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SOA from biogenic precursors

-Ozonolysis of monoterpenes

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  European Science Foundation, Interdisciplinary Tropospheric Research: from the Laboratory to Global Change

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Atmospheric Science, Department of Chemistry, GU

- Research focus
  - Experimental (Laboratory and Field)
  - Aerosol particles
  - Heterogeneous chemistry

- Personnel
  - Faculty members (Pettersson, Ljungström, Boman, and Hallquist), 10 PhD-students, 4 postdocs, 2 technicians, assistant professor (Andersson), guest professor (Prevot)
  - Modelling joint projects with Dr David Simpson

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Selected projects

SOA formation and properties

Flux measurements

Traffic emission factors and urban aerosol

Air quality in developing countries

Aerosol mass spectrometry (e.g. K and Na)

Levitation balance (freezing of cloud droplets)

Molecular bean studies (Interaction with ice surfaces)

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“SOA”, Atmospheric Science, Department of Chemistry, GU

- Research focus
  - Oxidation of BVOC and SOA

- Personnel
  - Faculty members: Evert Ljungström, Mattias Hallquist and David Simpson (Associated)
  - Postdocs: Åsa Jonsson and Claudia Hak
  - PhD Students: Robert Bergström, Eva Emanuelsson, Helene Holmgren and Kent Salo

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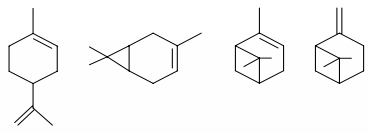
Secondary Organic Aerosol (SOA) Formation

- Gas-to-particle conversion
  - nucleation
  - condensation
  - gas-to-particle partitioning

- One important group contributing to SOA
  - Monoterpenes, e.g. limonene, Δ^3-carene, α-pinene and β-pinene



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Degradation of unsaturated compounds

- Oxidation initiated by
  - OH
  - O_3
  - NO_3
- Importance depends on
  - Atmospheric conditions
  - Application

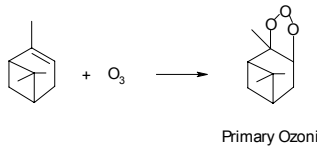
Table 1
Calculated atmospheric lifetimes of biogenic volatile organic compounds

Biogenic VOC	Lifetime[a] for reaction with		
	OH^b	O_3^c	NO_3^d
Isoprene	1.4 h	1.3 day	1.6 h
Monoterpenes			
Camphene	2.6 h	18 day	1.7 h
2-Carene	1.7 h	1.7 h	4 min
3-Carene	1.6 h	11 h	7 min
Limonene	49 min	2.0 h	5 min
Myrcene	39 min	50 min	6 min
cis-/*trans*-Ocimene	33 min	44 min	3 min
α-Phellandrene	27 min	8 min	0.9 min
β-Phellandrene	50 min	8.4 h	8 min
α-Pinene	2.6 h	4.6 h	11 min
β-Pinene	1.8 h	1.1 day	27 min
Sabinene	1.2 h	4.8 h	7 min
α-Terpinene	23 min	1 min	0.5 min
γ-Terpinene	47 min	2.8 h	2 min
Terpinolene	37 min	13 min	0.7 min

Source: Atkinson and Arey 2003 AE

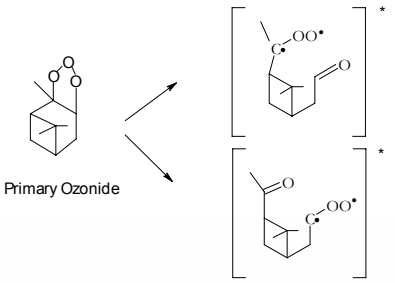
Ozonolysis

- In the reaction with ozone an ozonide is initially formed



Primary Ozonide

- This ozonide is energy rich and decomposes into carbonyls and biradicals, i.e. Criegee Intermediates



