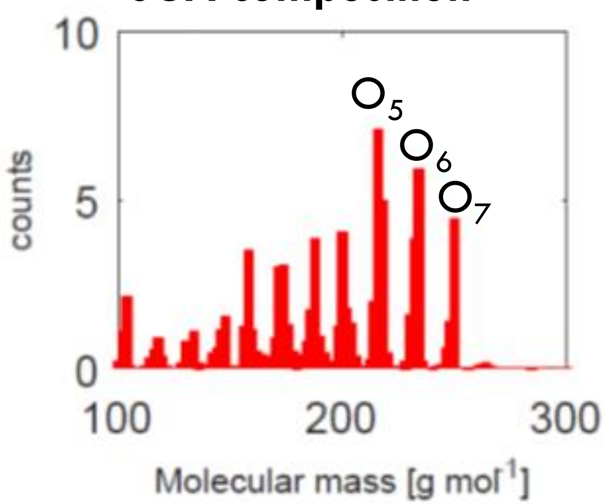
Pathways absent from community mechanisms



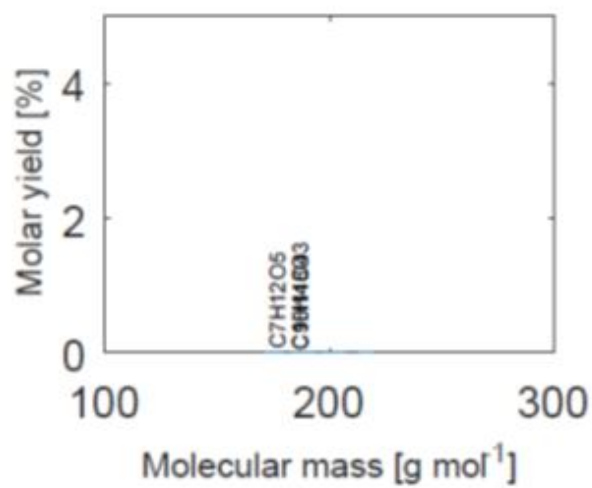
+ OH

	Observed	Predicted
SOA Yield	**12%**	**<1%**

SOA composition

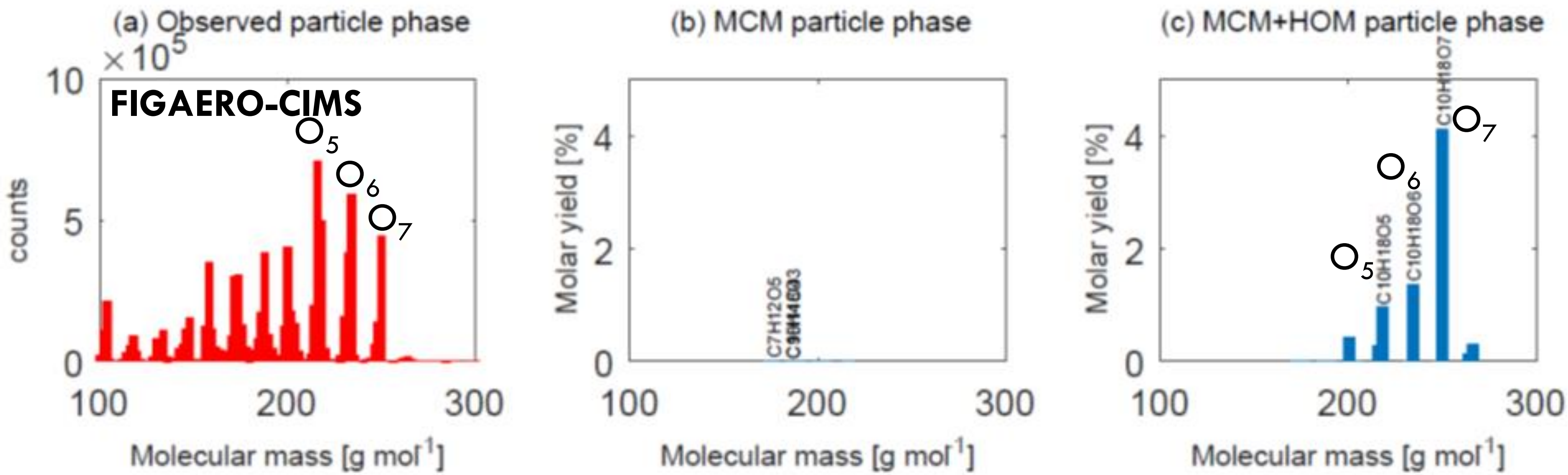


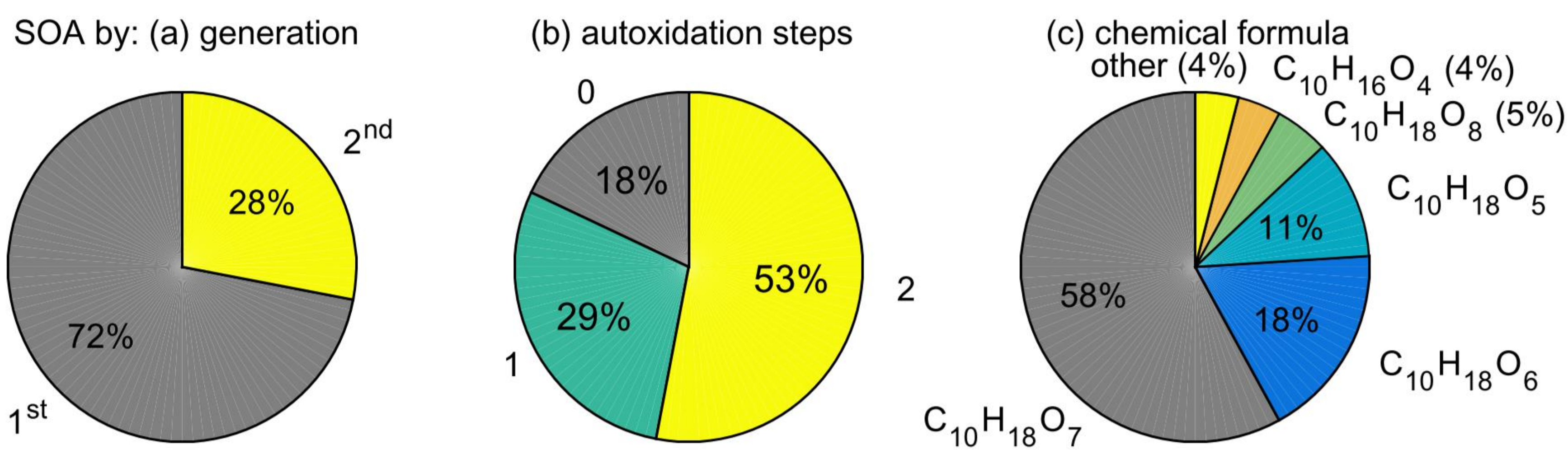
Master Chemical Mechanism

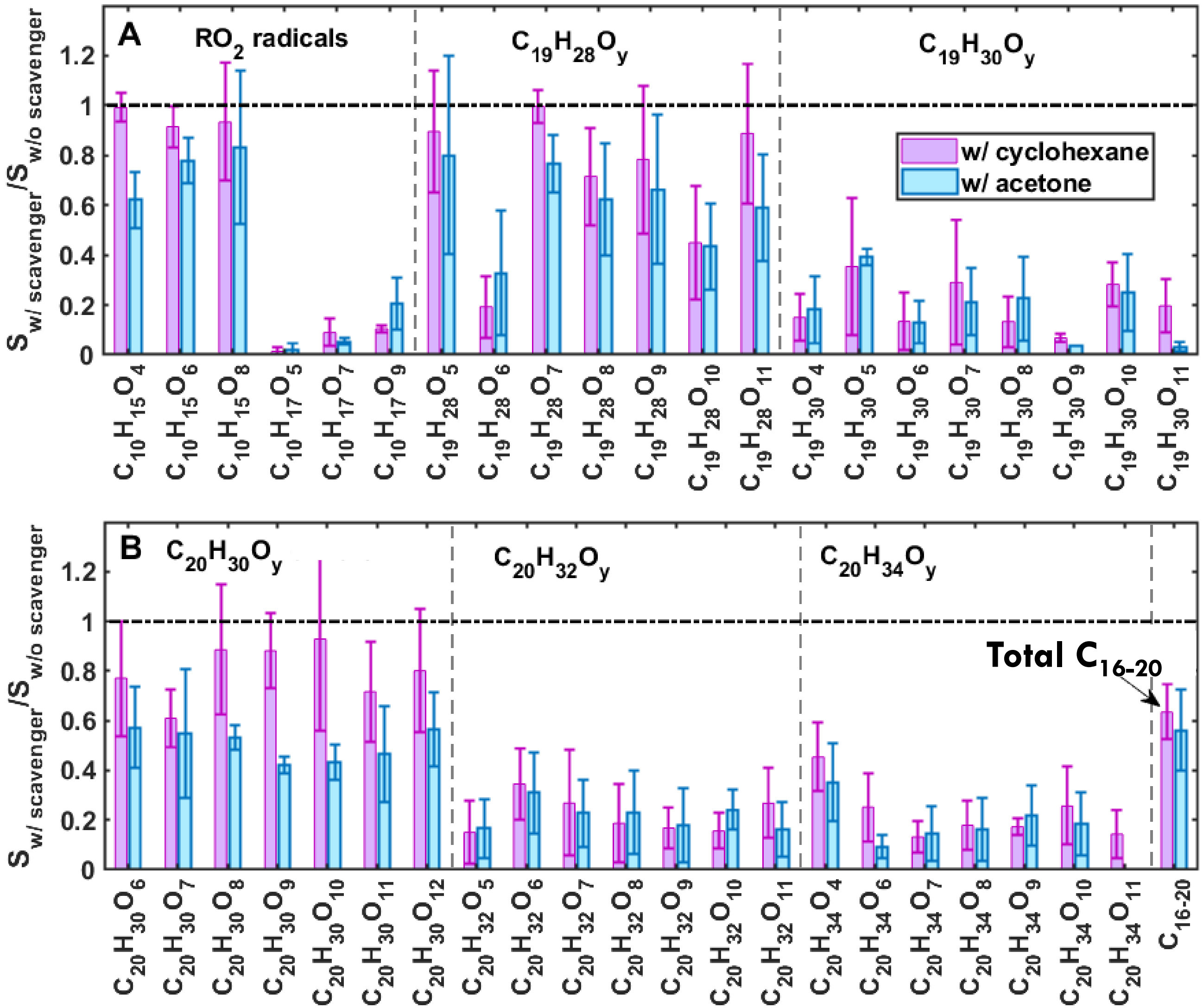


Pye et al, in review

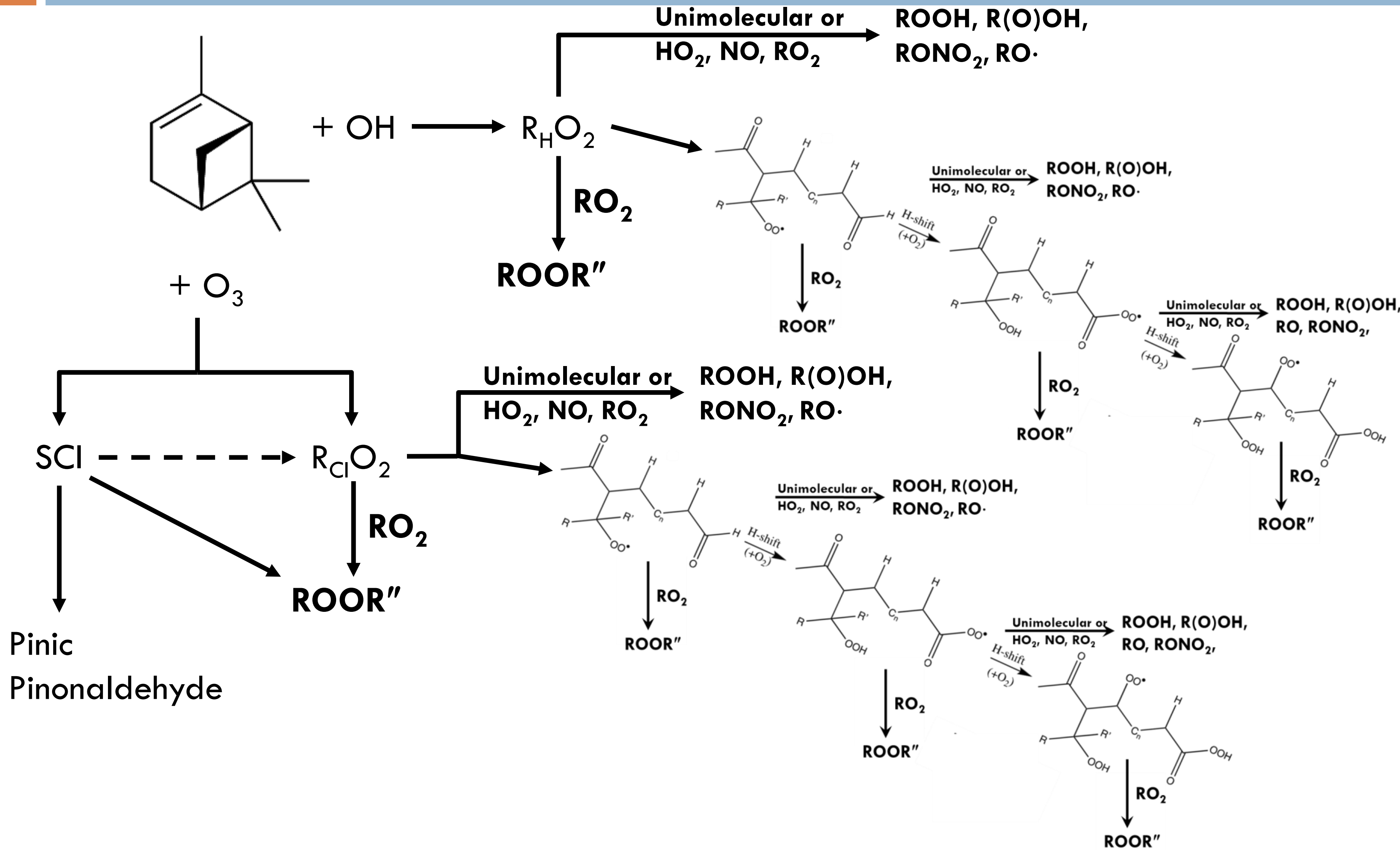
Comparison to SOAFFEE Chamber Experiments



