Temperature dependence of secondary organic aerosol yield from the ozonolysis of monoterpenes

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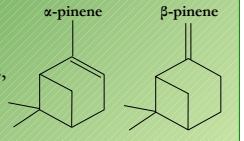
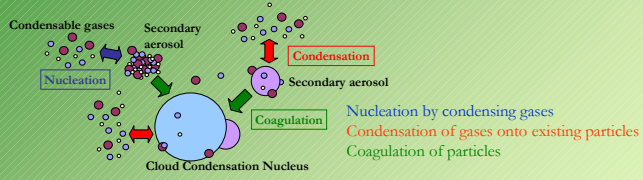
Introduction

Biogenic volatile organic compounds (BVOCs) such as monoterpenes are emitted in significant amounts by vegetation, especially in forests. They are oxidized primarily by O_3, OH and NO_3 radicals, and some of their oxidation products play an important role in the growth of secondary organic aerosol (SOA).

α-pinene β-pinene



Formation of secondary particle:

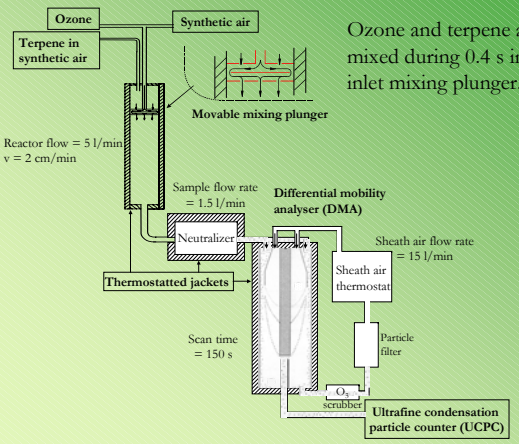


Temperature affects the formation of condensable gases, as well as nucleation and condensation. It has been shown to be anticorrelated with SOA yields and is one of the most important factors in SOA formation (Takekawa *et al.*, 2003).

In this study we measure the temperature dependence of SOA-yields and particle size distributions from the reaction of ozone with the monoterpenes α-pinene and β-pinene.

Laboratory study of temperature dependence

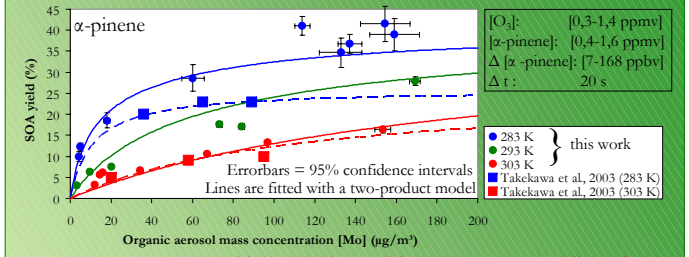
Experiments were performed in a flow reactor connected to a scanning mobility particle sizer (SMPS) system (long DMA and UCPC):



Ozone and terpene are totally mixed during 0.4 s in the movable inlet mixing plunger.

Results

Yield as a function of organic aerosol mass at three temperatures:



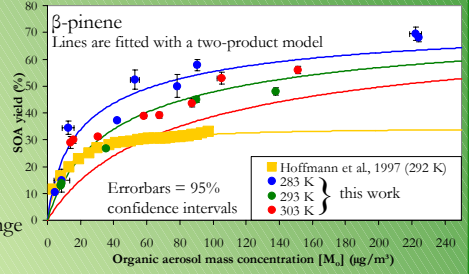
Lower temperature ➡ higher yield ΔT = -20 K ➡ Doubling of yield!

Yields are higher than reported by Takekawa *et al.* (2003) (chamber setup).

[O3]: [0,9-2,5 ppmv]
[β-pinene]: [1,0-2,6 ppmv]
Δ [β-pinene]: [7-59 ppbv]
Δ t : 20 s

293 K→ 283 K
➡ higher yields

303 K→ 293 K
➡ no significant change



Yields are higher than reported by Hoffmann *et al.* (1997) (chamber setup).