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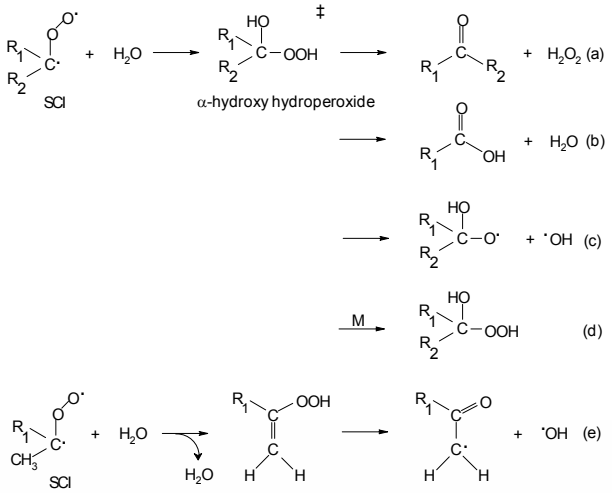
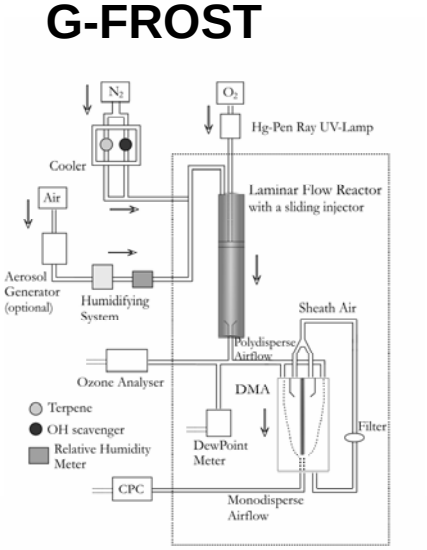
Ozonolysis

- The fate of the excited CI are e.g.
  - stabilisation, forming a stable CI (SCI)
  - unimolecular rearrangement
  - fragmentation
- In the ozonolysis OH radicals are formed
- The SCI can undergo reaction with e.g. water

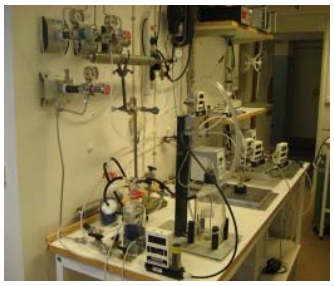
Ozonolysis



G-FROST



Temperature 243-323 K (-30-50°C)
Relative Humidity, RH ~0-80%
Reaction times 40-500 s



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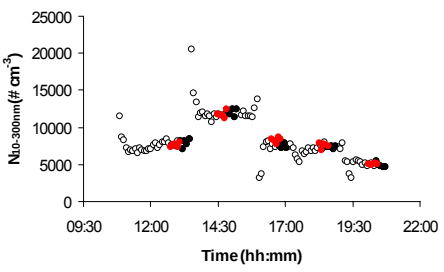
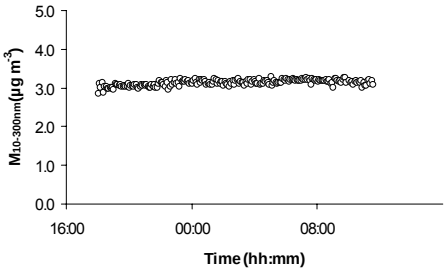
G-FROST