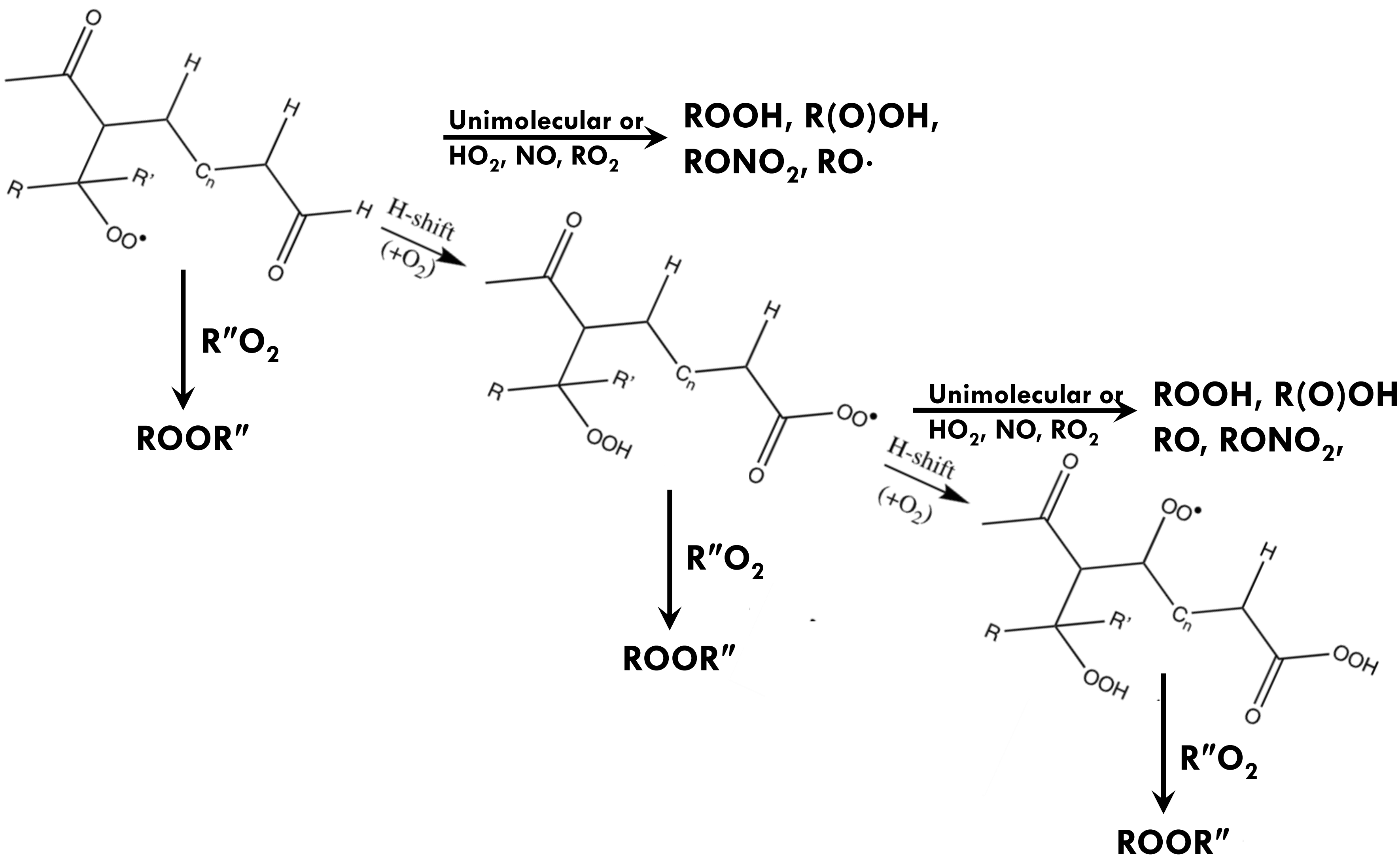



A
RO2 radicals
C19H28Oy
C19H30Oy
w/ cyclohexane
w/ acetone
Sw/ scavenger/Sw/o scavenger
B
C20H30Oy
C20H32Oy
C20H34Oy
Total C16-20

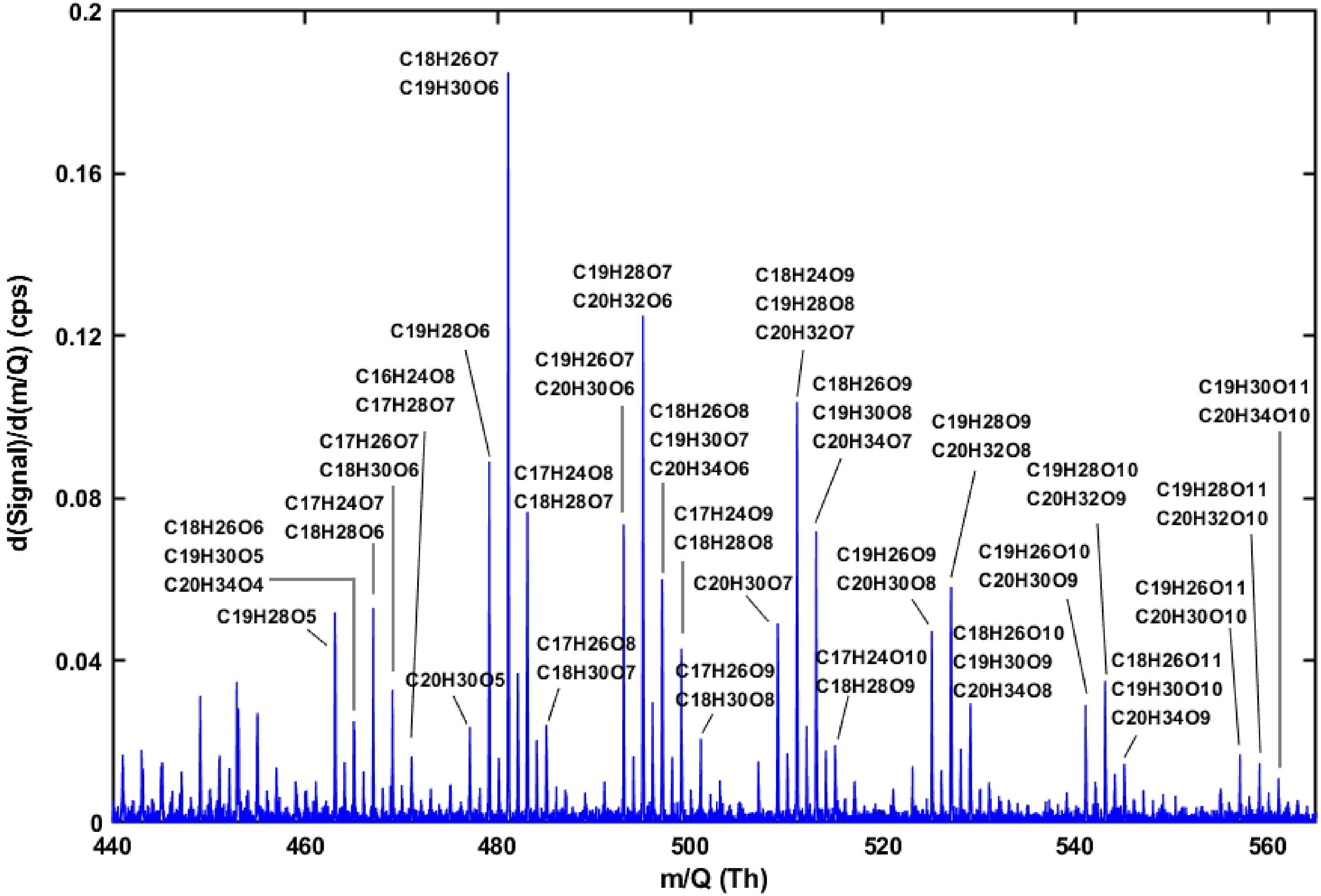
Updates to MCM-based mechanism

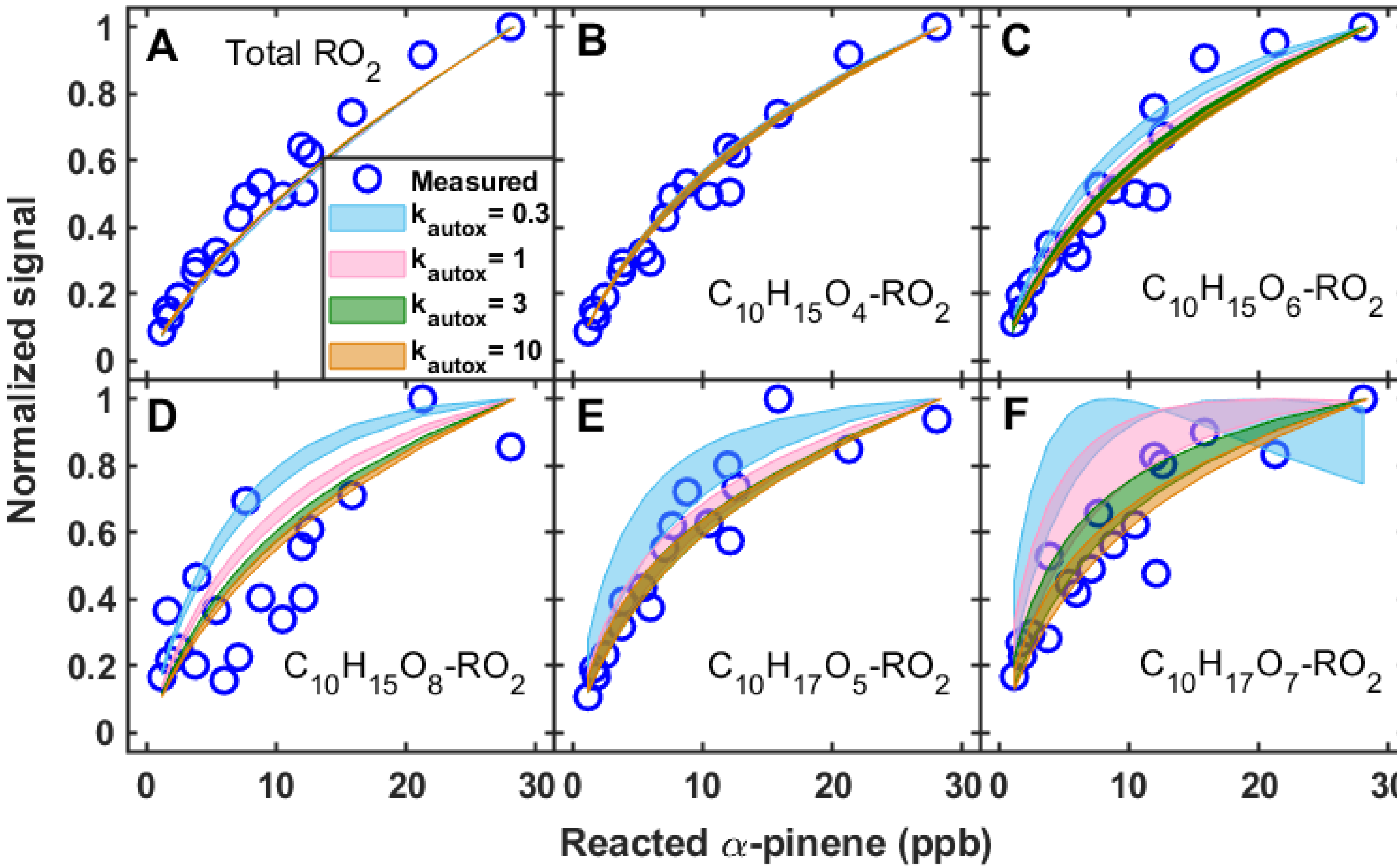


Vapor Pressure Lowering in a-Pinene Oxidation



C_{16} - C_{20} vapors during a-pinene ozonolysis





A
Total RO_2
B
C
D
E
F
Measured
k_{autox}= 0.3
k_{autox}= 1
k_{autox}= 3
k_{autox}= 10
$C_{10}H_{15}O_4$-RO_2
$C_{10}H_{15}O_6$-RO_2
$C_{10}H_{15}O_8$-RO_2
$C_{10}H_{17}O_5$-RO_2
$C_{10}H_{17}O_7$-RO_2
Normalized signal
Reacted α-pinene (ppb)
0
0.2
0.4
0.6
0.8
1
0
10
20
30

Gas-phase Accretion Chemistry

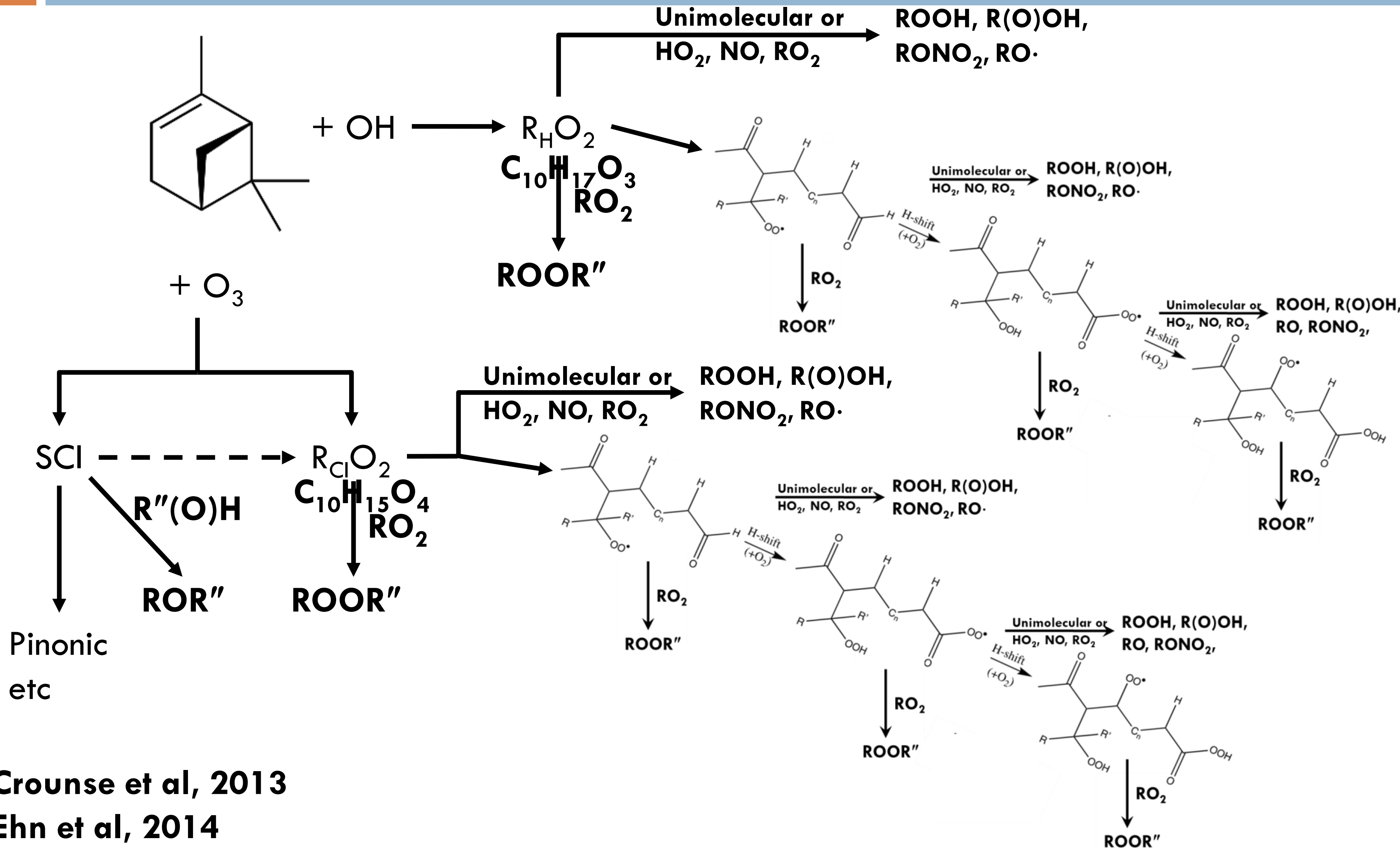
- Reaction of SCI w/closed-shell OVOC and RO_2

