Accretion product formation from self- and cross-reactions of RO_2 radicals

$RO_2 + R'O_2 \rightarrow ROOR' + O_2$

Torsten Berndt

Davis, 7.12.2018

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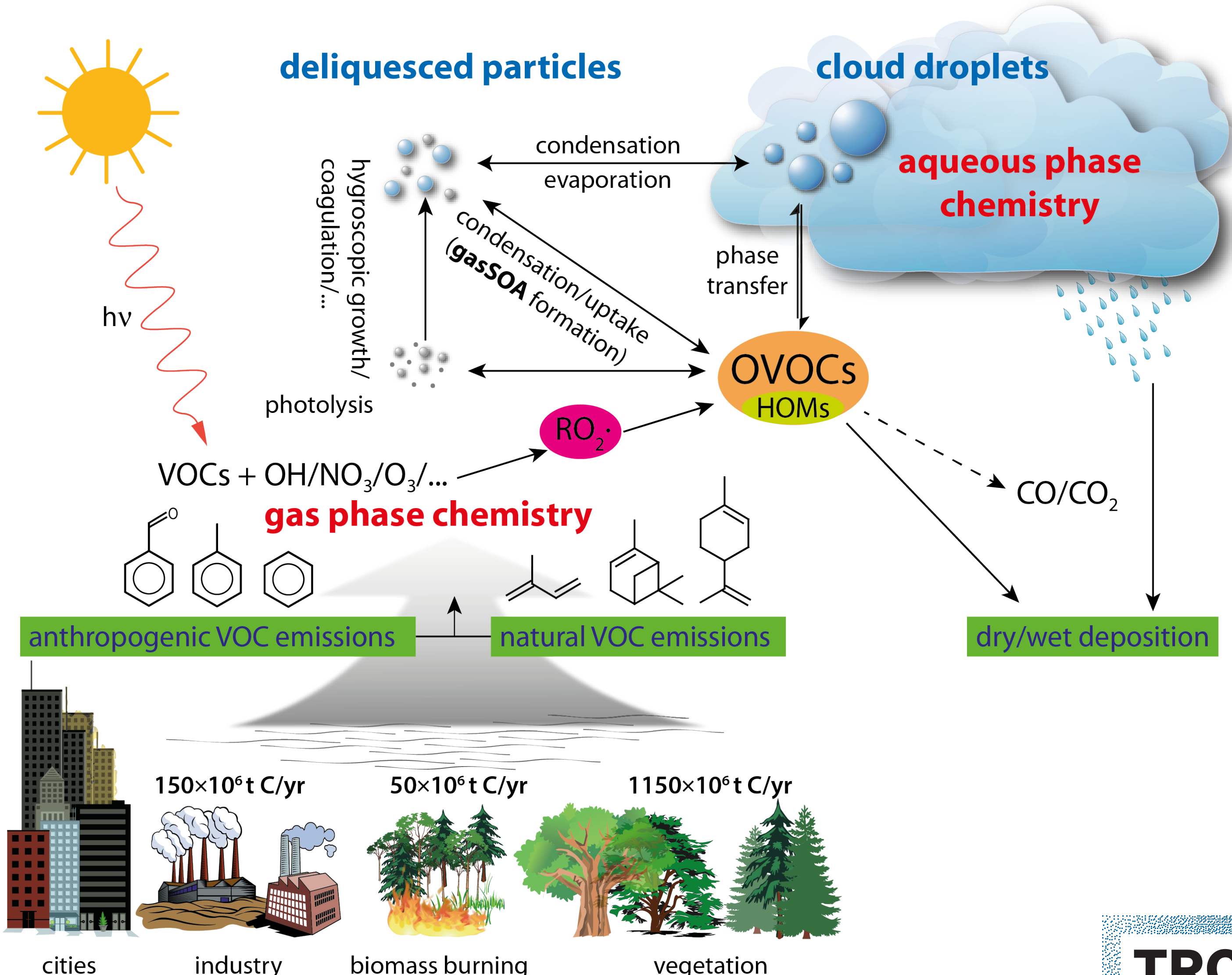
Motivation



Source: A. Tilgner

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RO_2 radical reactions I (traditional)

$RO_2 + NO \rightarrow RO + NO_2$
$\rightarrow RONO_2$

site	NO conc.	RO_2 lifetime
- urban	10 ppb	0.5 s
- rural	1 ppb	5 s
- forest	20 ppt	4 min

$RO_2 + HO_2 \rightarrow ROOH + O_2$

site	HO_2 conc.	RO_2 lifetime
- urban	5 ppt	9 min
- rural	20 ppt	2 min
- forest	50 ppt	1 min

