UNIVERSITY OF GOTHENBURG

SOA Formation from the Ozonolysis of Limonene, Δ^3-Carene and α-Pinene

-Influence of temperature and water

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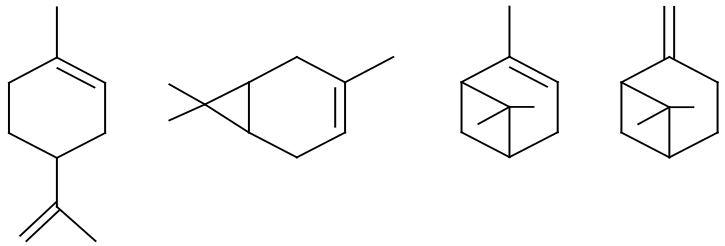
Secondary Organic Aerosol (SOA) Formation

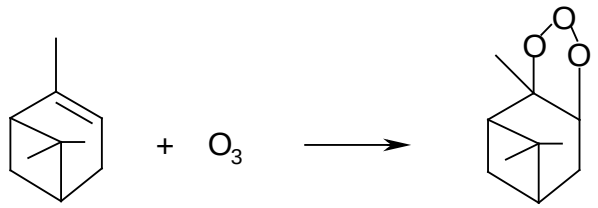
- Gas-to-particle conversion
  - nucleation
  - condensation
  - gas-to-particle partitioning

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

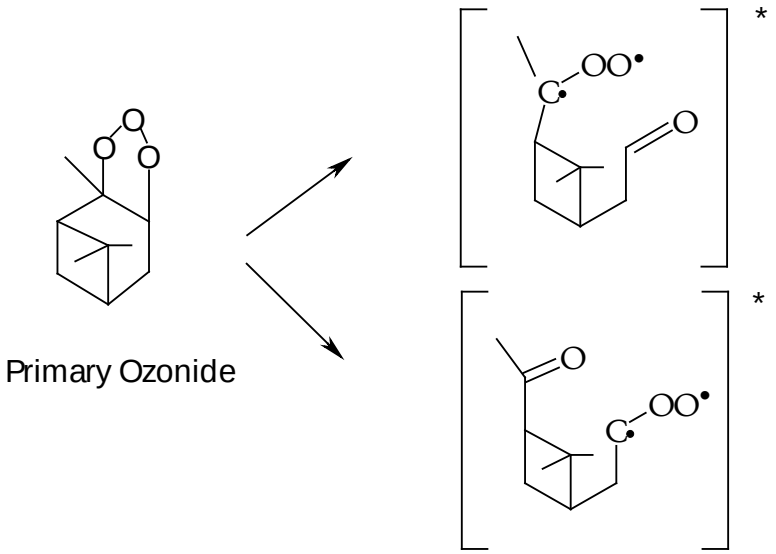


Ozonolysis

- In the reaction with ozone an ozonide is initially formed



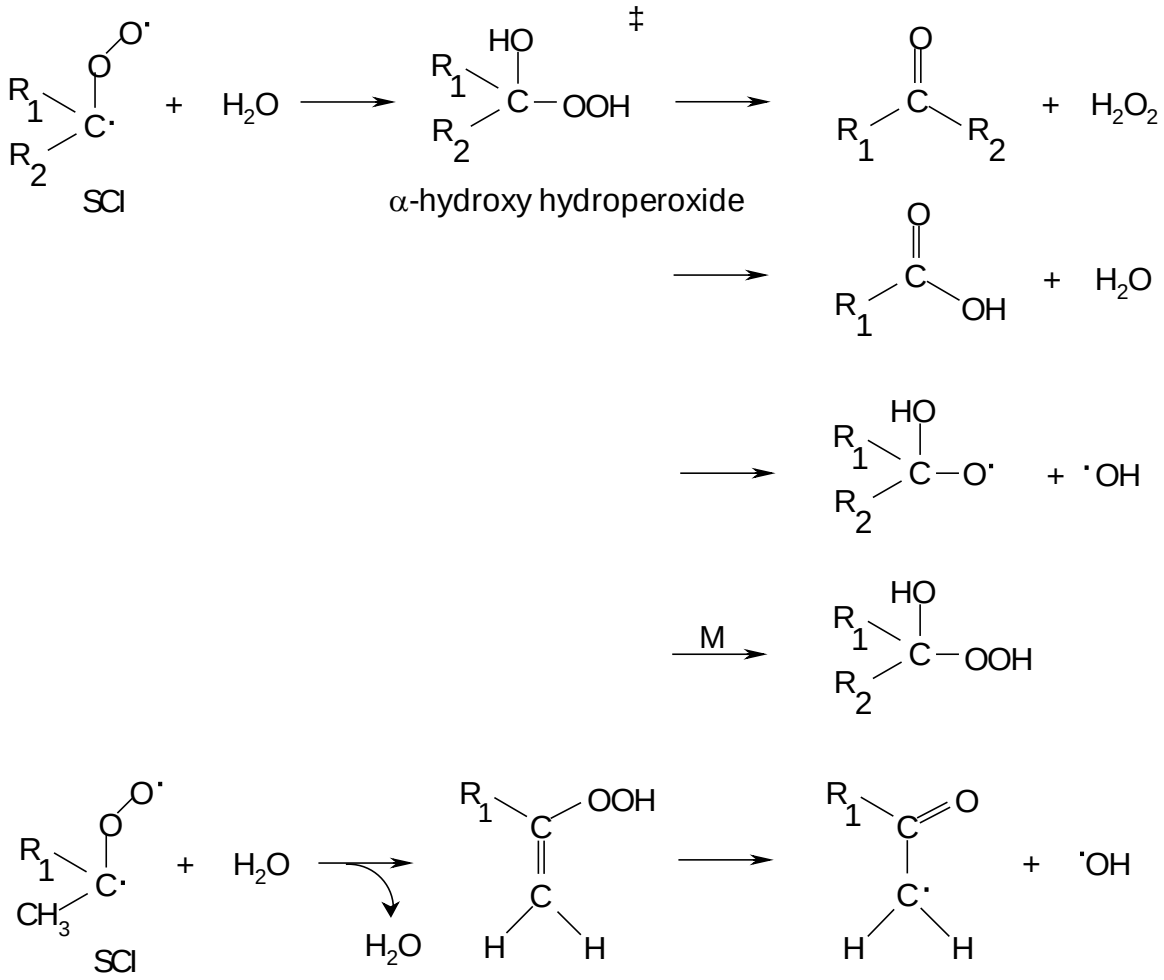
- This ozonide is energy rich and decomposes into carbonyls and biradicals, *i.e.* Criegee Intermediates



