Secondary organic aerosol formation and chemical composition

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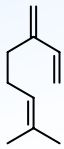
Introduction

This work is focused on the atmospheric degradation of biogenic acyclic VOCs. Myrcene (7-methyl-3-methylene-1,6-octadiene) has been chosen as initial species in the study of a series of biogenic monoterpenes including linalool and ocimene as well as larger compounds such as acyclic sesquiterpenes (α-farnesene, β-farnesene, (*E*)-4,8-dimethyl-1,3,7-nonatriene (DMNT), …). Myrcene is very reactive with the major atmospheric oxidants (OH, NO_3 and O_3) and its oxidation contributes to Secondary Organic Aerosol (SOA) formation.

Up to now, most of the studies have been performed in the presence of inorganic seed aerosol that favours condensation [1-3], and the chemical composition of the condensed phase has not been investigated so far.

Here is presented preliminary results performed in atmospheric simulation chambers (Orleans and Valencia) and in a aerosol flow reactor (Orleans). SOA formation has been studied in both systems and results on chemical composition of SOA is presented.



Atmospheric simulation chambers (SOA formation = f(t))

ICARE, Orleans
(7,3 m³, indoor chamber)

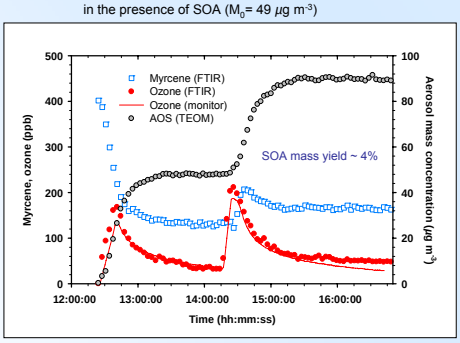
- **Gas-phase characterization:**
  FTIR, ozone monitor, P, T and RH
- **Particulate phase characterization:**
  ICARE: SMPS
  EUPHORE: TEOM, SMPS, GC-MS

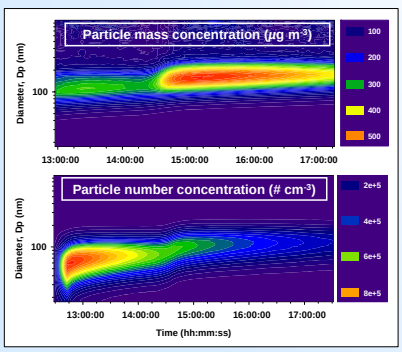
EUPHORE, Valencia
(204,5 m³, outdoor chamber)

Results

Ozonolysis of myrcene performed at the EUPHORE

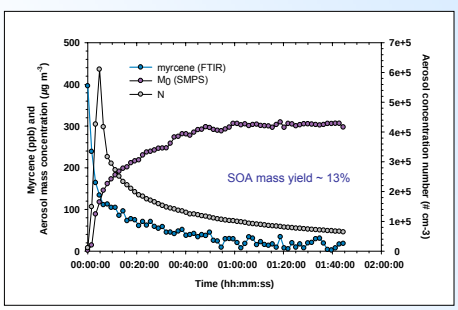
1st injection: Myrcene (402 ppb), Ozone (168 ppb) and cylohexane (used as OH scavenger)
2nd injection: myrcene (126 ppb), ozone (180 ppb)
in the presence of SOA (M_0= 49 μg m^{-3})

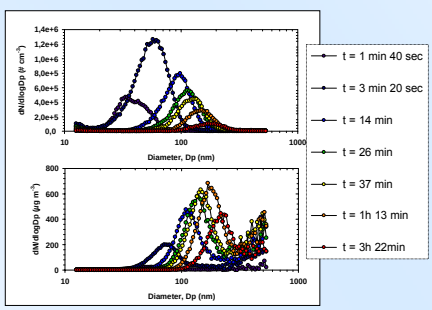




Ozonolysis of myrcene performed at the ICARE

Myrcene (400 ppb), Ozone (1500 ppb) – no OH scavenger used (SMPS: 12 < Dp < 533 nm)



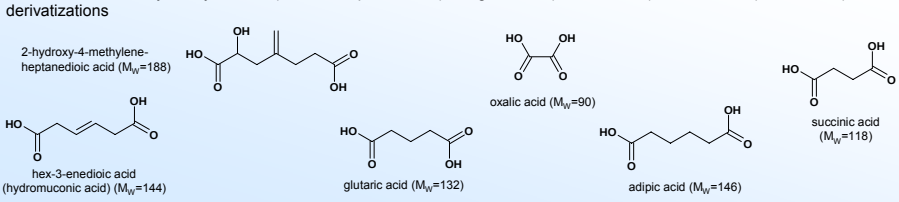


For particle number distribution, $Dp_{mode,\ max}$ = 57nm
For particle mass distribution, $Dp_{mode,max}$ = 168 nm