- RO_2 self and cross-reactions (either HOM-RO_2 or acyl-RO_2)

Kroll and Seinfeld, AE, 2008; Johnson and Marston, Chem. Soc. Rev., 2008

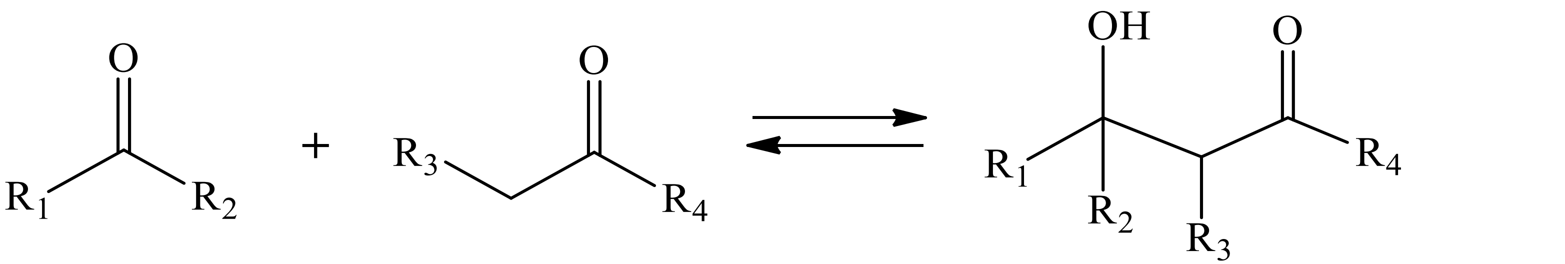
Sadezky et al., ACP, 2008; Zhao et al., PCCP, 2015

Autoxidation and Accretion in a-Pinene Oxidation



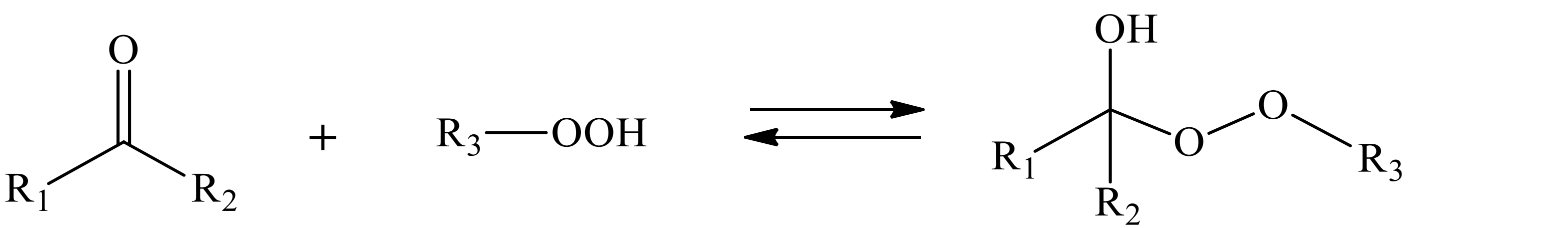
Crounse et al, 2013
Ehn et al, 2014

Particle Phase Accretion Chemistry



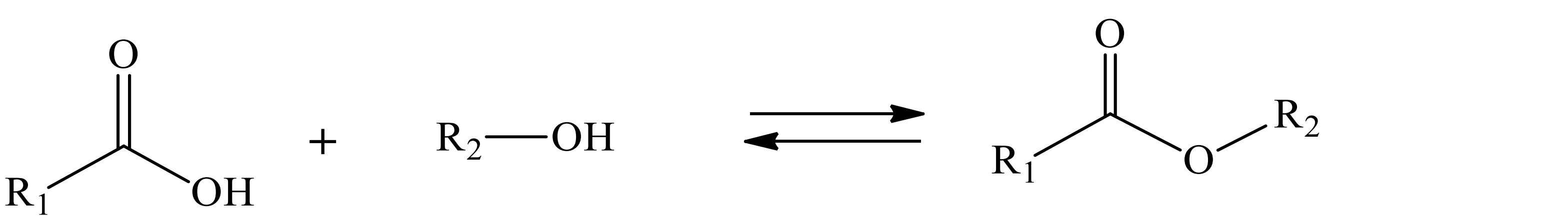
(R1)

Aldol



(R2)

Peroxyhemiacetal



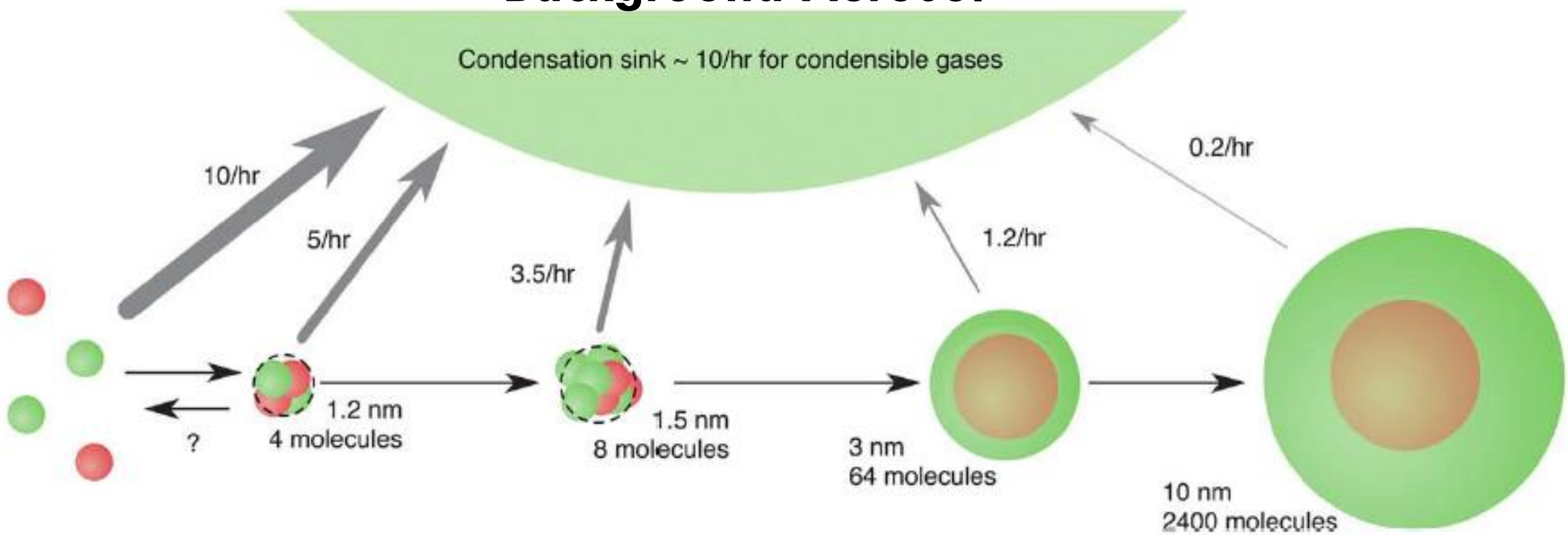
(R3)

Ester

Kroll and Seinfeld, AE, 2008; Ziemann and Atkinson, Chem. Soc. Rev., 2012

Growth model: MABNAG (T. Yli-Juuti)

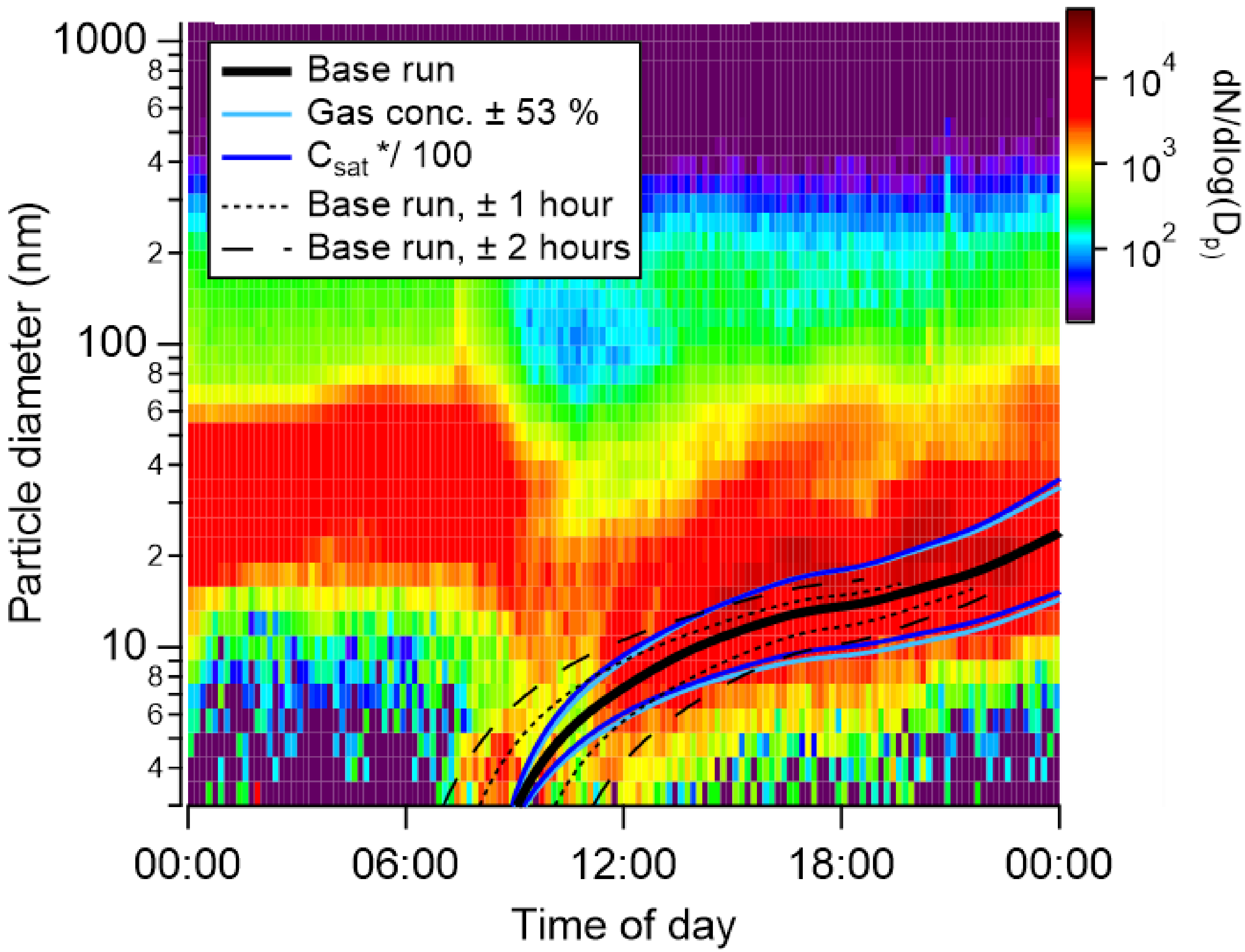
Background Aerosol



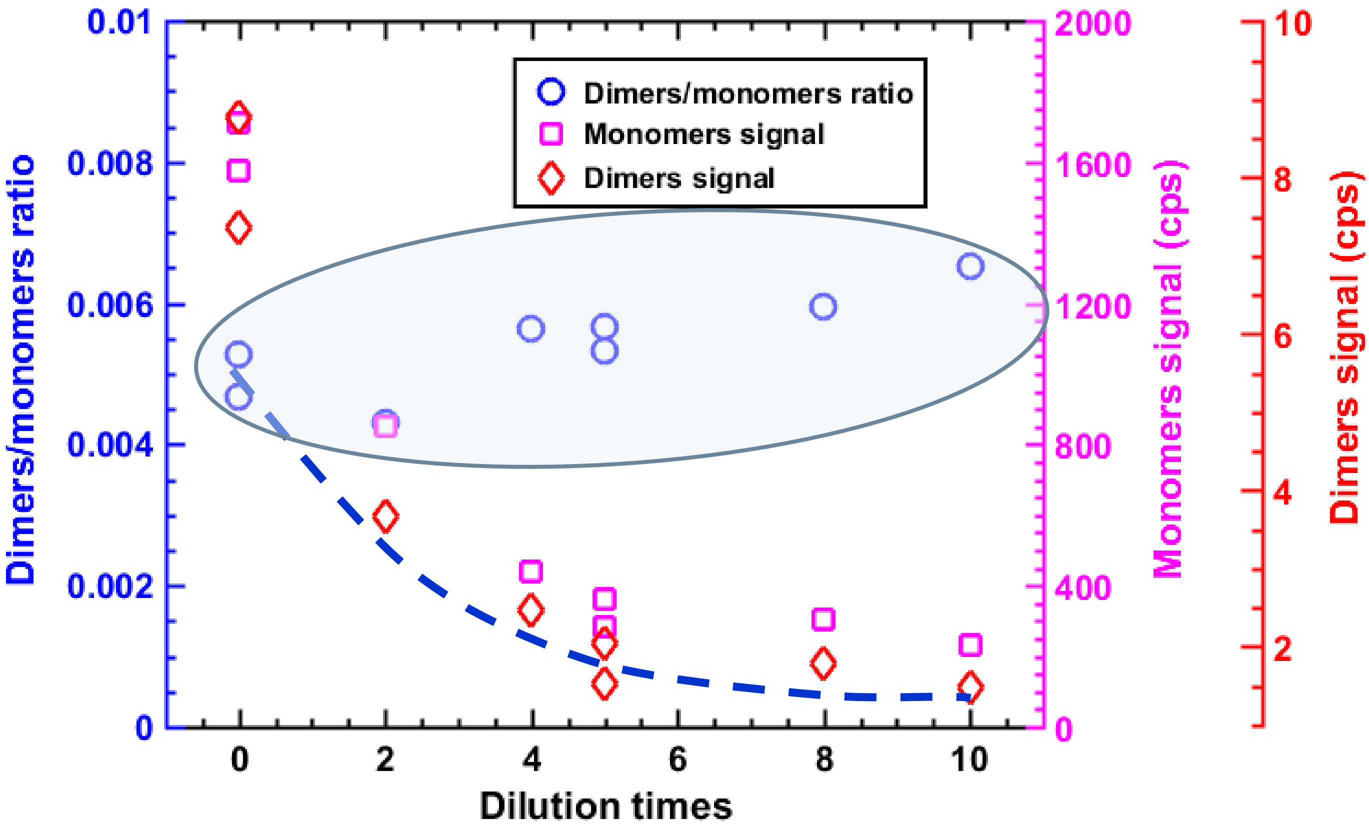
$$growth\,rate \propto [C_i^v - (a_i K) C_i^*]$$