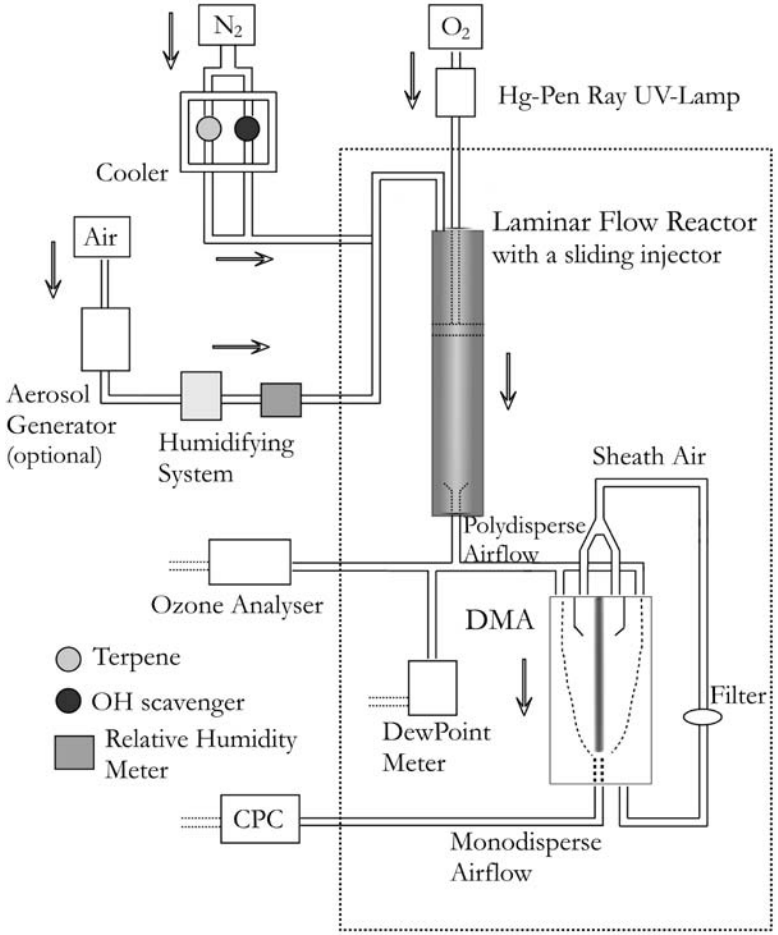
Ozonolysis

- 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

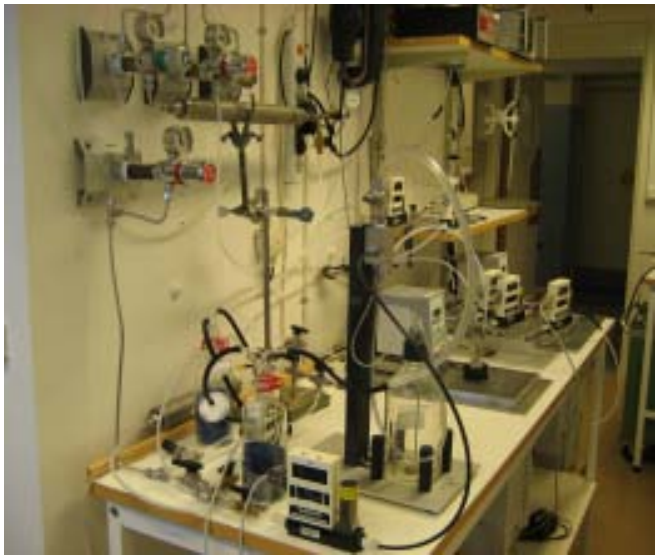
Ozonolysis



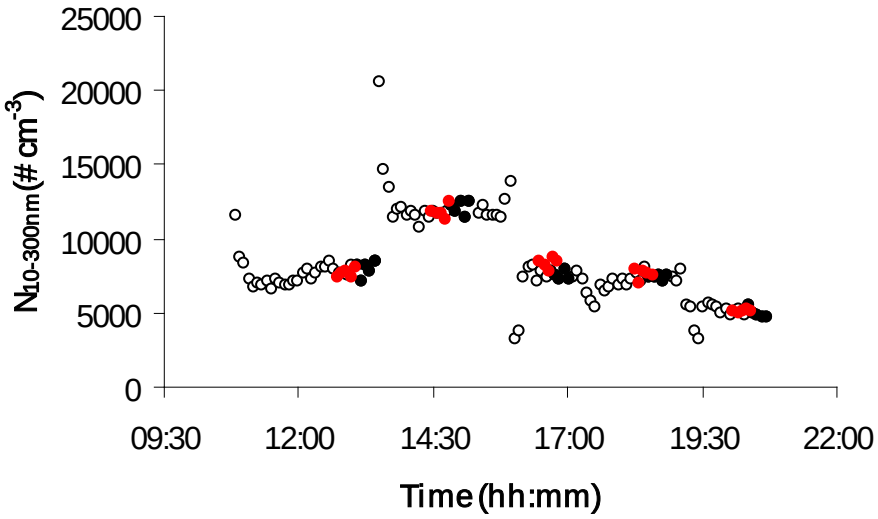
G-FROST

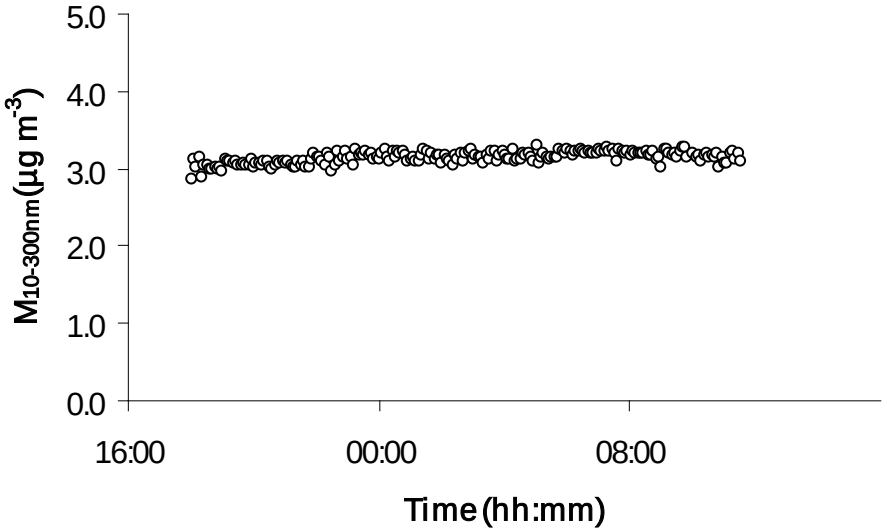


Temperature 243-323 K (-30-50°C)
Relative Humidity, RH ~0-80%
Reaction times 40-500 s