Reproducibility of SOA formed
Exp.run#1 black, run#2 red
RH changed stepwise

Example of the stability of SOA formed at constant T and RH

Source: Jonsson 2008 Thesis

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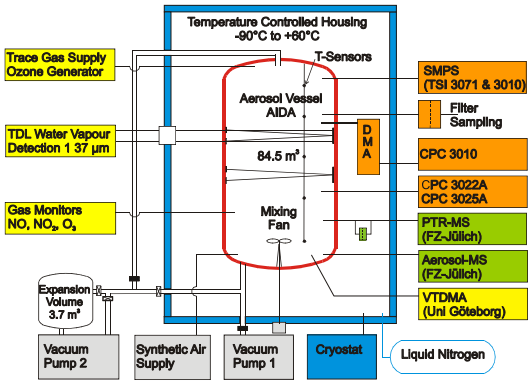
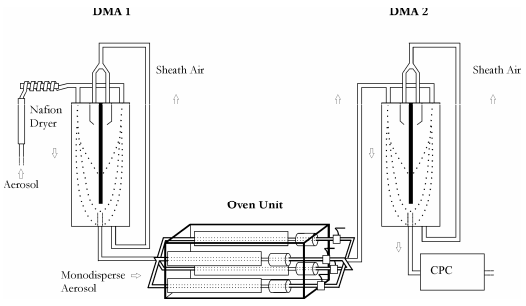
AIDA-Karlsruhe

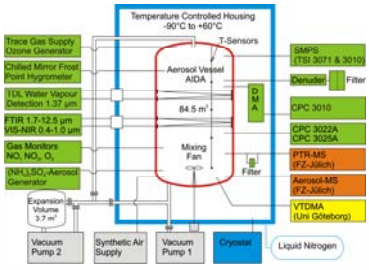
Temperature 243-313 K (-30-40°C)
Relative Humidity, RH ~0-44% (at 293)
Reaction times, days

Focus: Volatility

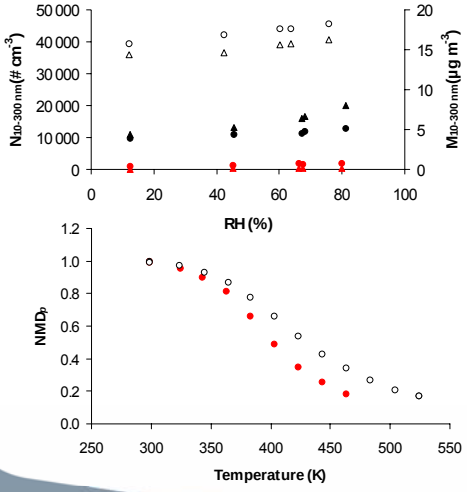


VTDMA (Volatility)





SOA Formation



Circles: number
Triangles: mass

White: limonene
Black: Δ^3-carene
Red: α-Pinene

White: limonene
Red: α-Pinene

Source: Jonsson et al 2006 (ES&T) & 2007(JAS)

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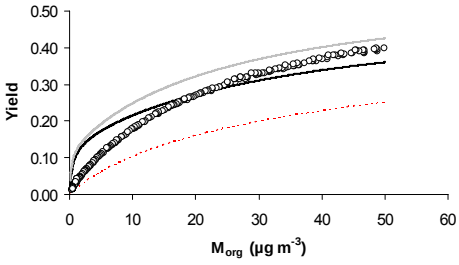
SOA Formation



Yield of limonene SOA

White circles: G-FROST, 298 K, 60% RH
Black line: AIDA, 303 K, 44% RH
Grey line: AIDA, 293 K, 42% RH
Red dashed line: photochemical oxidation, ~311 K, 5% RH, (Griffin et al., 1999)

Source: Jonsson 2008 (Thesis)

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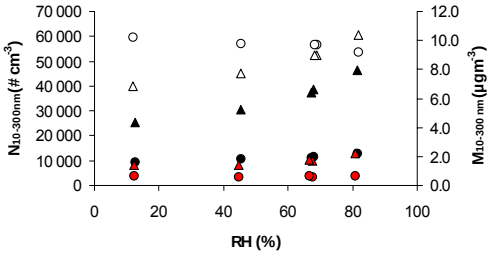
SOA Formation and Scavenger



298 K

○ : number
△ : mass

White: no OH-s
Black: 2-butanol
Red: cyclohexane

Number and mass
No OH-s > 2-b > cyclohexane

Source: Jonsson et al 2008 (ES&T)