Donahue et al, Faraday Discussions 2013
Tröstl et al Nature 2016

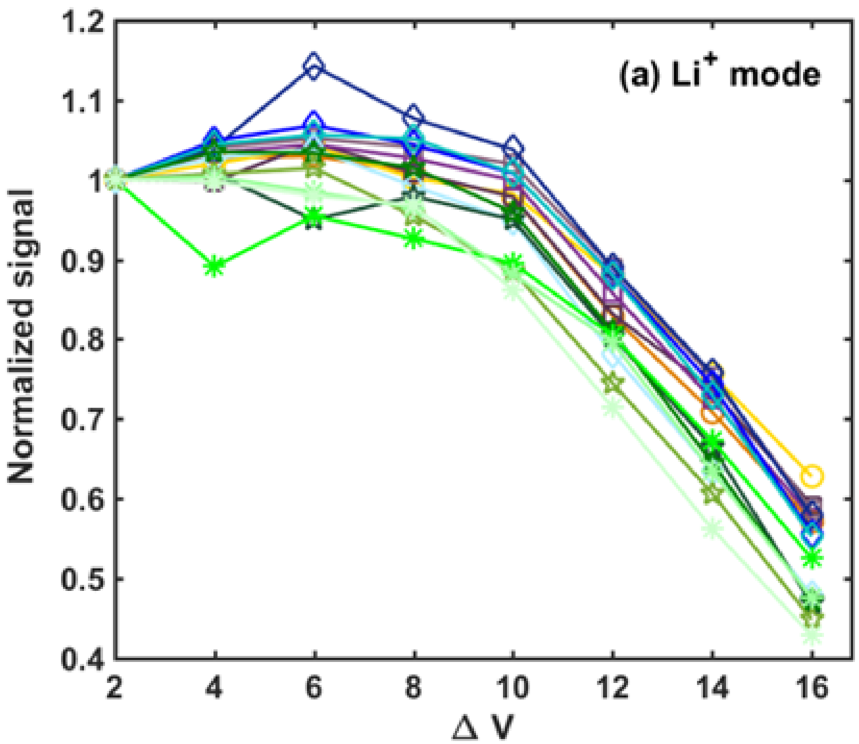
Molecular explanation of new particle growth