G-FROST

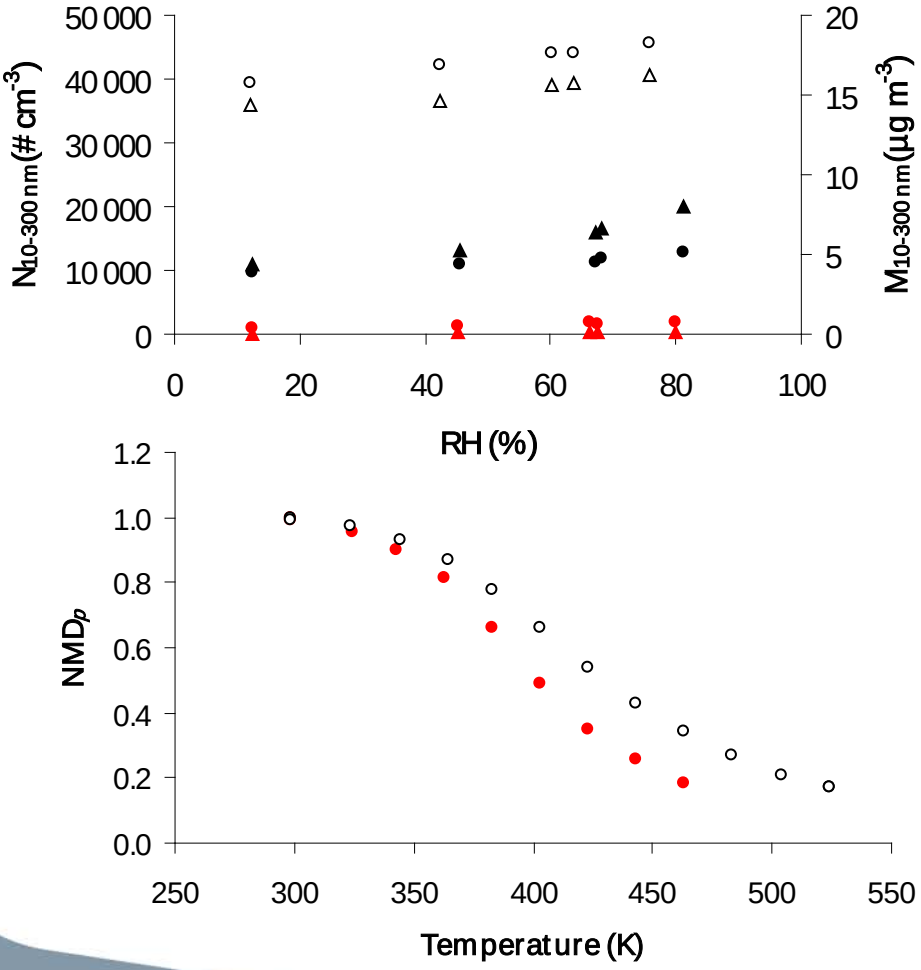




Reproducibility of SOA formed
Exp.run#1 black, run#2 red
RH changed stepwise

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

SOA Formation



Circles: number
Triangles: mass

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

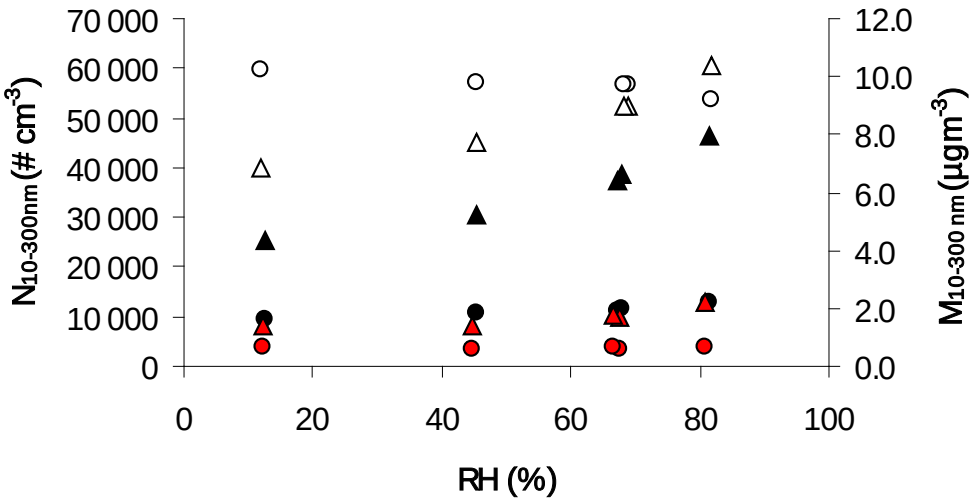
White: limonene
Red: α-Pinene

Static chamber-AIDA

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

Experimental

SOA Formation and Scavenger



298 K

○ : number

△ : mass

White: no OH-s

Black: 2-butanol

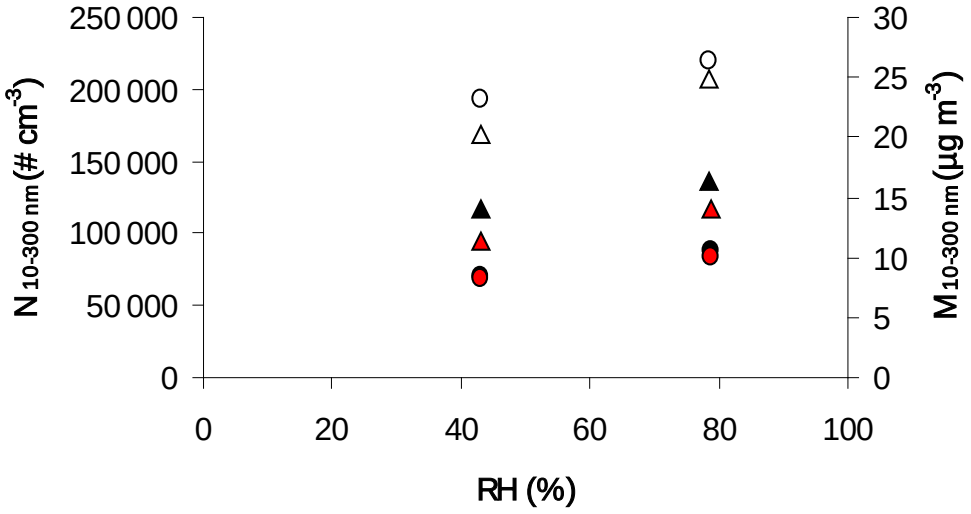
Red: cyclohexane

Number and mass

No OH-s > 2-b > cyclohexane

Source: Jonsson et al 2008 (ES&T)

