Formation of organosulfates from the sulfate radical induced oxidation of methacrolein and methyl vinyl ketone

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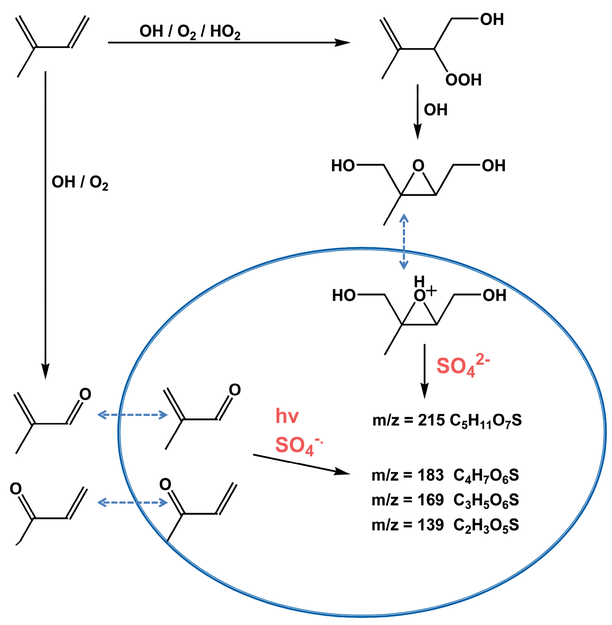
PEGASOS Pan-European Gas-AeroSOls-climate interaction Study

TROPOS Leibniz Institute for Tropospheric Research

Member of the Leibniz Association

Introduction



Organosulfates in ambient aerosols:

- Can add up to 10% to organic mass and 12% to total sulfur concentration[1,2]
- Isoprene-organosulfate m/z 215 is most abundant one
- Masses of C_2 – C_4 organosulfates related to isoprene oxidation products[3,4]

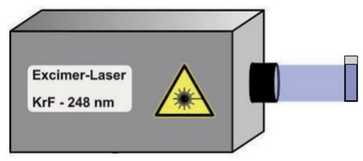
formation

- Partitioning of MACR and MVK into the particle phase
- Reaction with sulfate radicals

Experiments

Bulk phase studies:

- MACR / MVK + SO_4^-
- Radical source: $K_2S_2O_8$
- Photolysis with laser pulses (n = 5, 10 and 20)



Ambient aerosol:

- PM_{10} filter samples
- Seiffen (rural East German Village)
- Po valley (PEGASOS field campaign 2012)

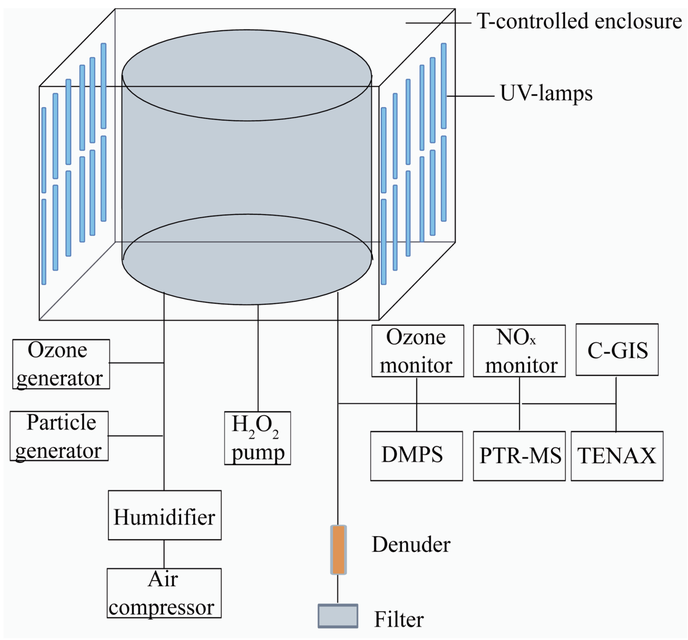
Offline analysis of filter extracts and bulk phase samples:

UPLC-TOF-MS

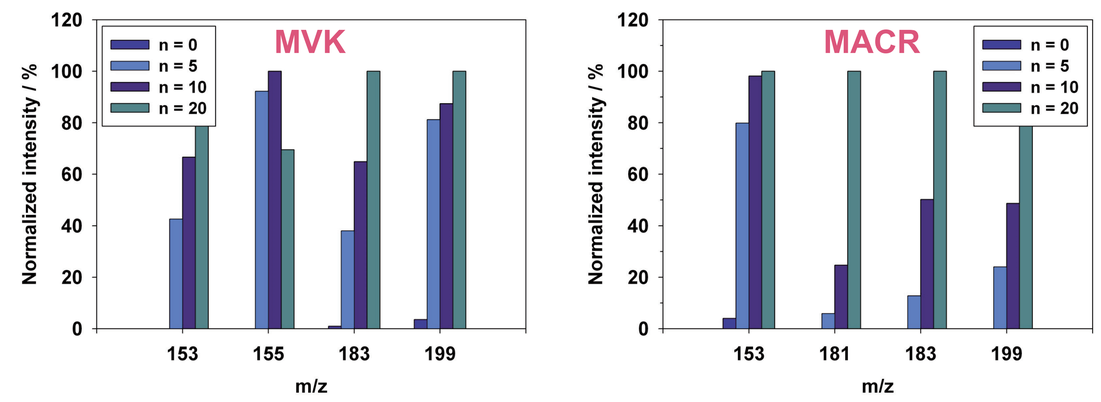
Chamber studies:

- MACR / MVK (1 ppm)
- 16 UV lamps + 8 Hg lamps (254 nm)
- RH 70%
- Seed: ($K_2S_2O_8$/)H_2SO_4
- Setups:
  $K_2S_2O_8/H_2SO_4$ - hν
  H_2SO_4 - hν
  H_2SO_4 - dark

Material: FEP foil
Volume: 19 m^3

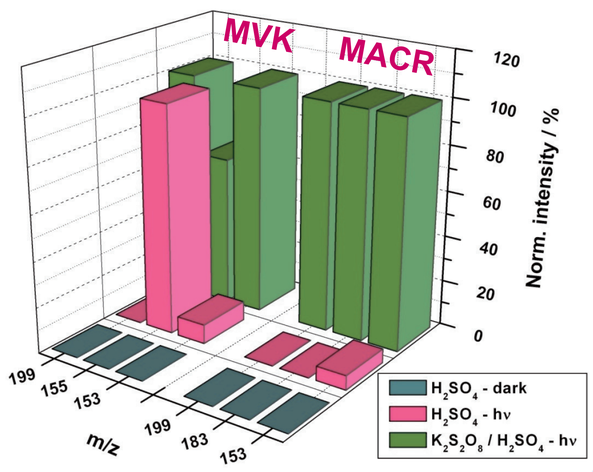


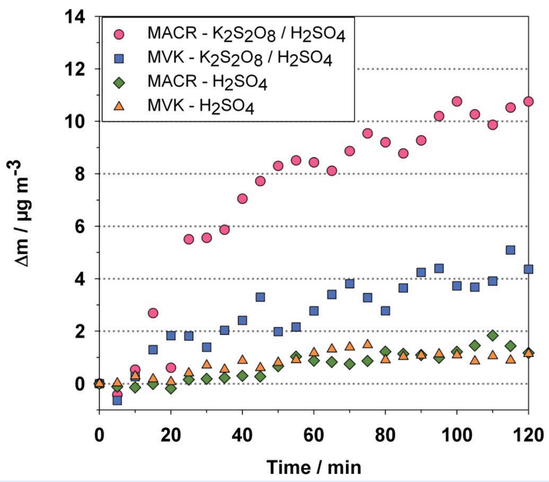
Results



Bulk phase and chamber experiments:

- Monomeric compounds with m/z 153, 155, 183 and 199
- Several isomers (e.g. 6 isomers for m/z 183 from MACR)
- Dimers of C_3 and C_4, e.g. m/z 251 and 253
- Mass increase of 10 and 5 µg m^{-3} for MACR and MVK in chamber experiments