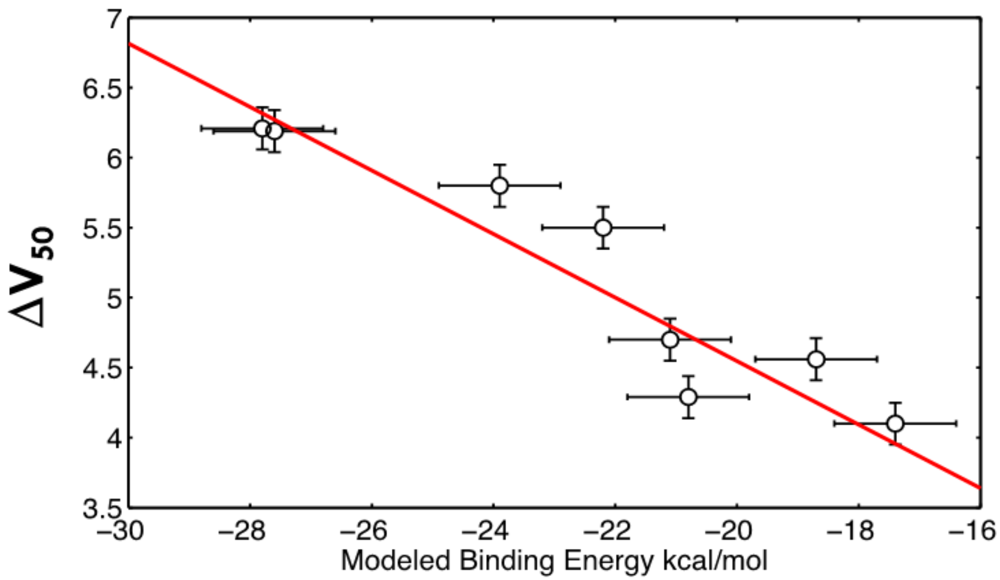


C_{16-20} products *not* ion-induced clusters

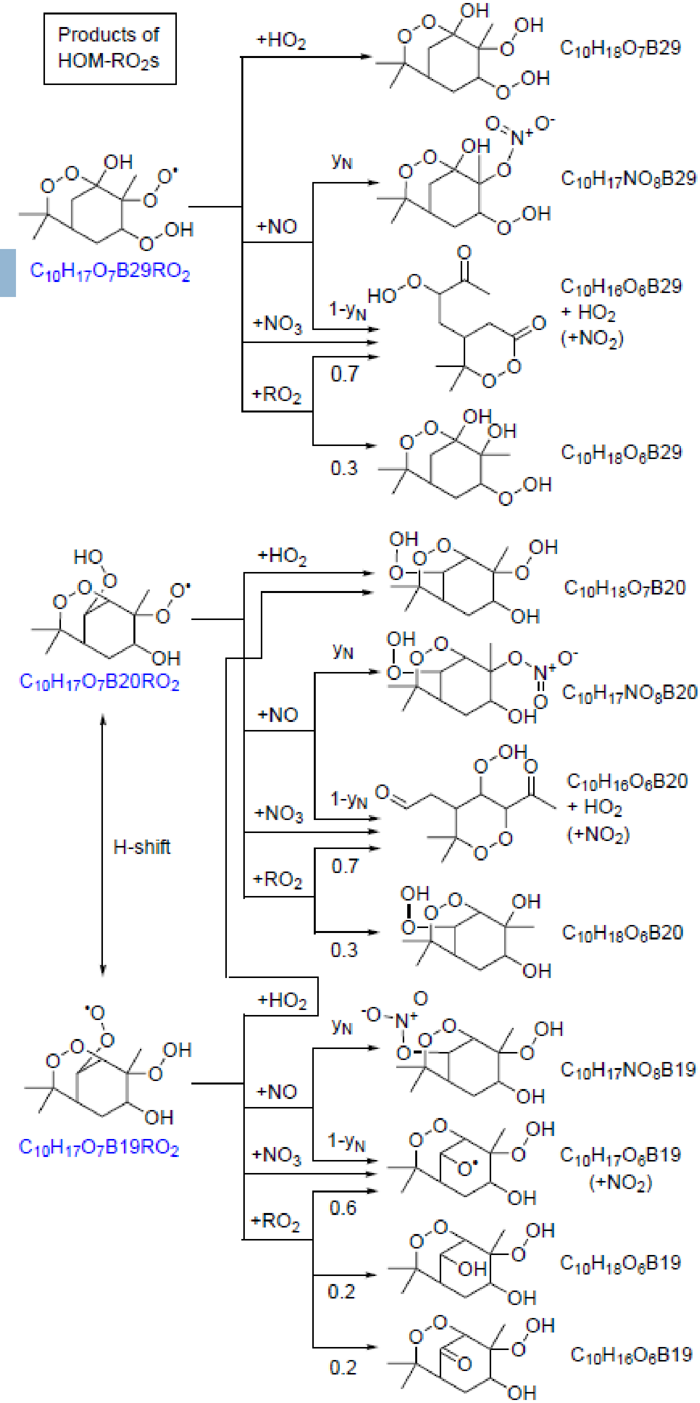


C_{16} – C_{20} products are covalently bound

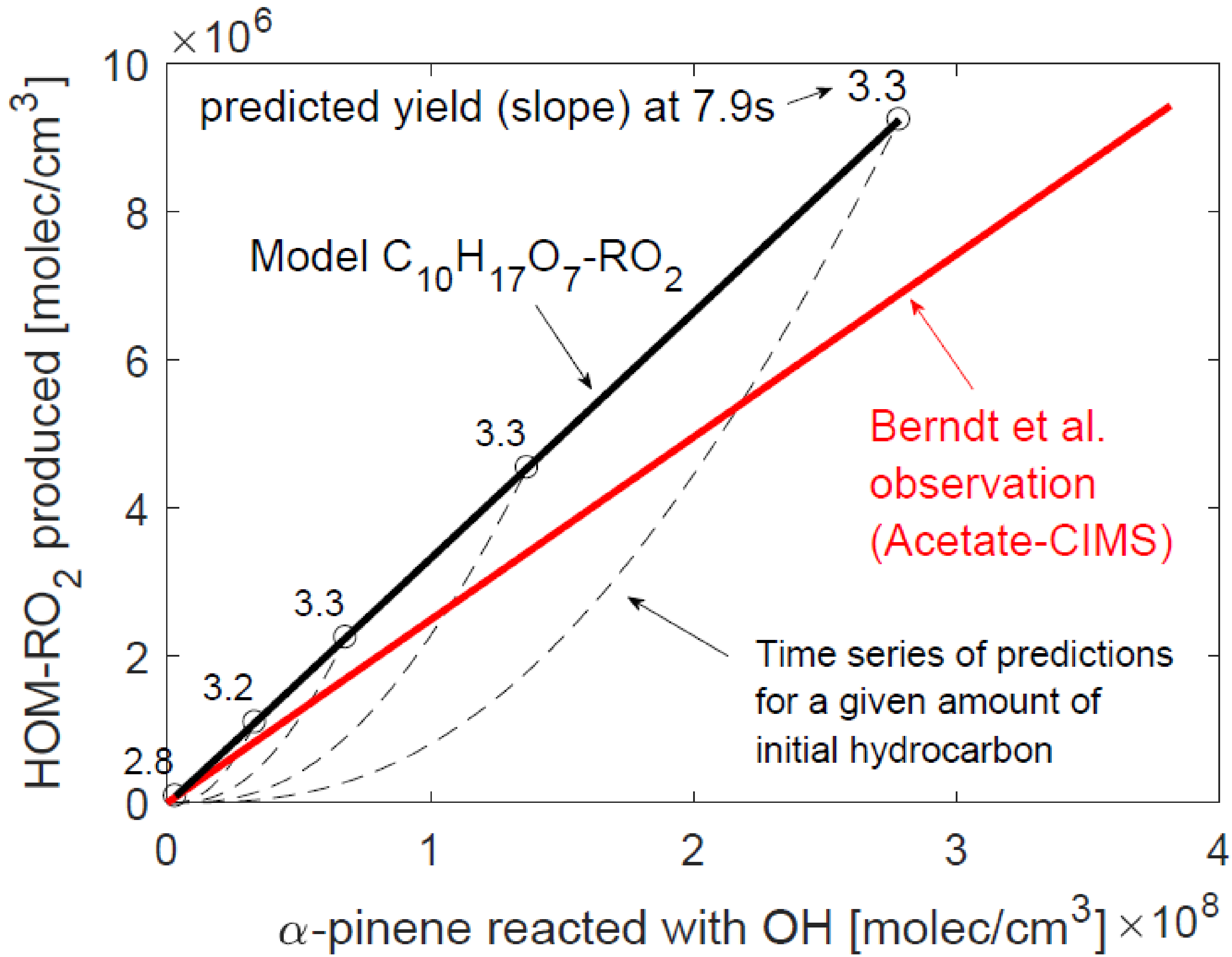




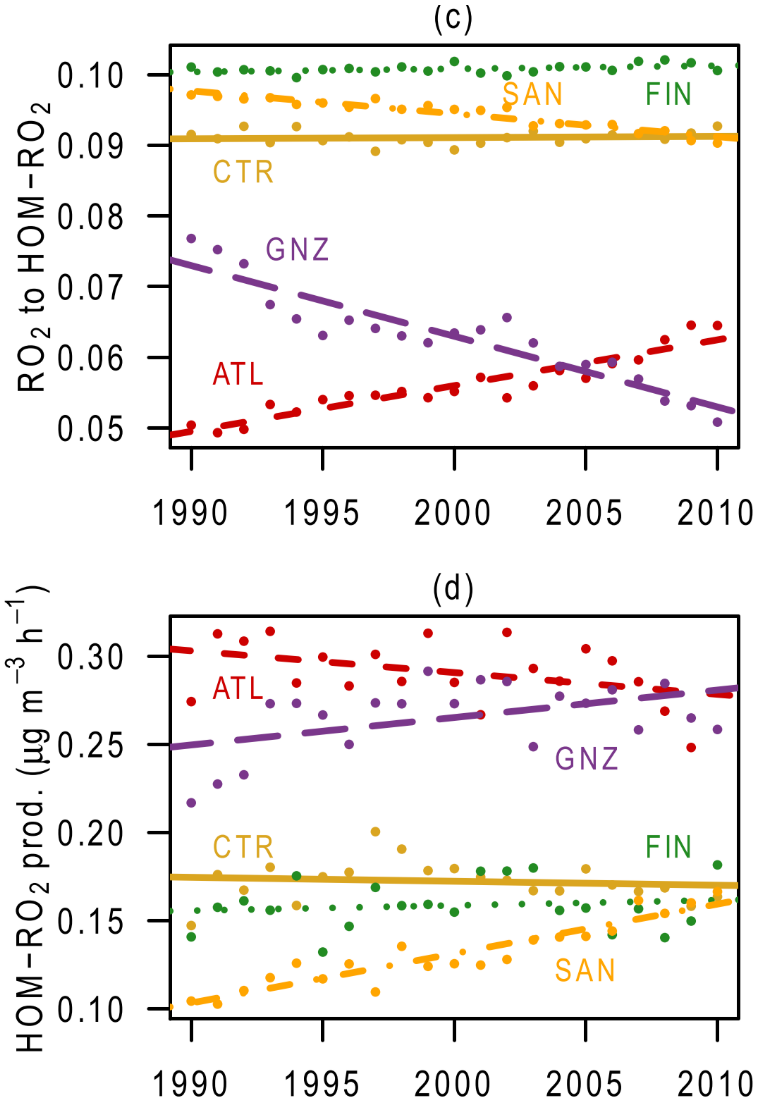
More chemistry

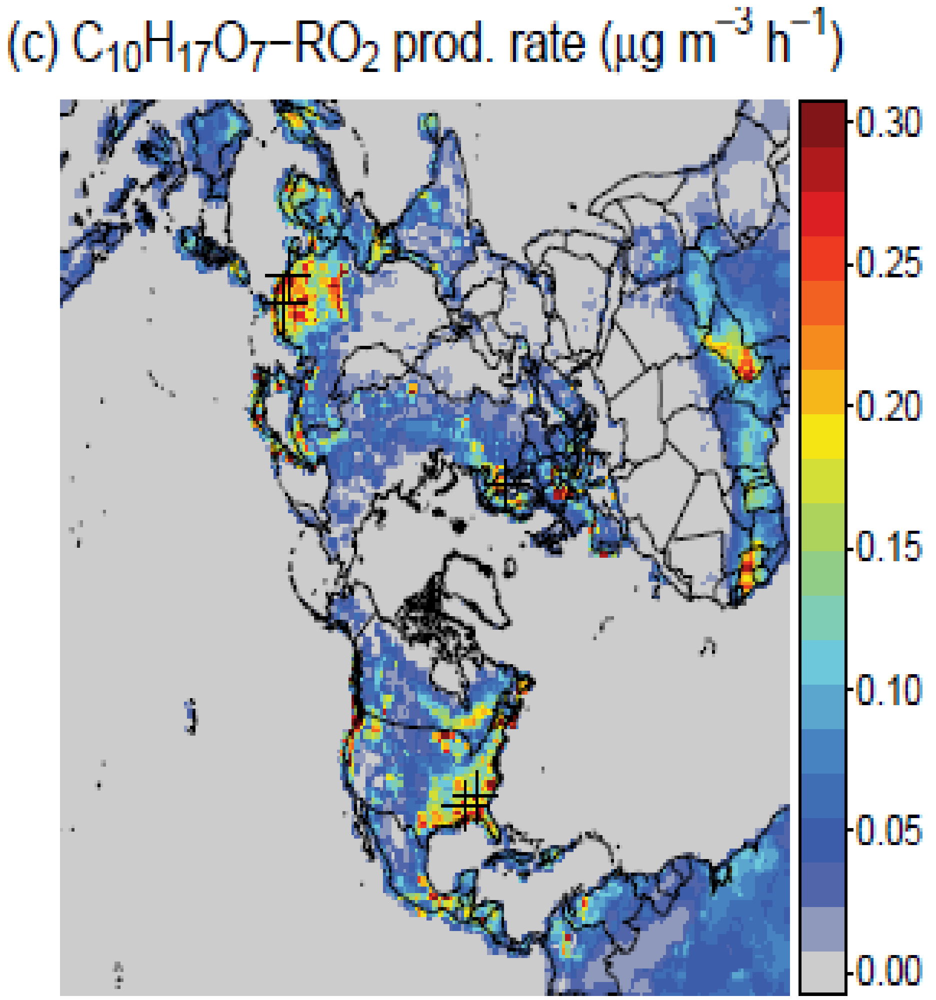


Fast-flow reactor studies (OH + α-Pinene)

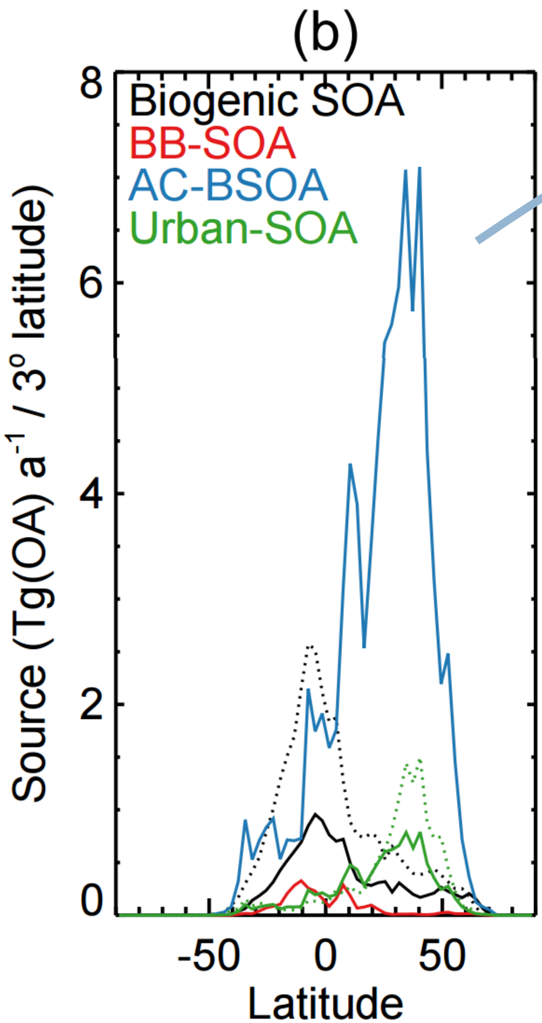


Regional NO_x emissions enhance autoxidation →Secondary Organic Aerosol



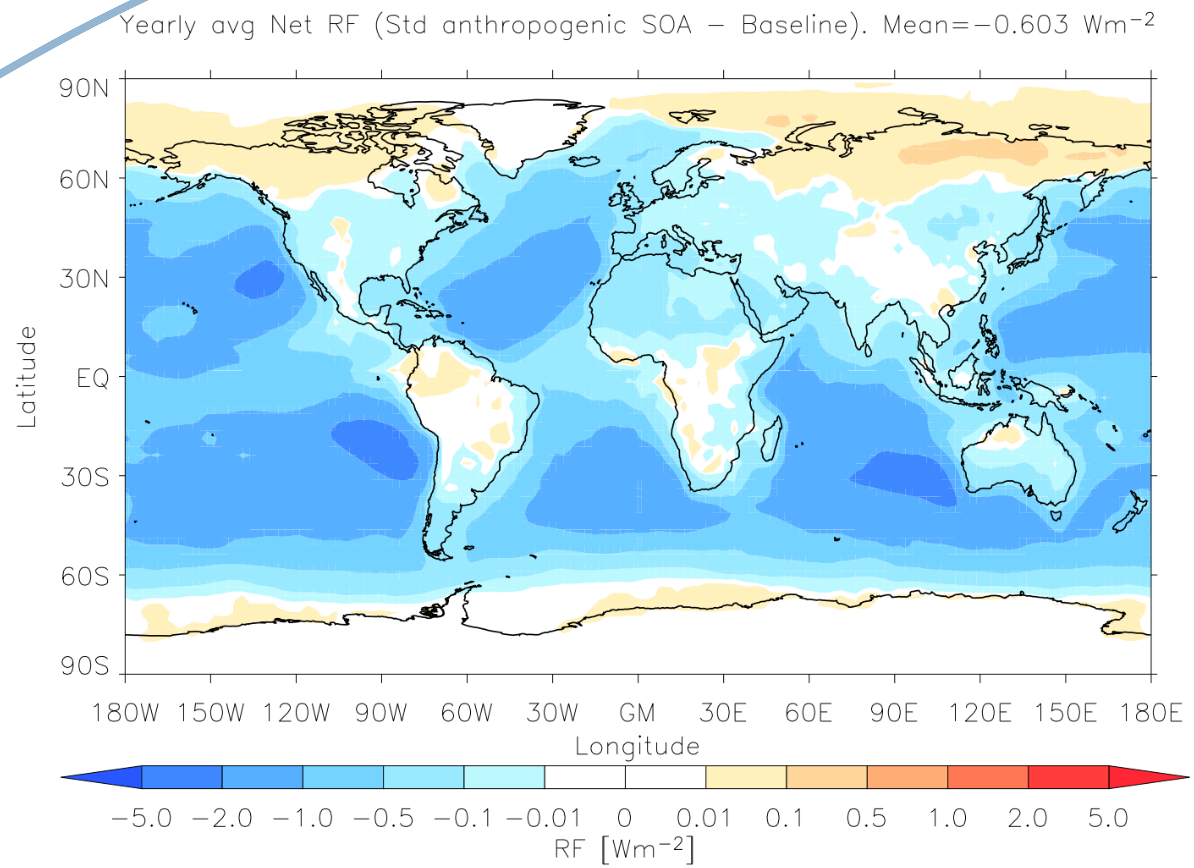


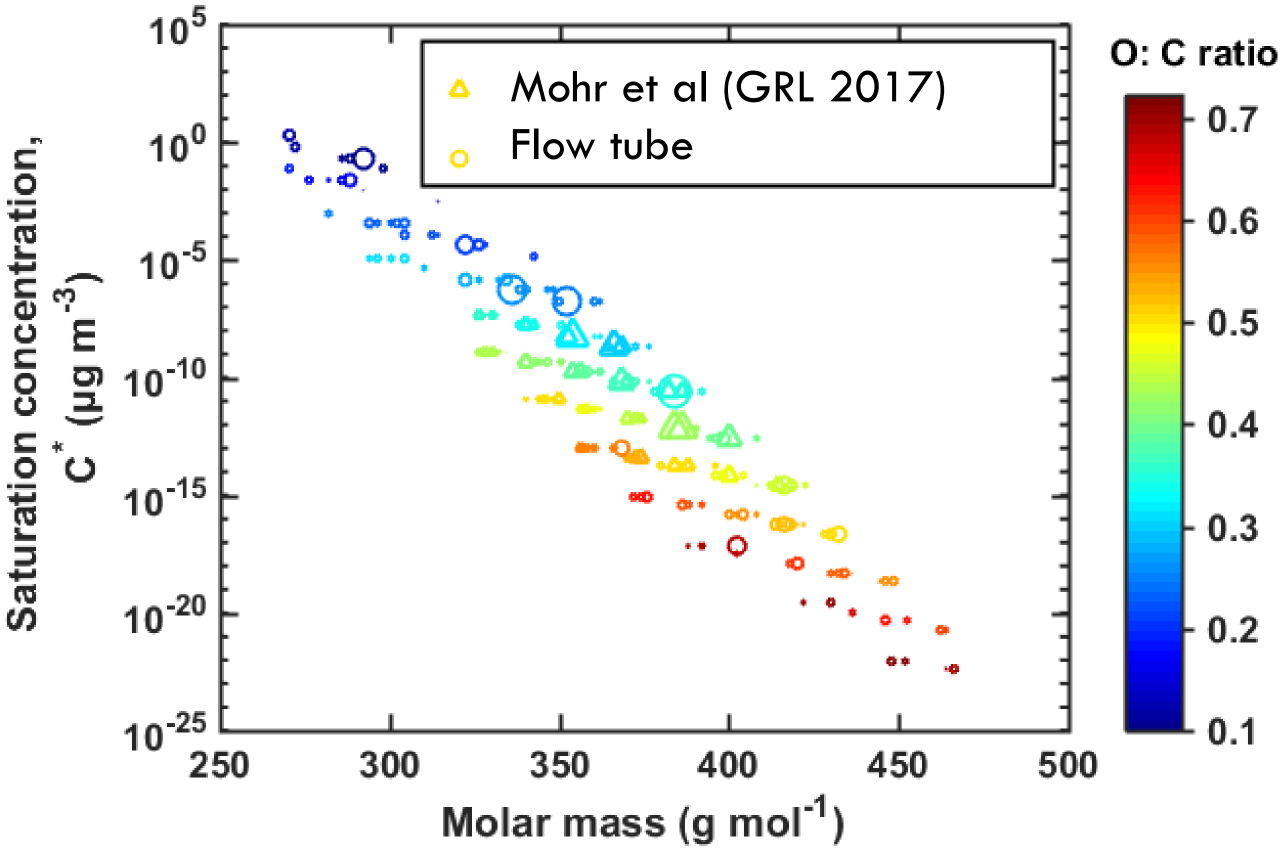
Secondary Organic Aerosol (SOA) - importance



Spracklen et al ACP 2011

ACRF ~ - 0.6 W/m²

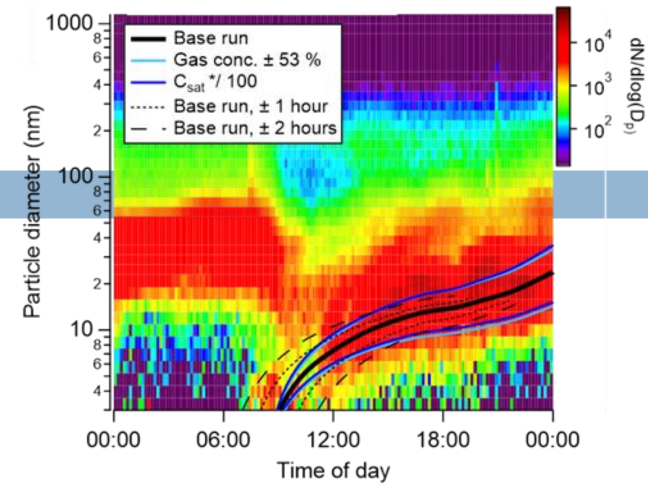




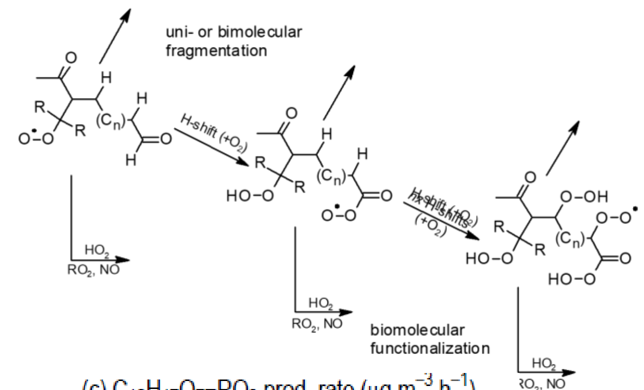
C estimated by Donahue et al. [ACP, 2011]*

Summary

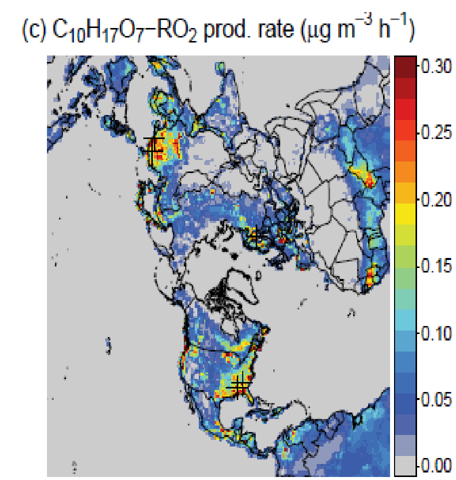
With one instrument, capture suite of low & extremely low volatility organics that explain nano-particle growth