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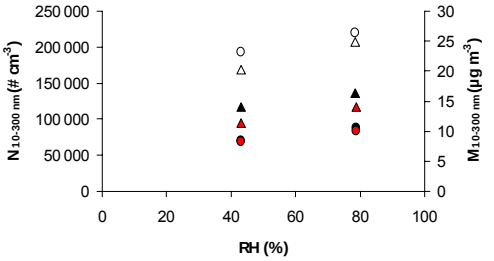
SOA Formation and Scavenger



243 K

○ : number
△ : mass

White: no OH-s
Black: 2-butanol
Red: cyclohexane

OH chemistry is influencing
the SOA formation even at low temperature

Source: Jonsson et al 2008 (ACPD)

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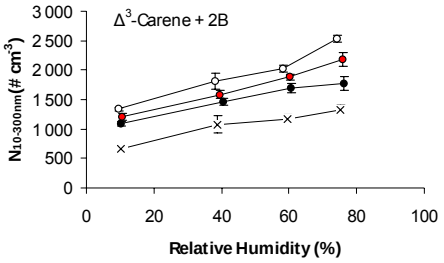
SOA Formation and Scavenger



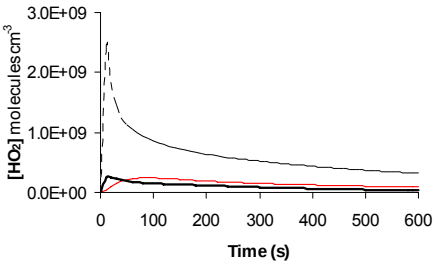
[2-Butanol]

3.5 x 10^{13} molecules cm^{-3}

32 x 10^{13} molecules cm^{-3}

Source: Jonsson et al 2008 (ES&T)

SOA Formation and Scavenger



Dashed line: 2-butanol
Black line: No OH-s
Red line: Cyclohexane
RH ~60%

Source: Jonsson et al 2008 (ES&T)

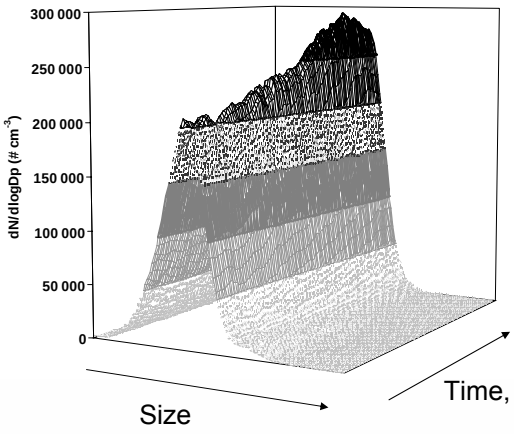
SOA Formation and Scavenger

Table 2. Effect of OH scavenger on SOA production from selected cyclic precursors. A comparison with literature data.

Reference	Org. Precursor	Scavenger	SOA Effect
This study	limonene α-pinene Δ^3-carene	cyclohexane, 2-butanol, without	$SOA_{WO}>SOA_{2\text{-}B}>SOA_{CH}$ $SOA_{WO}>SOA_{2\text{-}B}>SOA_{CH}$ $SOA_{WO}>SOA_{2\text{-}B}>SOA_{CH}$
Keywood et al. 2004 (18)	cyclohexene	cyclohexane, 2-butanol, CO	$SOA_{CO}>SOA_{2\text{-}B}>SOA_{CH}$
Iinuma et al. 2005 (19)	α-pinene	cyclohexane, 2-butanol	$SOA_{2\text{-}B}>SOA_{CH}$
Docherty and Ziemann, 2003 (30)	β-pinene	cyclohexane 1-propanol	$SOA_{CH}>SOA_{1\text{-}P}$
Docherty et al. 2005 (17)	α-pinene β-pinene Δ^3-carene sabinene	cyclohexane, 1-propanol, formaldehyde	$SOA_{1\text{-}P}\geq SOA_{CH}\geq SOA_{HCHO}$ $SOA_{CH}>SOA_{1\text{-}P}>SOA_{HCHO}$ $SOA_{1\text{-}P}\geq SOA_{CH}$ $SOA_{CH}\geq SOA_{1\text{-}P}$