$RO_2 + RO_2 \rightarrow 2\,RO + O_2$
$\rightarrow ROH + R'(C{=}O) + O_2$

RO_2 conc.	RO_2 lifetime
a few ppt	min - hours

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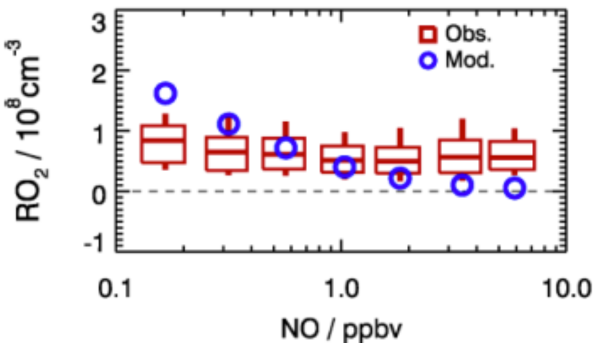
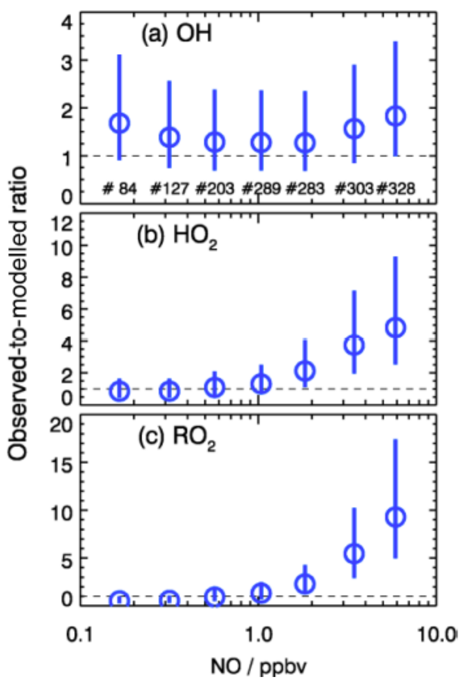
RO_2 radical measurements in the atmosphere

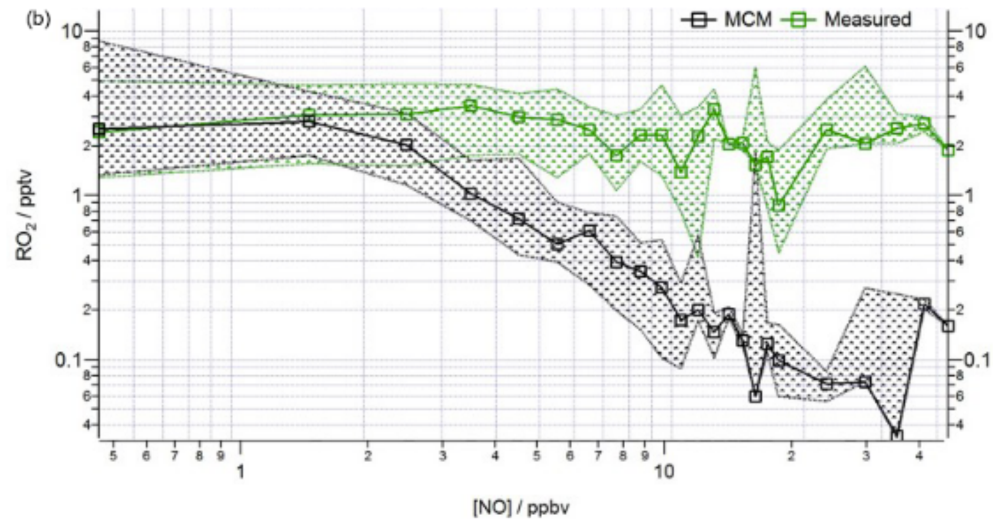
Winter 2016, near Beijing





Tan et al., *Atmos.Chem.Phys.* (2018)

Summer 2012, London



Whalley et al., *Atmos.Chem.Phys.* (2018)

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RO_2 radical reactions II

		RO₂ lifetime
$RO_2 + NO$	$\rightarrow RO + NO_2$ $\rightarrow RONO_2$	0.5 s - 4 min
$RO_2 + HO_2$	$\rightarrow ROOH + O_2$	1 - 9 min
$RO_2 + RO_2$	$\rightarrow 2\,RO + O_2$ $\rightarrow ROH + R'(C{=}O) + O_2$	min - hours
RO_2 isomerization		< 1 s possible
$RO_2 + RO_2$	$\rightarrow ROOR + O_2$	min - hours

- 1960s/70s/80s: ROOR formation is unimportant! RO_2: CH_3O_2, $C_2H_5O_2$
  McDowell et al., *Can.J.Chem.*(1963); Weaver et al., *J.Photochem.*(1975)
- In the last years: rebirth of interest -> HOM formation from terpene ozonolysis

-> large molecules as 1st generation products during VOC degradation

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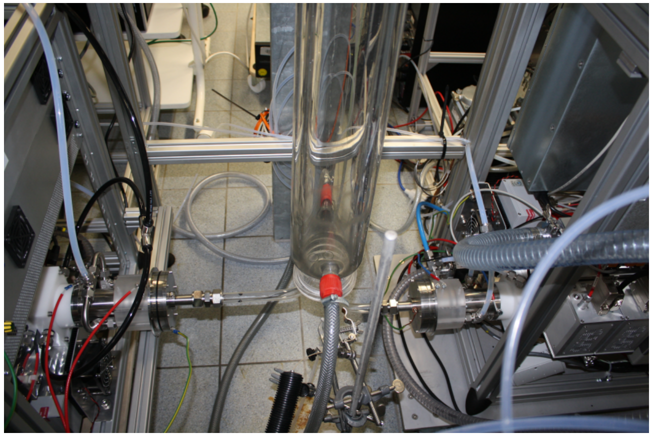
Experiment