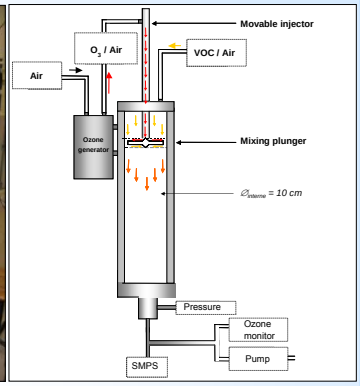
What could be the influence of OH and criegee scavengers on the SOA formation diameter?

Chemical composition of SOA from the ozonolysis of myrcene

SOA filters were analyzed by GC-MS (electron impact: 70 eV) using PFBHA (C=O function) and MSTFA (OH function) derivatizations



Aerosol flow reactor (SOA formation at t < 1min)



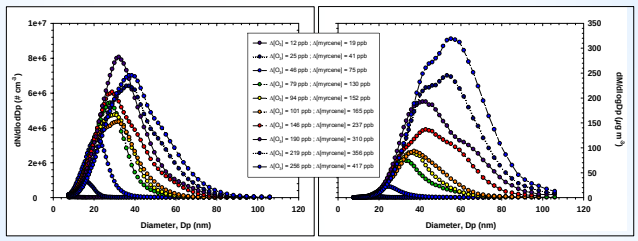
- [myrcene]$_0$ = 500 – 1000 ppb
- [ozone]$_0$ = 100-1600 ppb
- P=(760 ± 1)Torr ; T =(297 ± 2)K
- Reaction time t: 38 s
- Total flow: 4,6 ± 0,5 L min^{-1}
- $V_{Average}$ = 1,1 ± 0,1 cm s^{-1} ⇨ Re = 60 (laminar flow)

Ozone concentration decay in function of time have been deduced assuming a 2nd order reaction and OH formation from the ozonolysis reaction has been taken account according to:

$$\Delta[O_3] = \frac{[\text{Myrcene}]_0\left[1-\exp\left[\left([\text{Myrcene}]_0-[O_3]_0\right)k_{\text{Myrcene}}t\right]\right]}{\left[1-\frac{[\text{Myrcene}]_0}{[O_3]_0}\exp\left[\left([\text{Myrcene}]_0-[O_3]_0\right)k_{\text{Myrcene}}t\right]\right]} \quad \text{and} \quad \Delta[\text{Myrcene}] = (1+\alpha_{OH})\times\Delta[O_3]$$

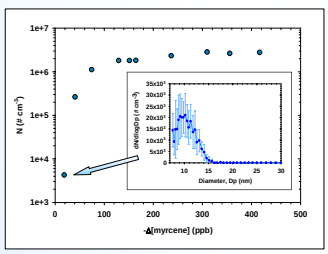
With α_{OH}: OH formation yield from the O_3 reaction with myrcene (α_{OH}=63% [4])
$k_{myrcene}$: rate constant of the O_3 reaction with myrcene ($k_{myrcene}$=(4.3 ± 0.4)×10^{-16} cm^3 molecule^{-1} s^{-1} at 298 K [this work])

Results



Nucleation threshold

Defines as the minimum amount of compound in order to initiate the formation of the first particles.



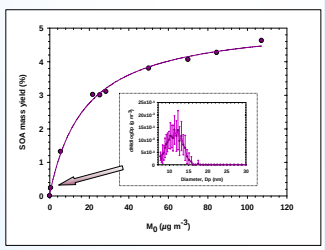
For this work, nucleation threshold has been estimated to 19 ± 2 ppb for detectable particles having a diameter Dp > 7 nm.

SOA yield

SOA mass yield has been calculated as follows :

$$Y = \frac{\Delta M_0}{\Delta HC}$$

With
Y: SOA mass yield
M_0: Mass of particles formed in μg m^{-3}
ΔHC: concentration of myrcene consumed in μg m^{-3}



SOA mass yield reach a maximum around 5% for the ozonolysis of myrcene for particle diameter range: 7 < Dp < 106 nm.

Perspectives

- Influences of temperature and relative humidity on particle nucleation and growth.
- Influences of OH and Criegee scavengers on the SOA formation yield and particle nucleation.

References

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Acknowledgements

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