SOA Formation and Scavenger



243 K

○ : number

△ : mass

White: no OH-s

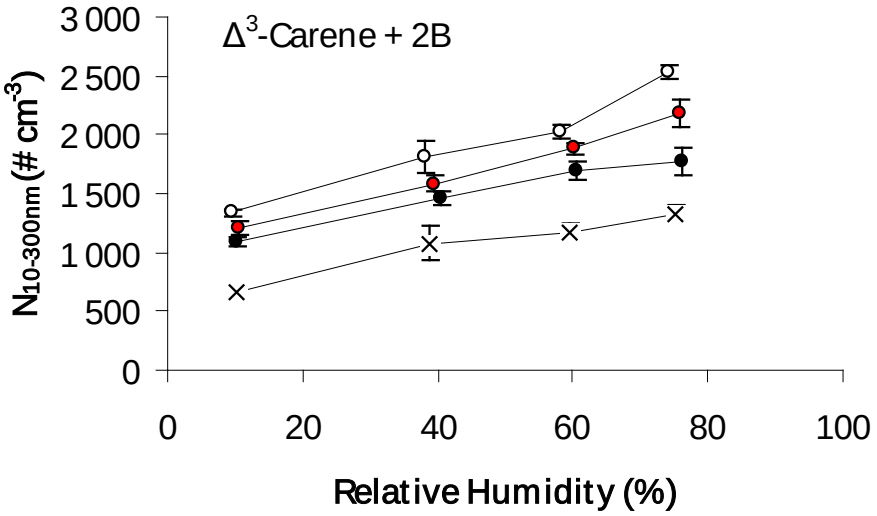
Black: 2-butanol

Red: cyclohexane

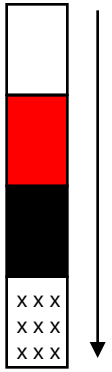
OH chemistry is influencing
the SOA formation even at low temperature

Source: Jonsson et al 2008 (ACPD)

SOA Formation and Scavenger



[2-Butanol]



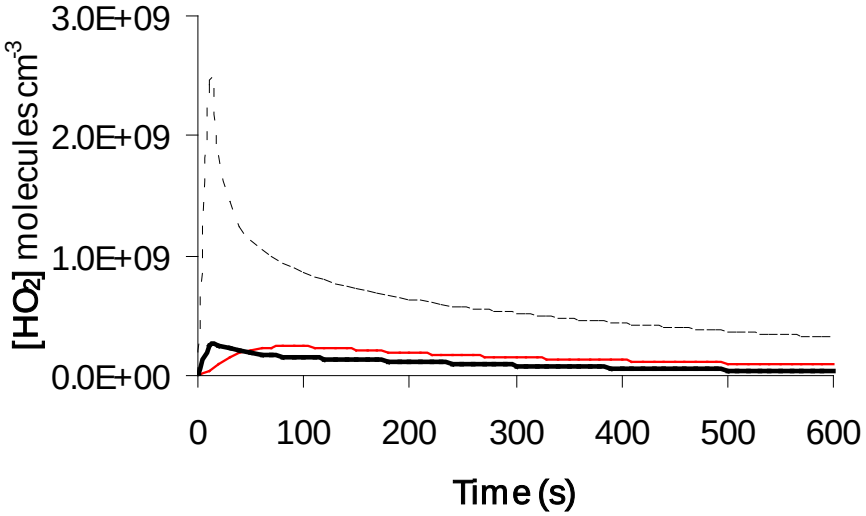
3.5 x 10^{13} molecules cm^{-3}

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

Source: Jonsson et al 2008 (ES&T)

Experimental

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)

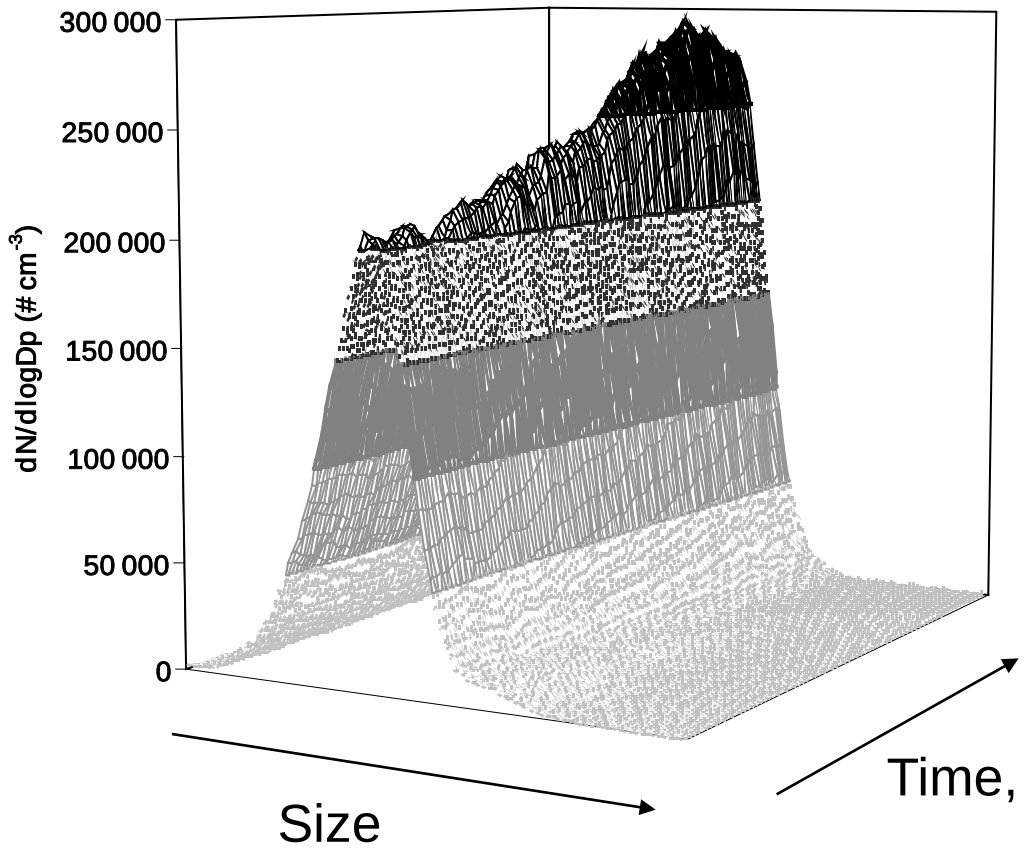
SOA Formation and Scavenger

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)