Source: Jonsson et al 2008 (ES&T)

SOA Formation and RH



Ozonolysis of Limonene
2-butanol
RH 10 → 80%, 298 K

Number of particles ↑
with increased RH

SOA Formation Temp & RH

N Temp		No OH-s	2-Butanol	Cyclohexane
298 K	Limonene	0	+	-
	Δ³-Carene	-	++	∨
	α-Pinene	-	++	++
273 K	Limonene	+	+	-
	Δ³-Carene	-	-	--
	α-Pinene	-	∧	--
243 K	Limonene	0	0	-
	Δ³-Carene	+	+	+
	α-Pinene	+	+	0

M Temp		No OH-s	2-Butanol	Cyclohexane
298 K	Limonene	++	+	+
	Δ³-Carene	++	++	++
	α-Pinene	+	++	++
273 K	Limonene	+	+	+
	Δ³-Carene	++	++	+
	α-Pinene	+	+	0 < 60% > -
243 K	Limonene	+	+	+
	Δ³-Carene	+	+	+
	α-Pinene	+	+	+

Influence of RH on N and M

increase +
decrease –
no change 0

Double symbols denote a change larger than 30 %.

-note these are endocyxlic terpenes
-β-pinene has basically opposite results (regarding mass and number at RT)

Source: Jonsson et al 2008 (ACPD)

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SOA Formation RH

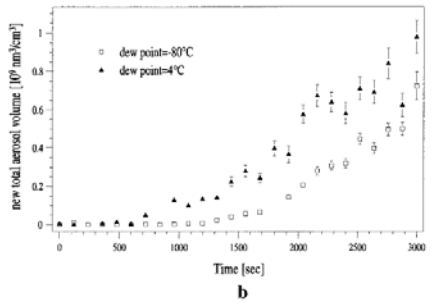

Figure 5. Influence of water vapor on (a) the aerosol number concentration and (b) the total aerosol volume formed in α-pinene ozonolysis at low concentrations (spherical reactor).

B

monoterpene	volume (dry)/ volume (humid)	N_{max} (dry)/ N_{max} (humid)	structure (bold: dominating type)
sabinene	59 ± 7	not measurable	**exo**cyclic
α-pinene	0.74 ± 0.13	1.8 ± 0.3	**endo**cyclic

Source: Bonn et al 2002 JPC

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SOA Formation RH

TABLE 2. Comparison of Literature on the Impact of Relative Humidity on Integrated Number and Mass[a]

org. precursor (ppb)[b]	type of study	OH scavenger	temp (K)	RH (%)	M_{tot}[c]	N_{tot}[c]	source
L (1000)	static reactor	cyclohexane	295 ± 2	0.01 & 31	no effect	−	Bonn et al. (*9*)
L (19.5 ± 1.2)	flow reactor	n.s	295 ± 2	15, 30 & 43	no effect	no effect	Fick et al. (*18*)
L (15 & 30)	flow reactor	2-butanol	298 ± 0.4	< 2−85	+	+	this study
C (1000)	static reactor	cyclohexane	295 ± 2	0.01 & 31	no effect	−	Bonn et al. (*9*)
C (18.5 ± 1.2)	flow reactor	n.s	295 ± 2	15, 30 & 43	no effect	no effect	Fick et al. (*18*)
C (15 & 30)	flow reactor	2-butanol	298 ± 0.4	< 2−85	+	+	this study
AP (1000)	static reactor	cyclohexane	295 ± 2	0.01 & 31	no effect	no effect	Bonn et al. (*9*)
AP (50)	static reactor	cyclohexane	295 ± 2	0.01 & 31	+	−	Bonn et al. (*9*)
AP (41−124 reacted)	static reactor	2-butanol	301−303	< 2−58	+	n.s	Cocker et al. (*11*)
AP (49−713)	flow reactor	cyclohexane	295 ± 0.5	0.2 & 40	n.s	− (small)	Berndt et al. (*10*)
AP (20.1 ± 1.3)	flow reactor	n.s	295 ± 2	15, 30 & 43	no effect	no effect	Fick et al. (*18*)
AP (56000 − 266000)	flow reactor	n.s	293−302	13−41	no effect	no effect	Rohr et al. (*17*)
AP (15 & 30)	flow reactor	2-butanol	298 ± 0.4	< 2−85	+	+	this study