Yields are calculated from the measurements and used to fit a two-product model (Odum *et al.*, 1996):

$$Yield = \frac{[SOA](\mu g/m^3)}{\Delta[terpene](\mu g/m^3)} = M_o\left(\frac{\alpha_1 * K_{om,1}}{1+K_{om,1} * M_o} + \frac{\alpha_2 * K_{om,2}}{1+K_{om,2} * M_o}\right)$$

$$[SOA] = \varrho * V_{aerosol} \qquad \varrho = 1 g * cm^{-3}$$

$$\Delta[terpene] = [terpene]_0 * \left(1 - e^{-k[O_3]_0 \Delta t}\right)$$

M_o = organic aerosol mass
$K_{om,i}$ = partitioning coefficient
α_i = stoichiometric coefficient
$B_i = \Delta H_{vap,i}/R$

Temperature dependence of the reaction constant for ozonolysis:

	k (cm^3*$molec^{-1}$*sec^{-1})	
T	α-pinene	β-pinene
283 K	$7{,}7*10^{-17}$	$1{,}2*10^{-17}$
293 K	$8{,}2*10^{-17}$	$1{,}4*10^{-17}$
303 K	$8{,}7*10^{-17}$	$1{,}6*10^{-17}$

(Atkinson and Arey, 2003)

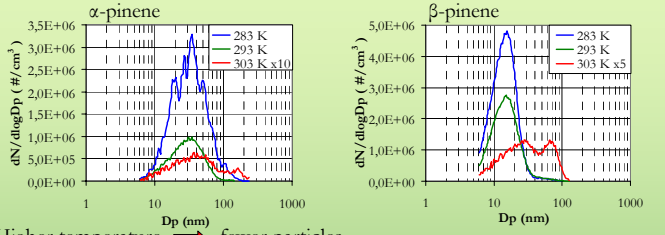
α_i is assumed to be constant, but $K_{om,i}$ is expected to be temperature dependent:

$$K_{om,i} = K_{om,i,303K} \frac{T}{303K} \exp\left[B_i\left(\frac{1}{T} - \frac{1}{303K}\right)\right]$$

(Sheehan and Bowman, 2001)

Results

Particle size distributions as a function of temperature:

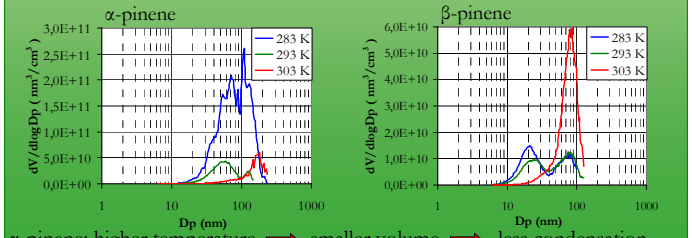


Higher temperature ➡ fewer particles
➡ less nucleation.

	Δα-pinene	Δβ-pinene
283 K	278 µg/m³	59 µg/m³
293 K	270 µg/m³	61 µg/m³
303 K	252 µg/m³	52 µg/m³

α-pinene vs. β-pinene: much fewer but larger particles
➡ less nucleation and larger growth
➡ less low volatile products.

Particle volume distributions as a function of temperature:



α-pinene: higher temperature ➡ smaller volume ➡ less condensation.
β-pinene: 303 K high proportion of large particles (more effectively detected).

Questions and ideas

Q1: Is the calculation of Δterpene a major source of uncertainty?
I1: Experiments with low $[O_3]$; $\Delta[terpene] = [O_3]_0$

Q2: Is the large surface (many and small particles) resulting in too large yields?
I2: Add seed-aerosol to the system.

Q3: Are there any effects from the walls in the flow reactor?
I3: Experiments with the same amount of reacted terpene with different inlet heights.

Ideas for the future: other terpenes, CCN properties of particles partitioning coefficients of products.

References

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Hoffmann, T., *et al.* **1997**. *Journal of Atmospheric Chemistry* (26) 189-222
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