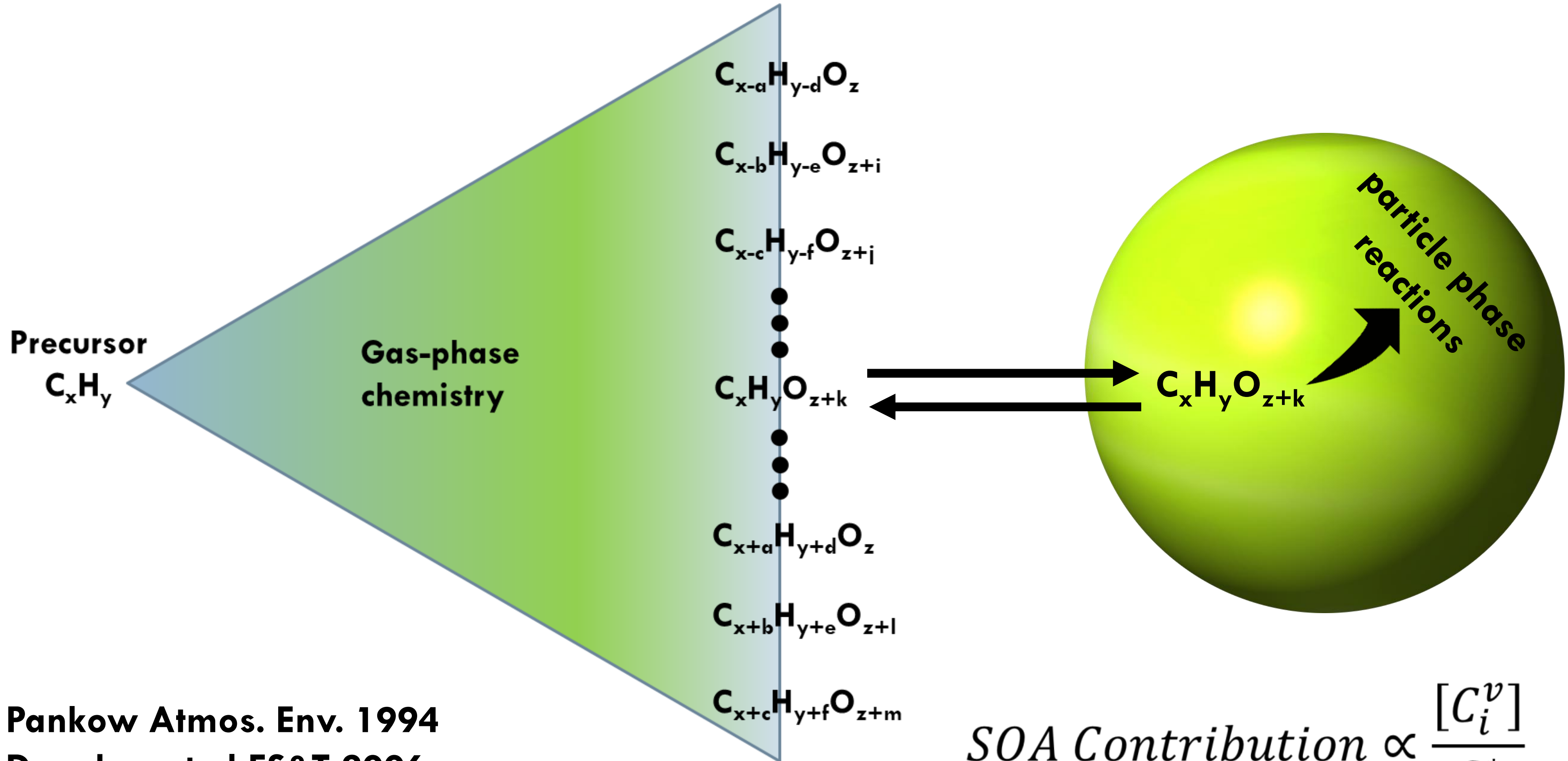
Autoxidation and dimer formation are key peroxy radical pathways to such vapors, drive *prompt* SOA formation



Prompt LVOC and ELVOC formation provides means for SOA formation rates to be sensitive to regional perturbations in oxidants