SOA Formation RH

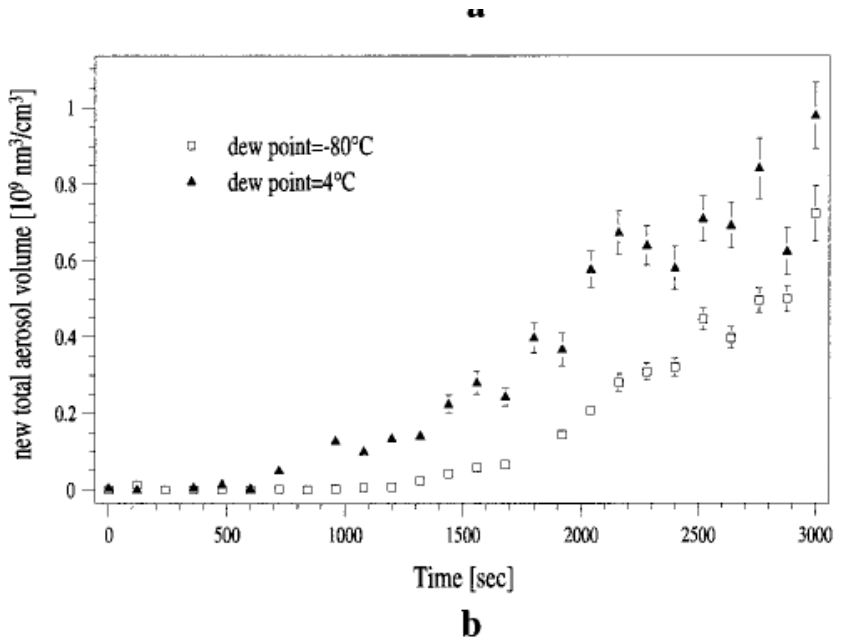


Figure 5. Influence of water vapor on (a) the aerosol number concentration and (b) the total aerosol volume formed in α-pinene ozonolysis at low concentrations (spherical reactor).

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

Experimental

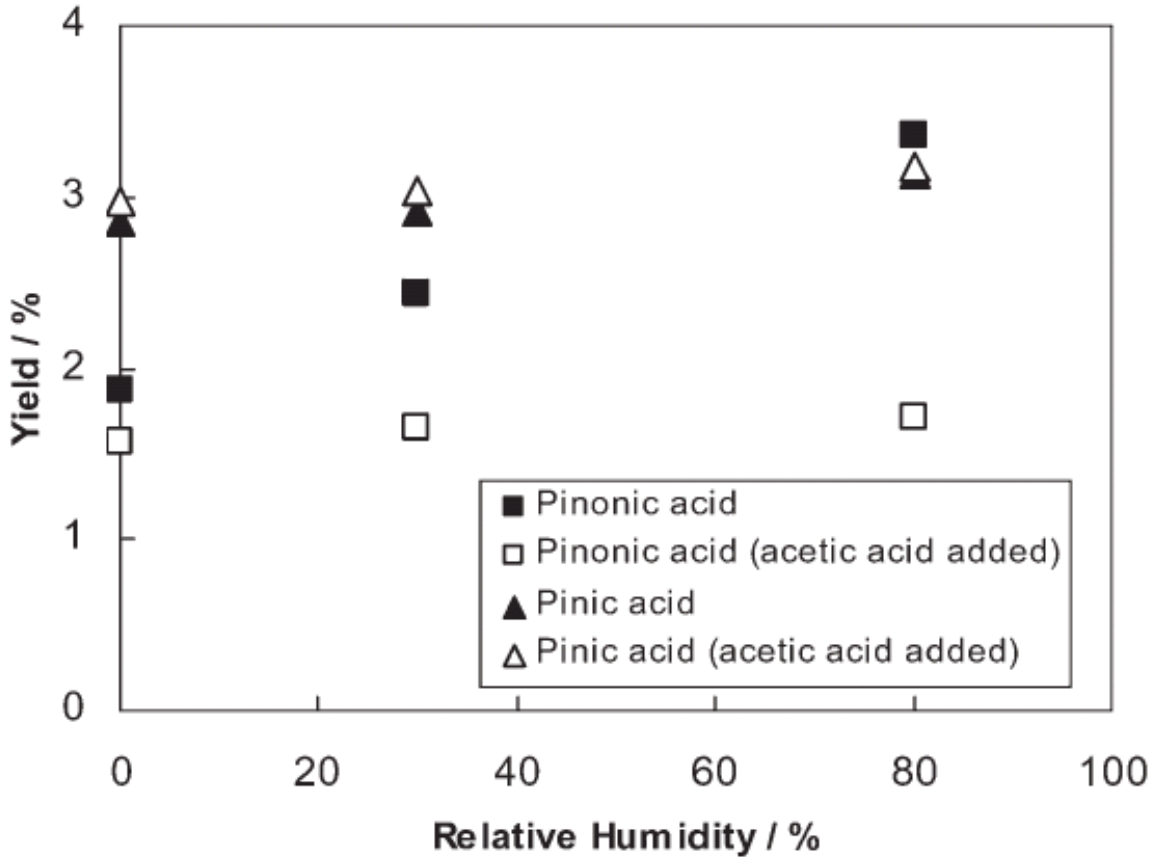


Fig. 1 Acid yields from the ozonolysis of α-pinene under various conditions.

Source: Ma et al 2007

Experimental

Conclusions

- **Scavenger effect**

  For endocyclic terpenes *no OH-s > 2-butanol > cyclohexane.*

  The concentration of the scavenger important. Important to select your system!

  The HO_2/RO_2 ratio, important for SOA formation

- **Water effect**

  SOA mass is increasing with elevated RH, whereas SOA number (nucleation) varies with terpene/scavenger system