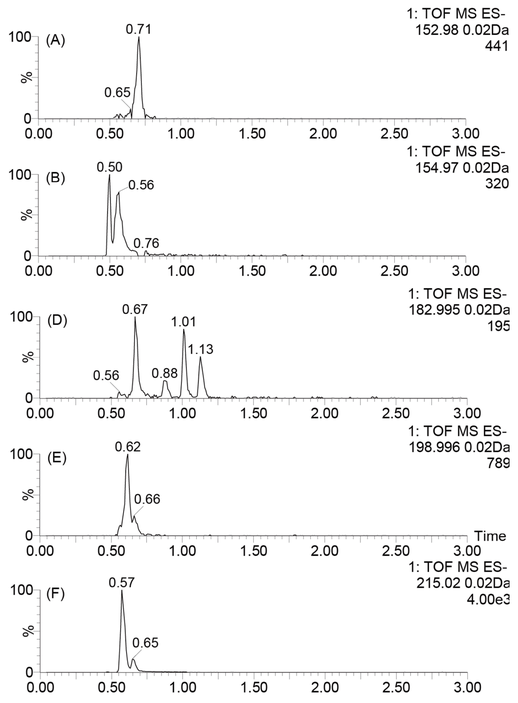




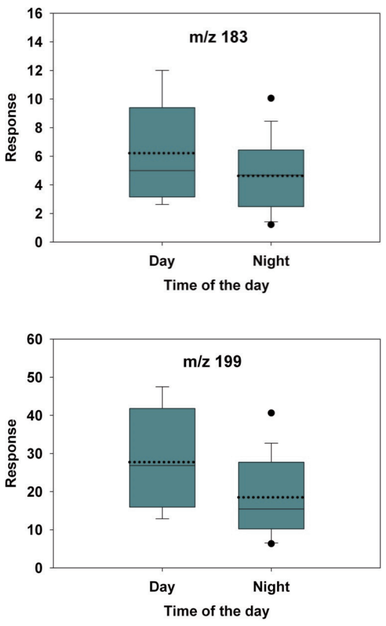
Ambient Aerosol:

- Masses agree with masses detected in lab experiments
- They correlate with each other
- Mean values are higher at day time

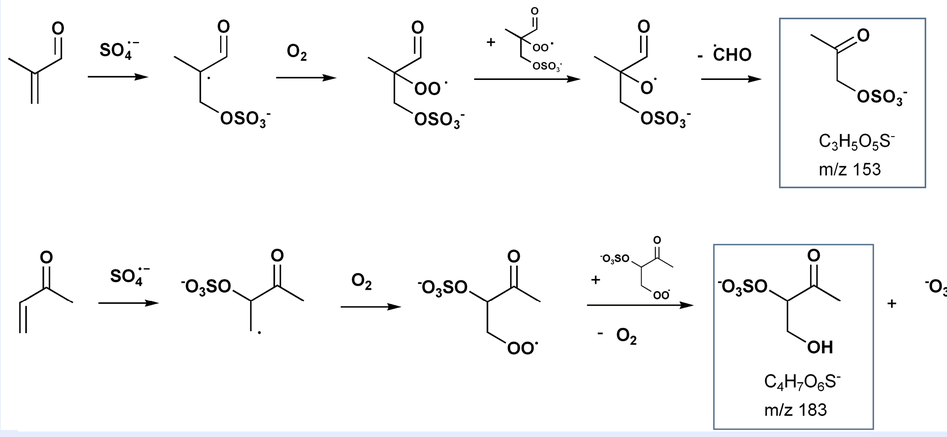
Seiffen (Germany)



San Pietro Capofiume (Italy)

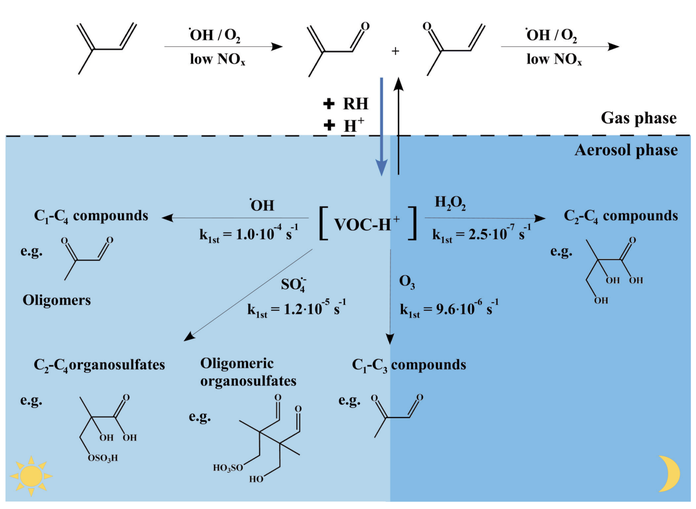


Peroxyl radical mechanism: (examples)



- Addition to double bond
- Peroxyl radical formation
- Tetroxide formation and decay

Atmospheric Implication



Reactivity:

- OH radical reactions are the major sink in the particle phase
- ~ 10% of MACR can react with sulfate radicals

Environmental conditions:

- Presence of SO_2
- Lower temperatures
- High relative humidity

➡ free troposphere
➡ radiation fog

References

1 Tolocka and Turpin, *Environ. Sci. Technol.* (2012), **46**, 7978-7983.
2 Lukács et al., *Atmos. Chem. Phys.* (2009), **9**, 231-238.
3 Froyd et al., *Proc. Natl. Acad. Sci. U. S. A.* (2010), **107**, 21360-21365.
4 Nozière et al., *Geophys. Res. Lett.* (2010), **37**, DOI: 10.1029/2009GL041683.

Acknowledgement

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