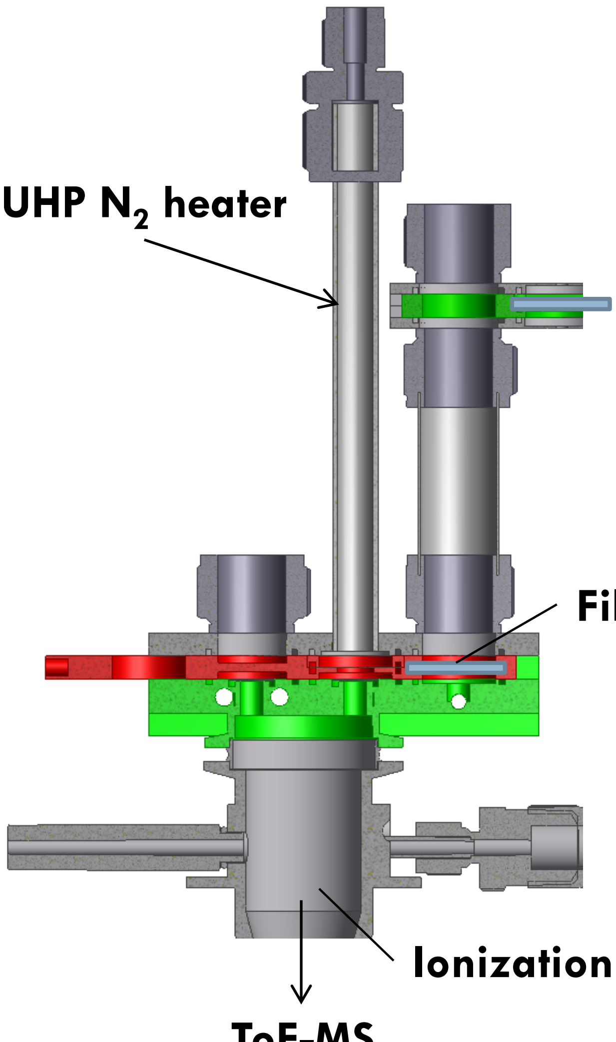
Insights from Molecular Composition

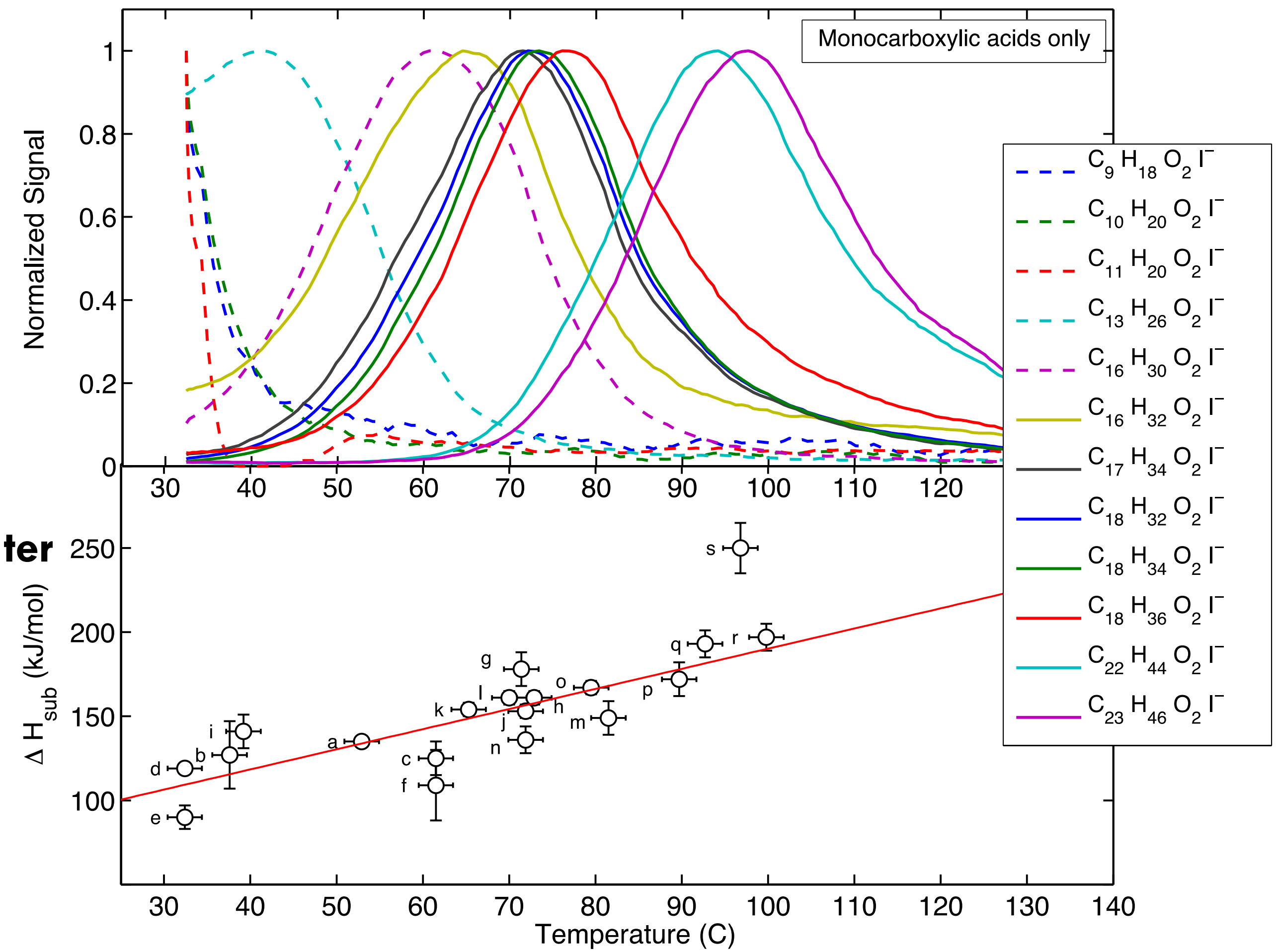


$$SOA\ Contribution \propto \frac{[C_i^v]}{C_i^*}$$

Pankow Atmos. Env. 1994
Donahue et al ES&T 2006
Trump and Donahue ACP 2014

UW FIGAERO HR-ToF-CIMS

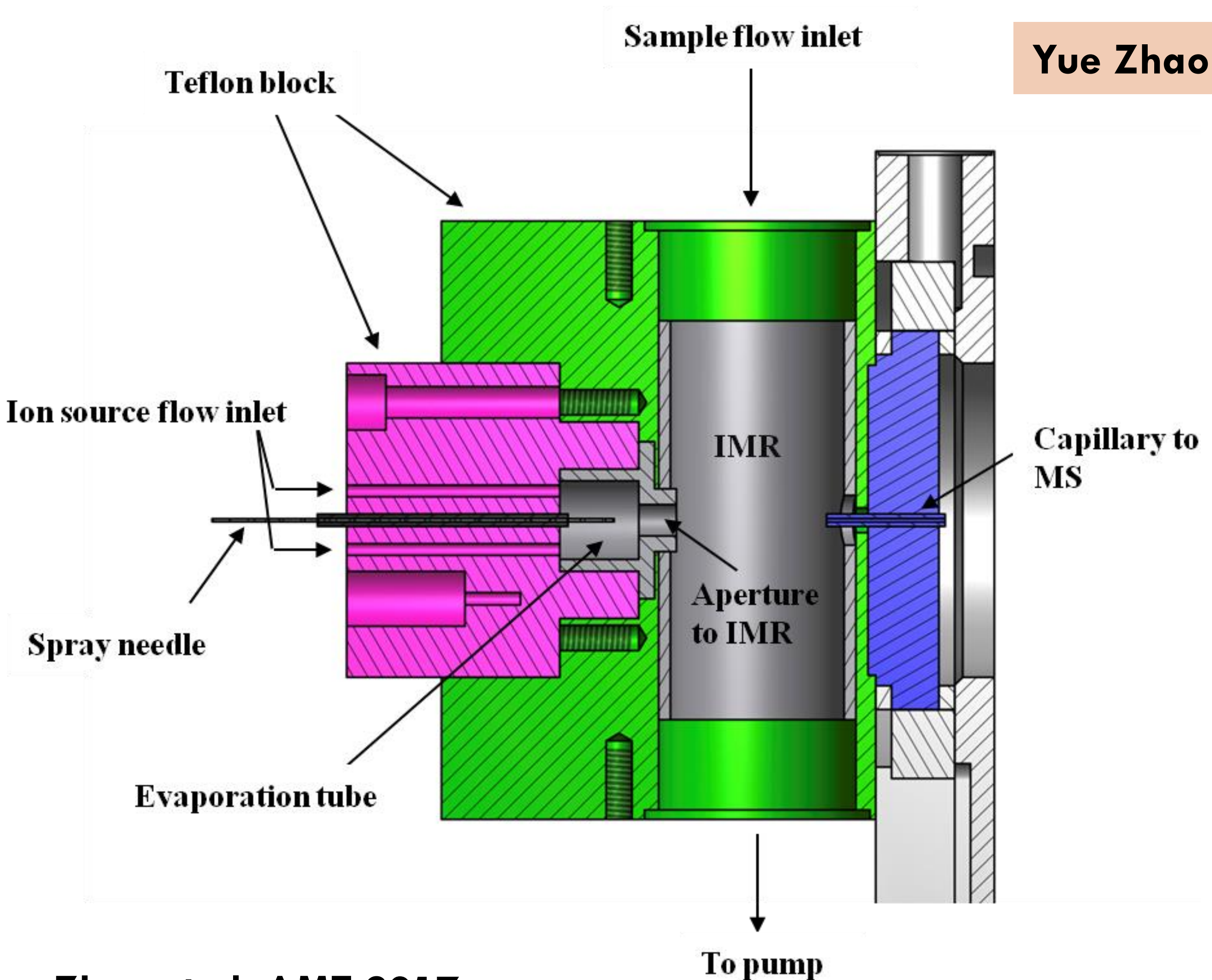




Lopez-Hilfiker et al AMT 2014

Electrospray Chemical Ionization

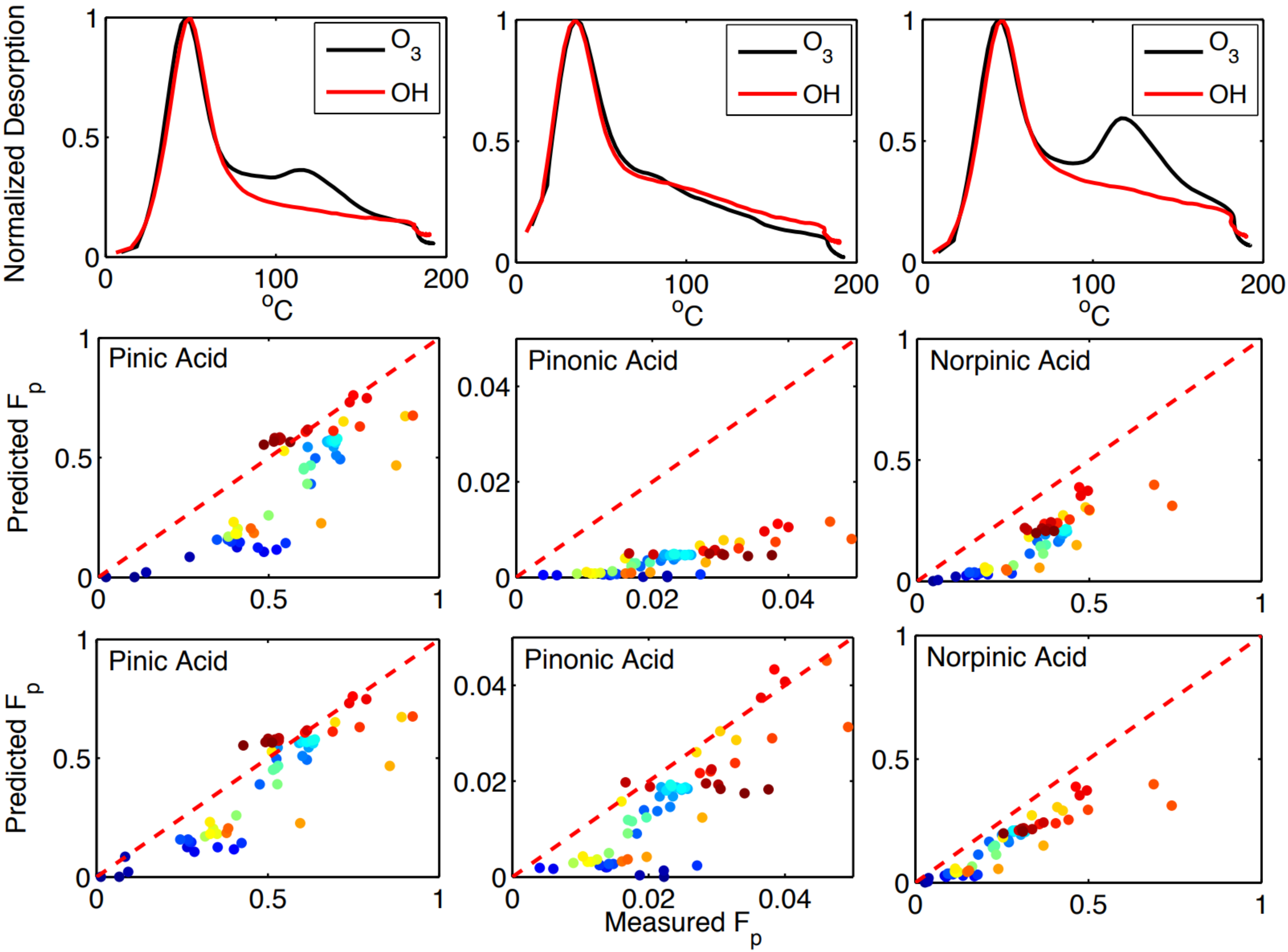
Yue Zhao 7IM.5



Yue Zhao

Jeremy Chan

Zhao et al, AMT 2017


Normalized Desorption
O3
OH
°C
Predicted Fp
Pinic Acid
Pinonic Acid
Norpinic Acid
Measured Fp

Atmos. Chem. Phys., 15, 7765–7776, 2015
www.atmos-chem-phys.net/15/7765/2015/
doi:10.5194/acp-15-7765-2015

Atmospheric Chemistry and Physics
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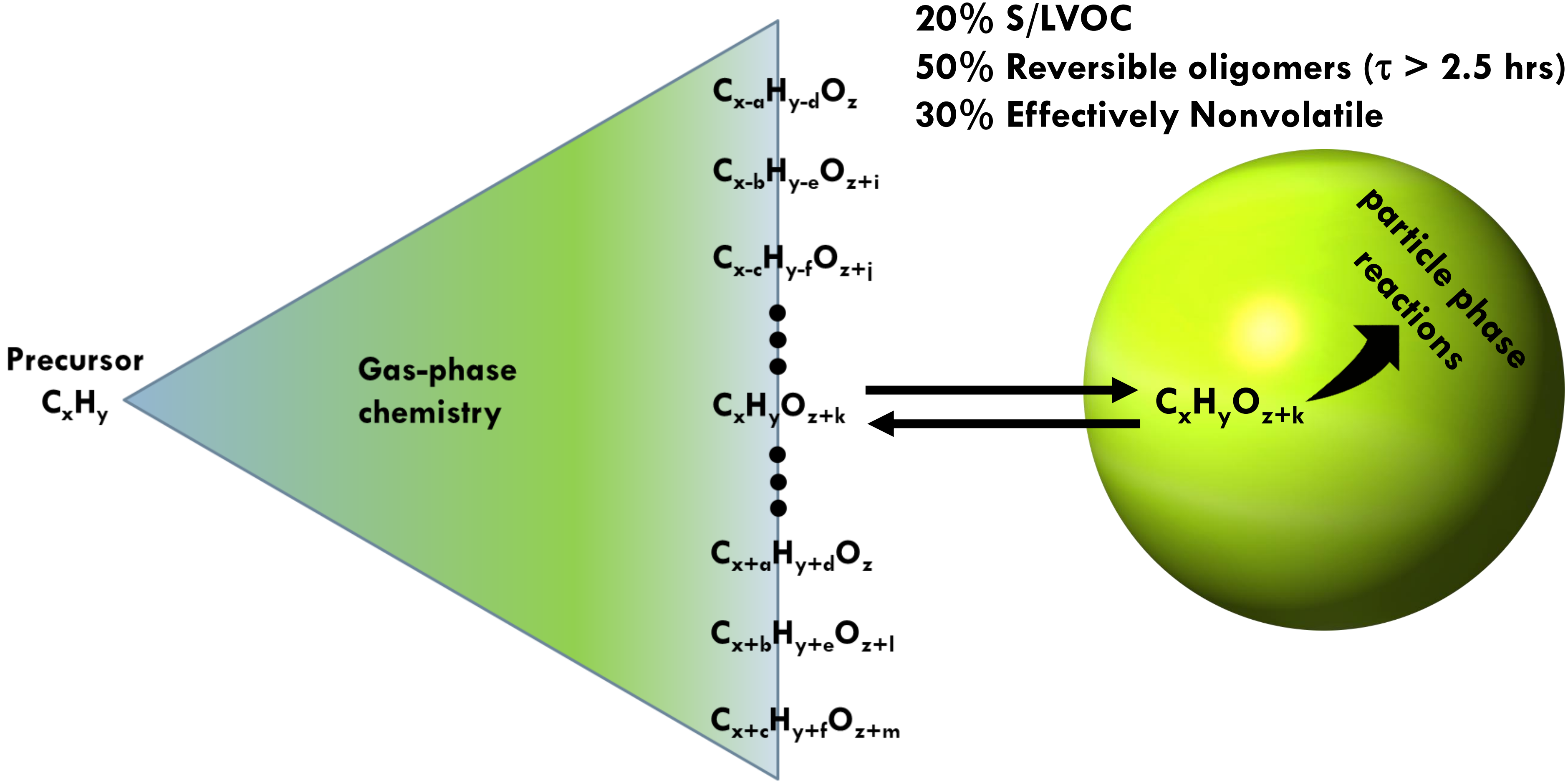
Phase partitioning and volatility of secondary organic aerosol components formed from α-pinene ozonolysis and OH oxidation: the importance of accretion products and other low volatility compounds

F. D. Lopez-Hilfiker[1], C. Mohr[1,7], M. Ehn[2,3], F. Rubach[3], E. Kleist[4], J. Wildt[4], Th. F. Mentel[3], A. J. Carrasquillo[5], K. E. Daumit[5], J. F. Hunter[5], J. H. Kroll[5], D. R. Worsnop[2,6], and J. A. Thornton[1,2,3]

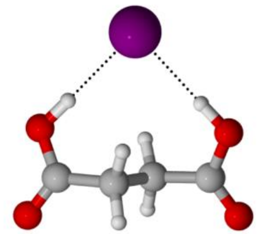
Lopez-Hilfiker et al ES&T 2017
D'Ambro et al ACP 2017
D'Ambro et al ES&T 2017

Conceptual model of MTSOA evolution

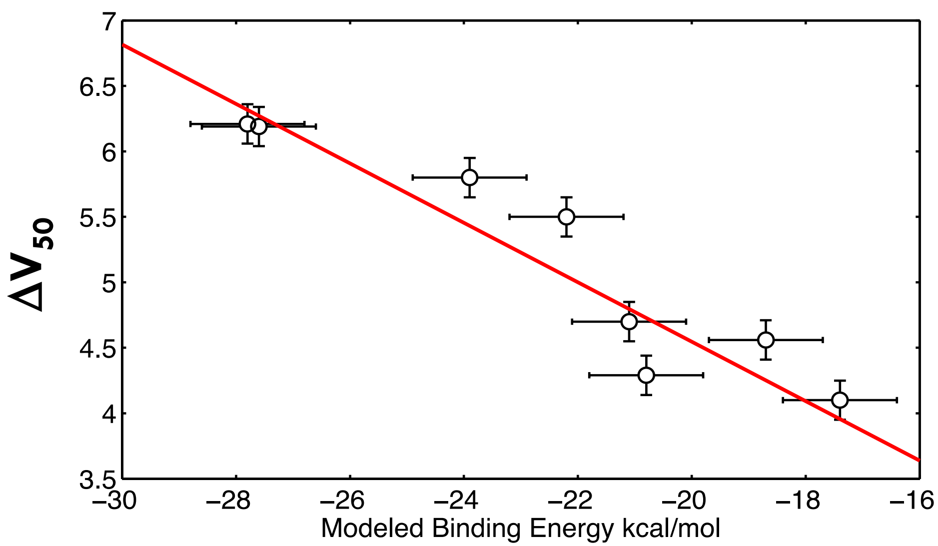
20% S/LVOC
50% Reversible oligomers (τ > 2.5 hrs)
30% Effectively Nonvolatile

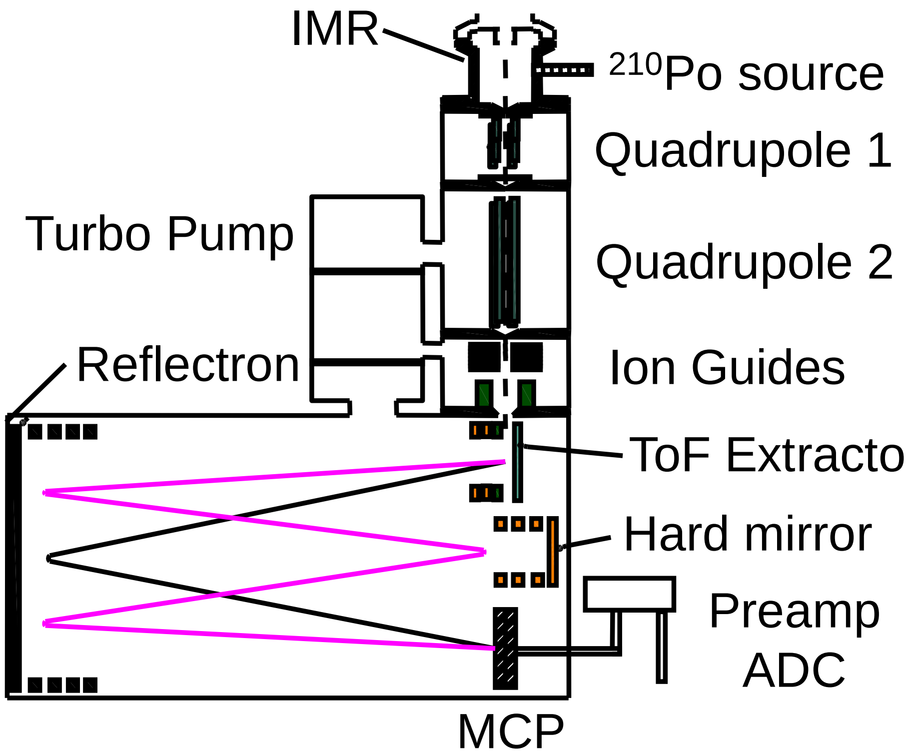


Adduct stability in transfer optics



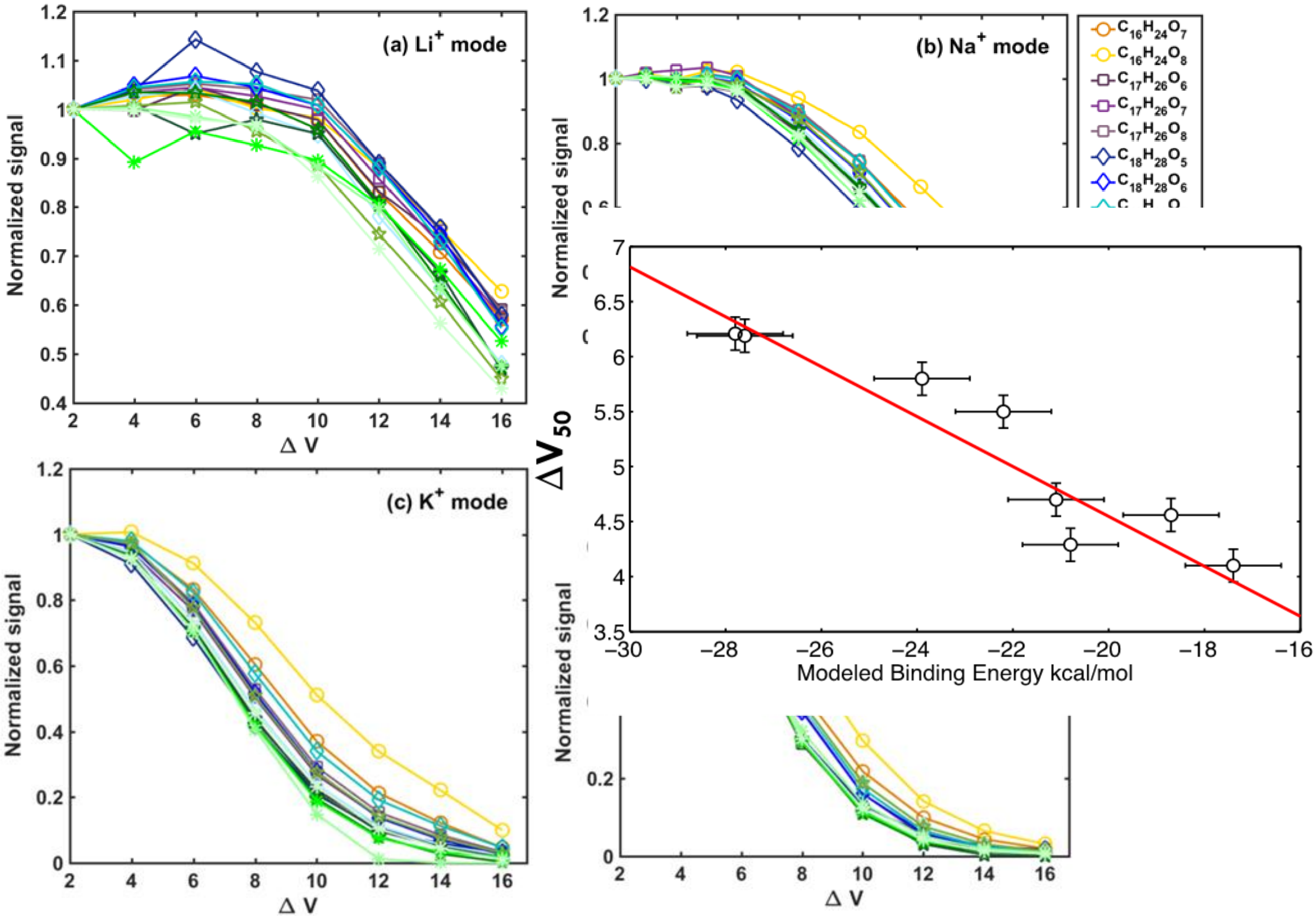
- $I^-(H_2O) + X \rightarrow I^-(X) + H_2O$
- $I^-(X) \xrightarrow{\Delta V} I^- + X$