[a] n.s = Not stated. L = Limonene. C = Δ^3-Carene. AP = α-pinene. [b] Concentrations are given as start concentrations in ppb. [c] A positive sign (+) means an increase with relative humidity and a negative sign (−) means a decrease with relative humidity.

Source: Jonsson et al 2006 JPC

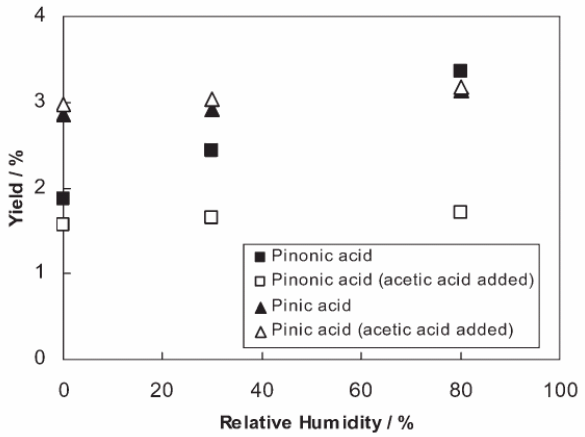
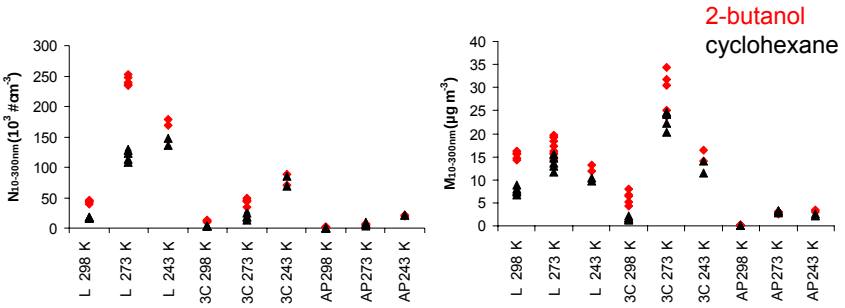


Fig. 1 Acid yields from the ozonolysis of α-pinene under various conditions.

Source: Ma et al 2007

SOA Formation and Temperature

L: Limonene, 3C: Δ^3-Carene, AP: α-Pinene



Source: Jonsson et al 2008 (ACPD)

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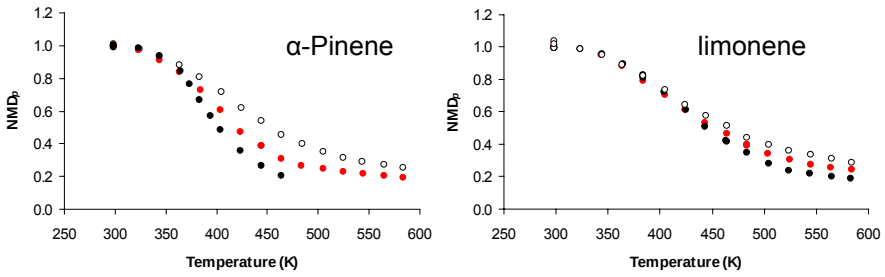
SOA Volatility and Temperature



White: 298 K, Red: 273 K and Black: 243 K

Decreased reaction temperature → more volatile SOA

Source: Jonsson et al 2007 (JAS)