- **Low temperature experiments**

  RH and scavenger still effect SOA formation

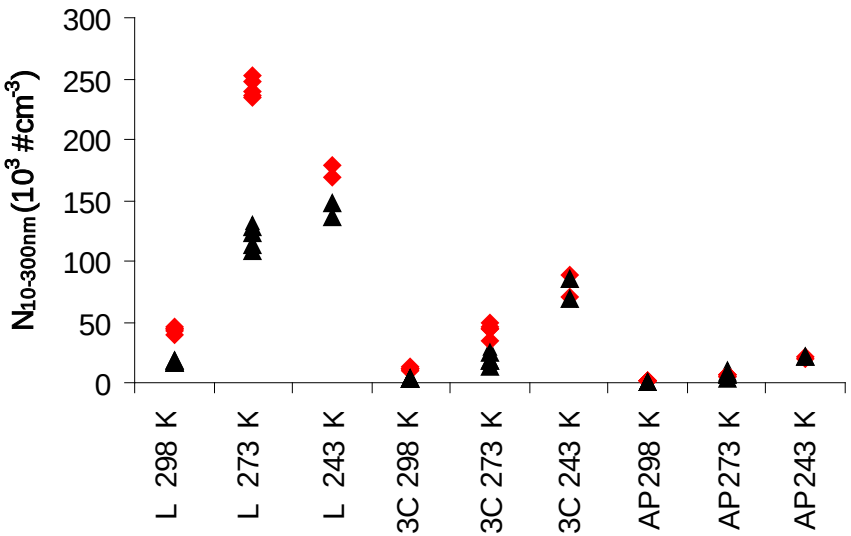
  OH chemistry still present at 243 K

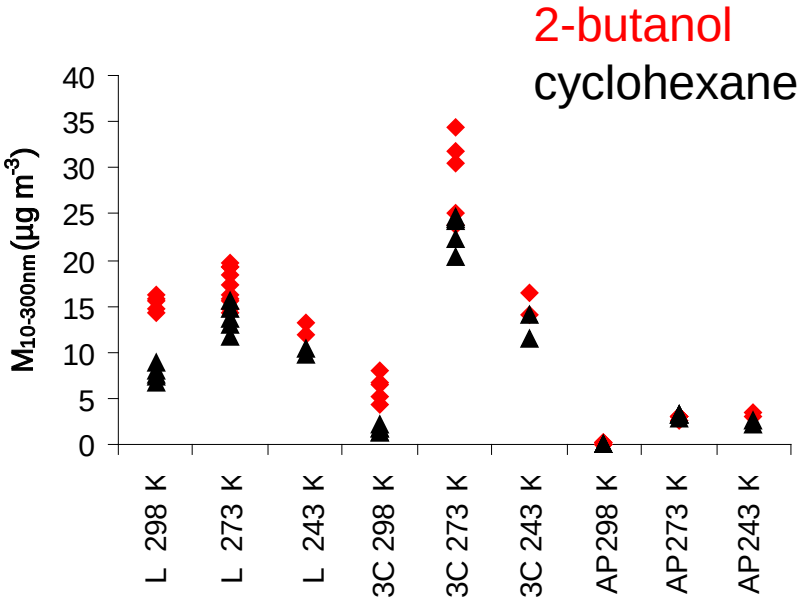
Acknowledgement

- Technical and Administrative support
- Financial support (Travelling grants from ICCPA, MISTRA, FORMAS, Climate and Mobility GU, VR)
- Donation of the climate chamber, SaabTech

SOA Formation and Temperature

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



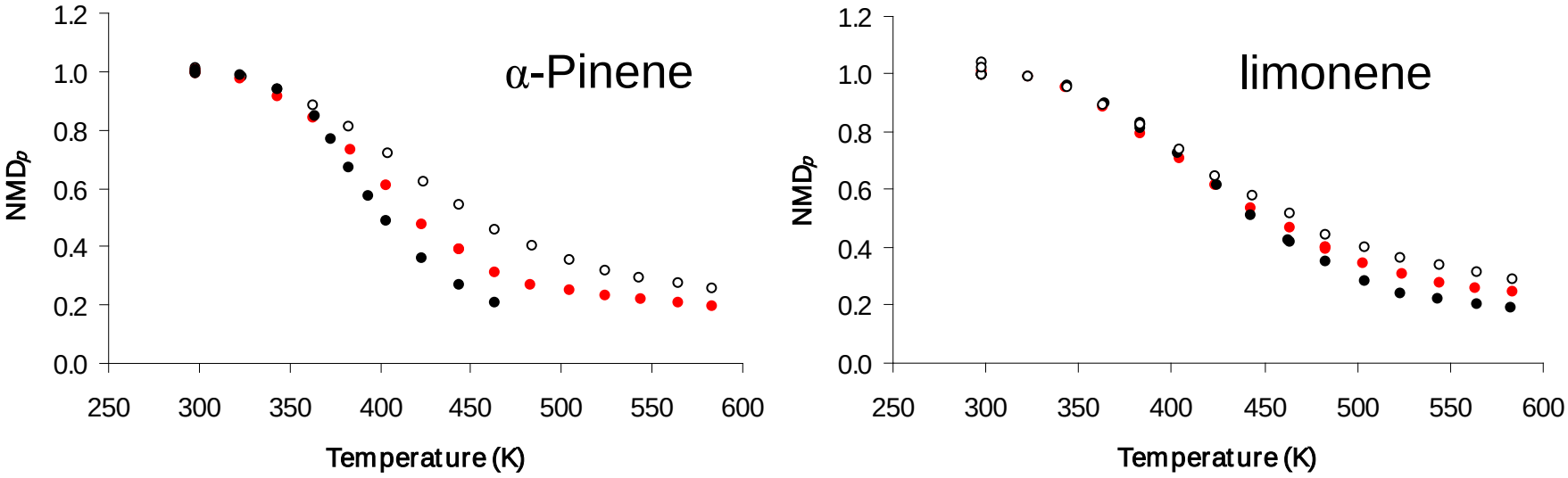


Experimental

Degradation of Unsaturated Compounds

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

SOA Volatility and Temperature

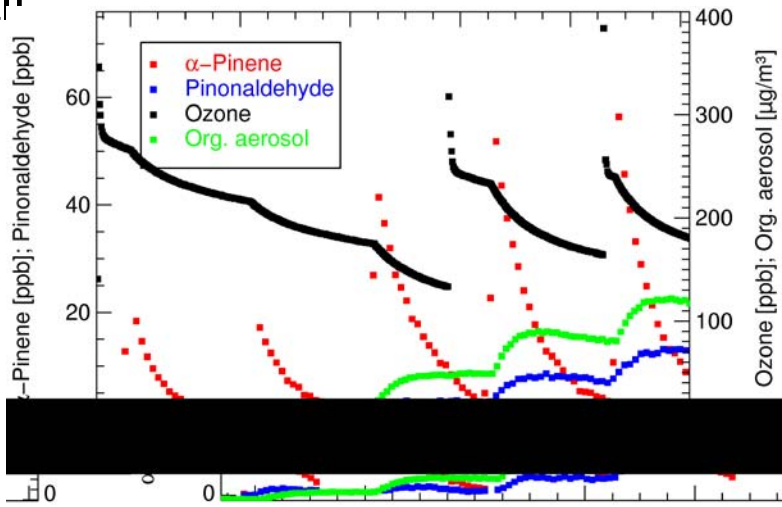


White: 298 K, Red: 273 K and Black: 243 K

Decreased reaction temperature → more volatile SOA

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



Atmospheric Science, Department of Chemistry, GU

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

- Personnel
  - 4 Faculty members (Professors Pettersson and Ljungström, Associate Professors Boman, and Hallquist), 13 PhD-students, 4 postdocs, 2 assistant professors, 2 technicians
  - Modelling joint projects with Dr David Simpson, e.g. Robert Bergström, Cornelia Richter, Dr Schultz Martin
- Part of GAC-Gothenburg Atmospheric Science Centre
  - www.chalmers.se/gmv/gac

Selected projects

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)

Flux measurements (Terpenes, particles)