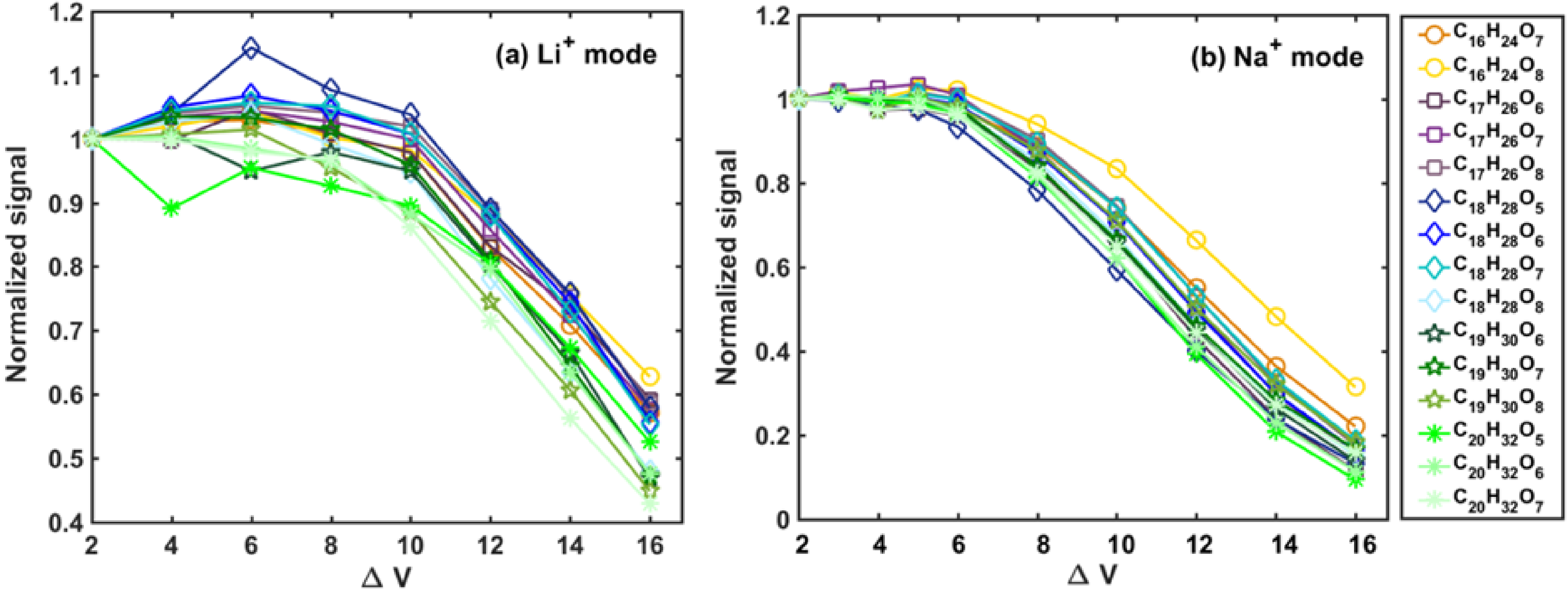


Lee and Lopez-Hilfiker et al 2014; Lopez-Hilfiker et al AMT 2016; Iyer et al, JPCA 2016

Binding Energies: $Li^+ > Na^+ > K^+ > NH_4^+$

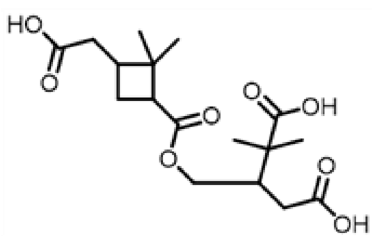


C_{16} – C_{20} "Dimers" are covalently bound

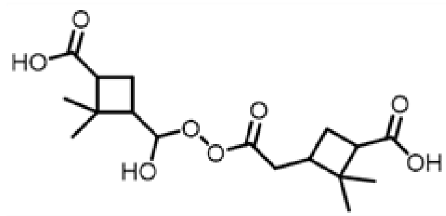


Possible structures from particle phase studies

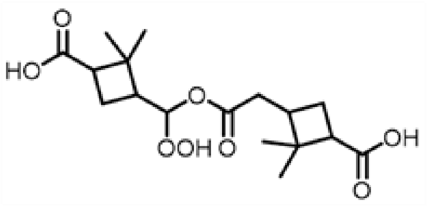
$C_{17}H_{26}O_8$



Ester

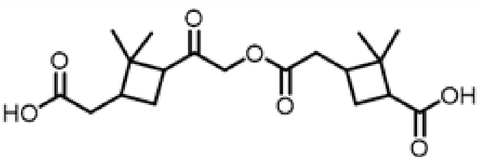


Peroxyhemiacetal

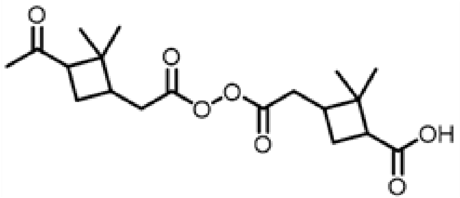


Hydroperoxyhemiacetal

$C_{19}H_{28}O_7$



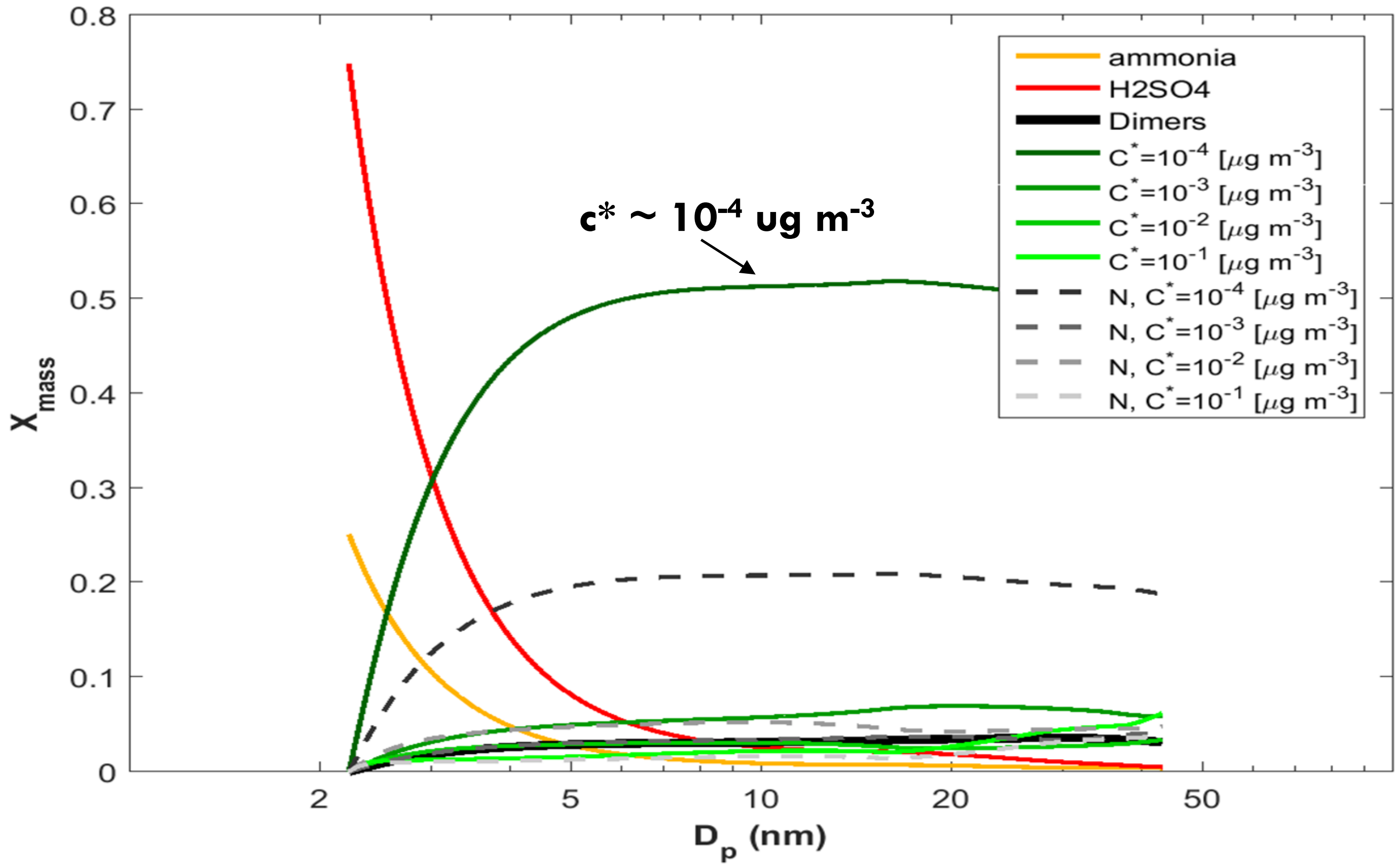
Ester



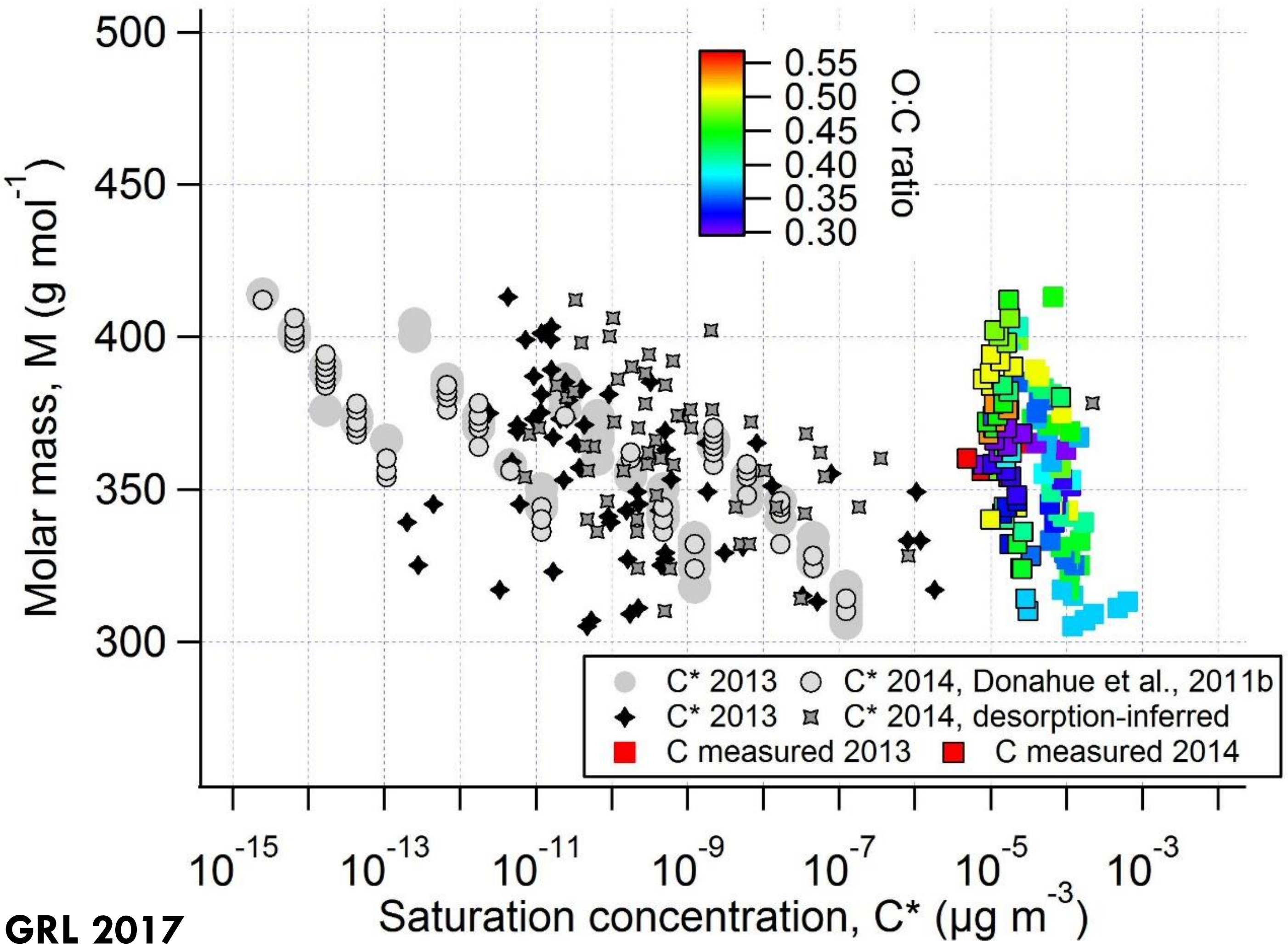
Diacyl peroxide

Kristensen et al ES&TL 2016
Kristensen et al ACP 2016
Zhao (Y) et al PCCP 2015
Zhao (J) et al PNAS 2015
Ziemann, JPCA 2002

Volatility distribution to explain growth



Measured vapor concentration >> c* estimates



Mohr, et al GRL 2017

RO_2 autoxidation and Self-Reaction: A Route to Prompt LVOC Formation