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SOA Formation Temperature

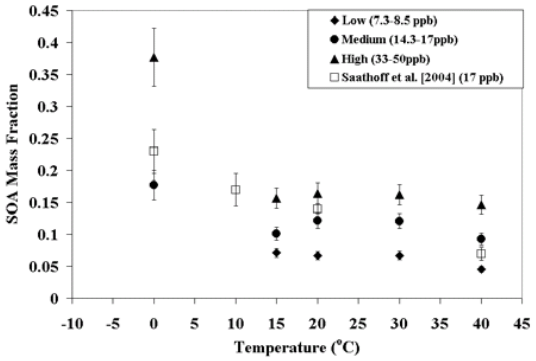

Figure 9. Comparison of the secondary organic AMFs for low, medium and high concentrations of α-pinene at 0° ± 5°C, 15° ± 0.5°C, 20° ± 0.5°C, 30° ± 0.5°C and 40° ± 0.5°C. The results of *Saathoff et al.* [2004] are also shown.

Source: Pathak et al 2007 JGR

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SOA Formation Temperature

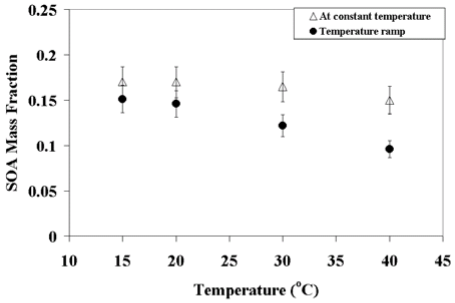

Figure 11. Comparison of α-pinene secondary organic average AMF measured for 38.3 ± 1.5 ppb α-pinene and 250 ppb ozone concentrations at constant temperature and secondary organic AMFs which were first obtained at 15°C and then later temperature ramp was carried out and secondary organic AMF were obtained at to 20°C, 30°C and 40°C.

Source: Pathak et al 2007 JGR

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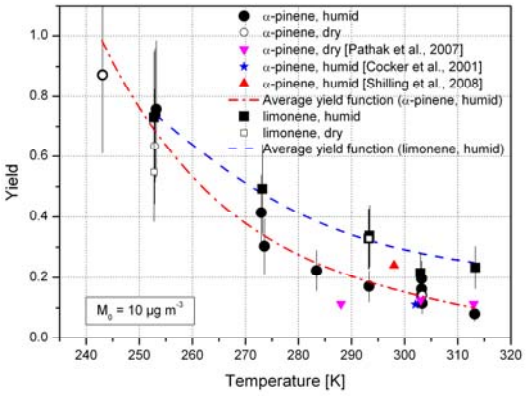
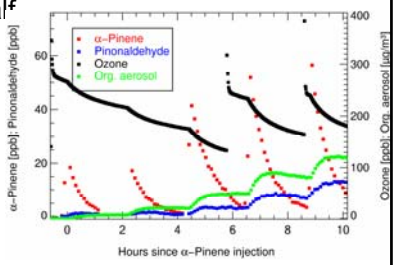
SOA Formation Temperature



Source: Saathoff et al 2008

Ozonolysis mechanism

- The observed influence on the chemical mechanism was supported by direct measurements. Done by Ralf Tillman, Astrid Kiendler-Scharr, Thomas F. Mentel
  - Pinonaldehyde, major product from α-pinene ozonolysis
    - Increased yield at high RH and partitioning significantly at low T
  - OH-radical production
    - Increased yield of OH-scavenger products at high RH
    - Still measure OH-scavenger products at low temperatures



Source: Tillman et al 2008

Conclusions

- The scavenger effect for endocyclic terpenes *no OH-s > 2-butanol > cyclohexane.* The concentration of the scavenger important. Important to select your system!
- OH chemistry still present at 243 K
- The HO_2/RO_2 ratio, important for SOA formation
- SOA mass is increasing with elevated RH, whereas SOA number (nucleation) varies with terpene/scavenger system

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- Donation of the climate chamber by SAAB Tech