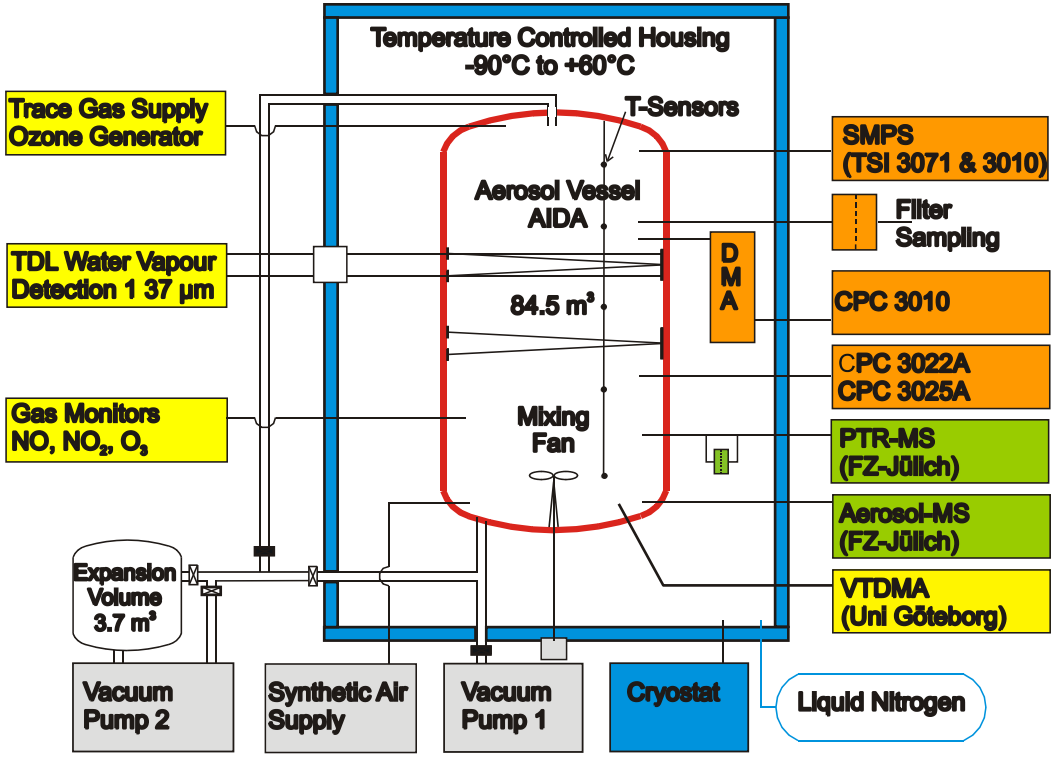
Todays topic: SOA

- Formation (dependence on humidity and Temperature)
- Properties (volatility)

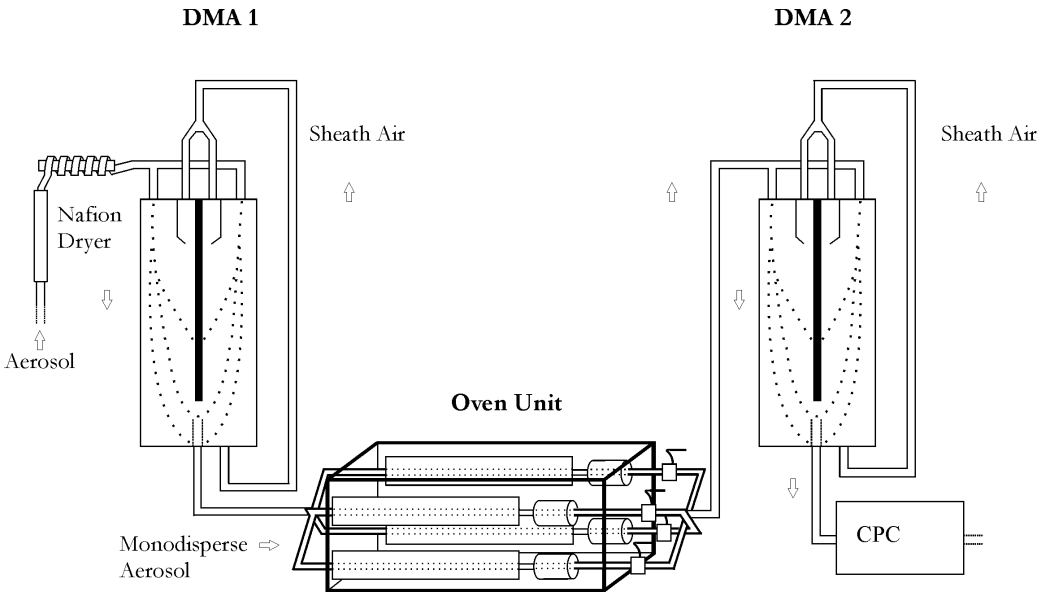
AIDA-Karlsruhe

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

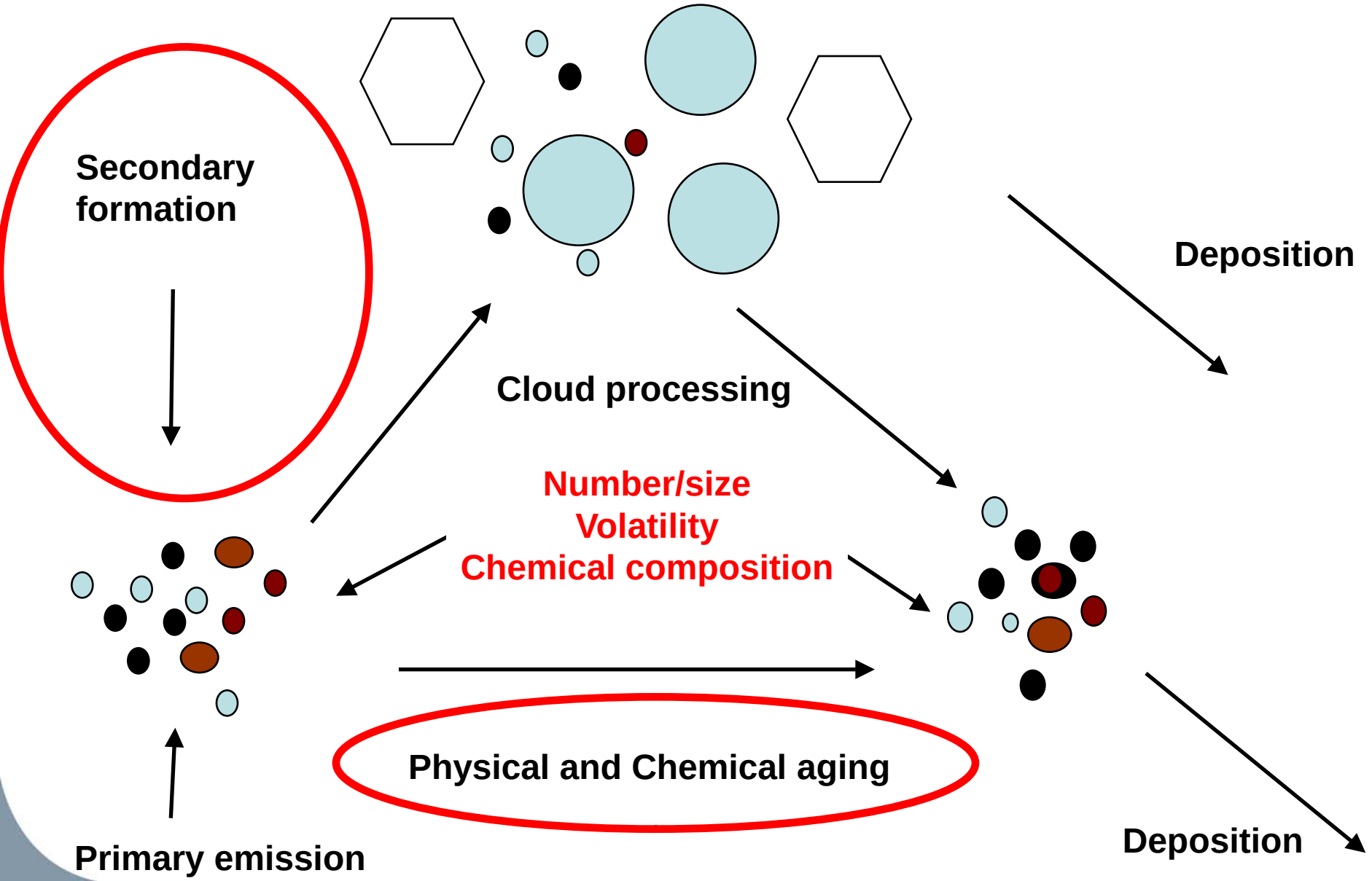
Focus: Volatility



VTDMA (Volatility)



Experimental


Secondary formation
Deposition
Cloud processing
Number/size
Volatility
Chemical composition
Physical and Chemical aging
Primary emission
Deposition

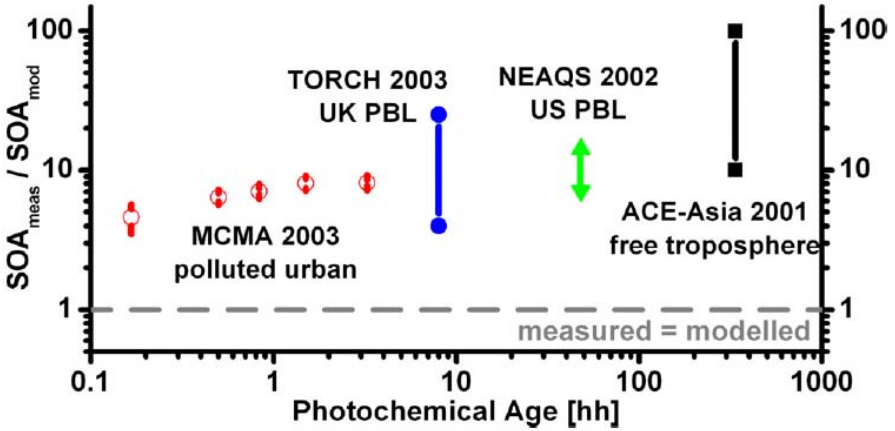
SOA in the Atmosphere

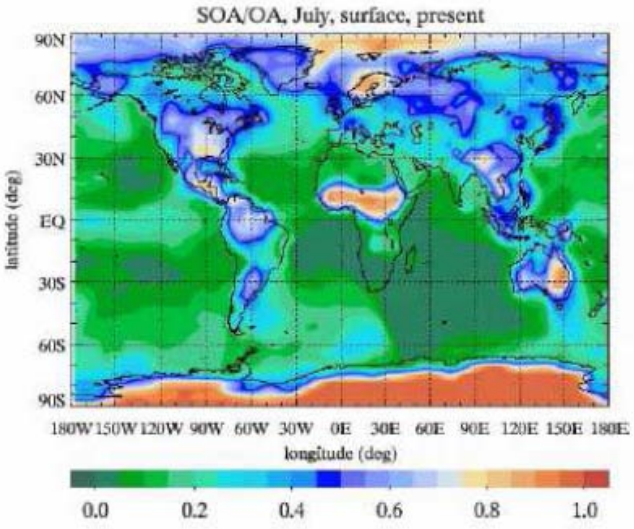
Models generally underestimates SOA formation (Volkamer et al. 2006→)

Global formation, uncertain but estimated to 12-72 Tg/year (Kanakidou et al 2005)

Estimates! Based on rather chemically simplified models, e.g. mostly α-pinene degradation

However , it is clear that SOA can dominate the OC fraction and that biogenic precursor gives significant input





Experimental

SOA Formation RH

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

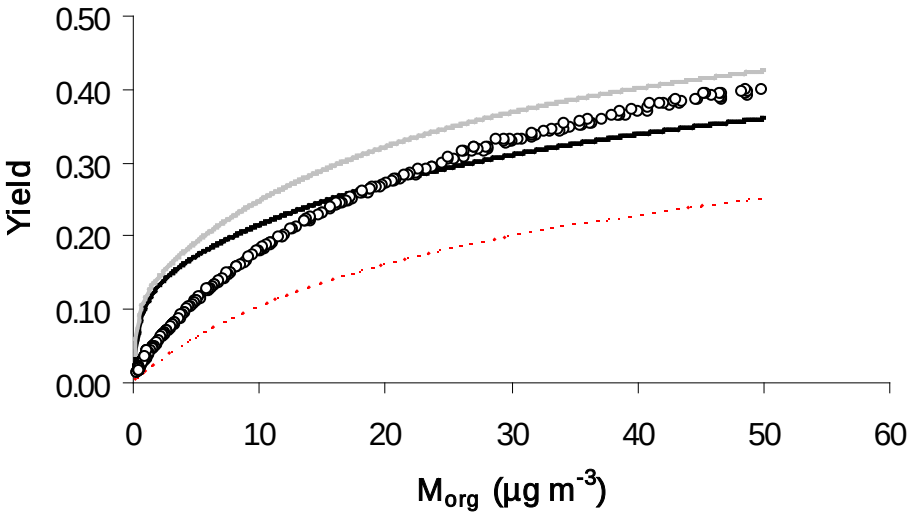
org. precursor (ppb)[b]	type of study	OH scavenger	temp (K)	RH (%)	M_{tot}[c]	N_{tot}[c]	source
L (1000)	static reactor	cyclohexane	295 ± 2	0.01 & 31	no effect	−	Bonn et al. (*9*)
L (19.5 ± 1.2)	flow reactor	n.s	295 ± 2	15, 30 & 43	no effect	no effect	Fick et al. (*18*)
L (15 & 30)	flow reactor	2-butanol	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 ES&T

Experimental

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)