Free jet flow system

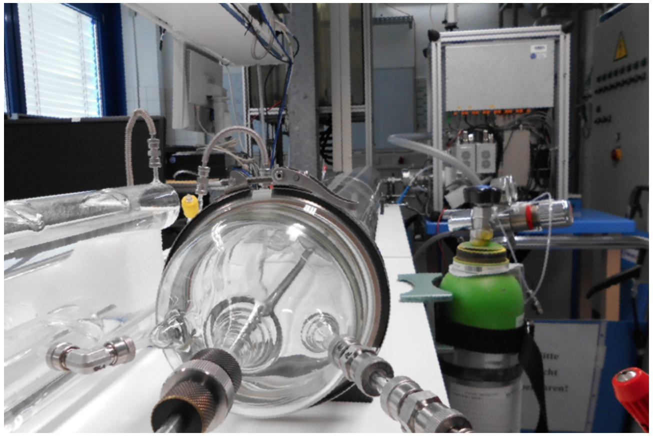
- 1 bar purified air
- Residence time: 3.0 - 7.9 s
- “early stage” of a reaction
- RO_2 radical formation/isomerization
- Controlled bimolecular RO_2 steps
- <u>benefit:</u> „wall-free“ conditions



CI-APi-TOF mass spectrometry

- Boulder-Typ inlet system
- Detection limit:
  10^3 - 10^4 molecules cm^{-3}
- Different ionisation schemes:
  CH_3COO^-, I^-, RNH_3^+, $H_2NNH_3^+$
- Lower limit concentrations

Additionally NH_4^+-CI3-TOF



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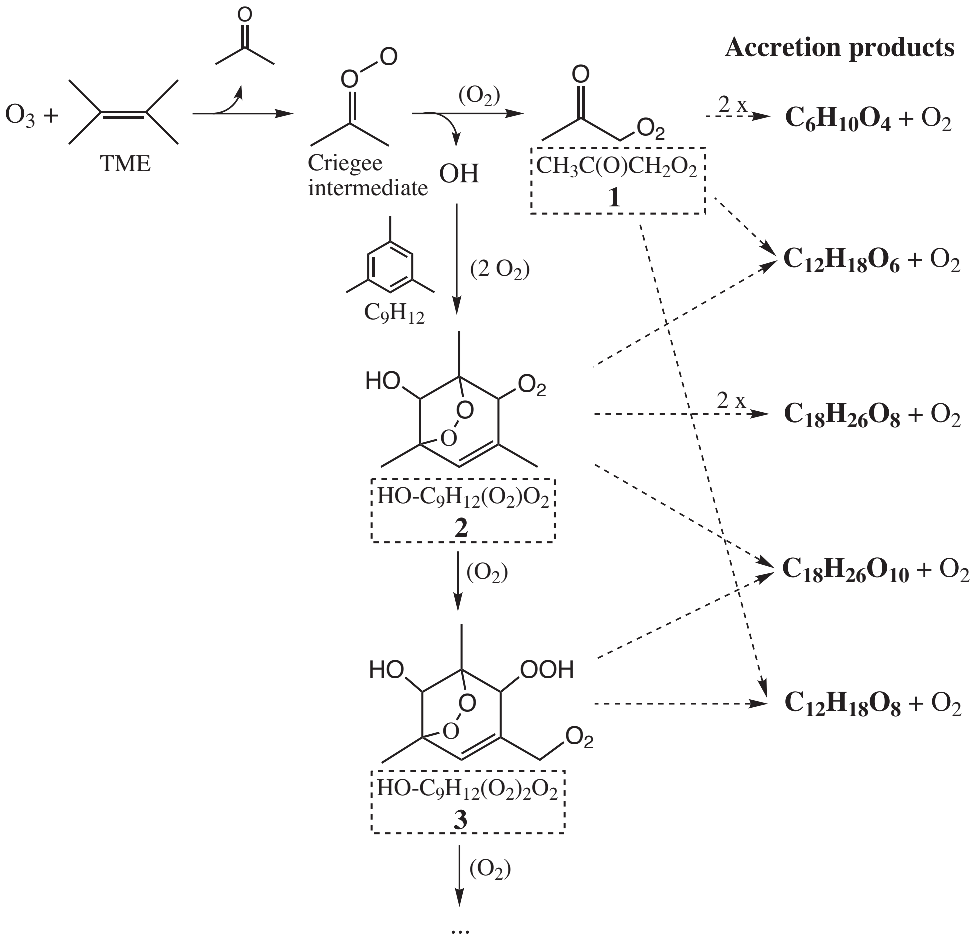
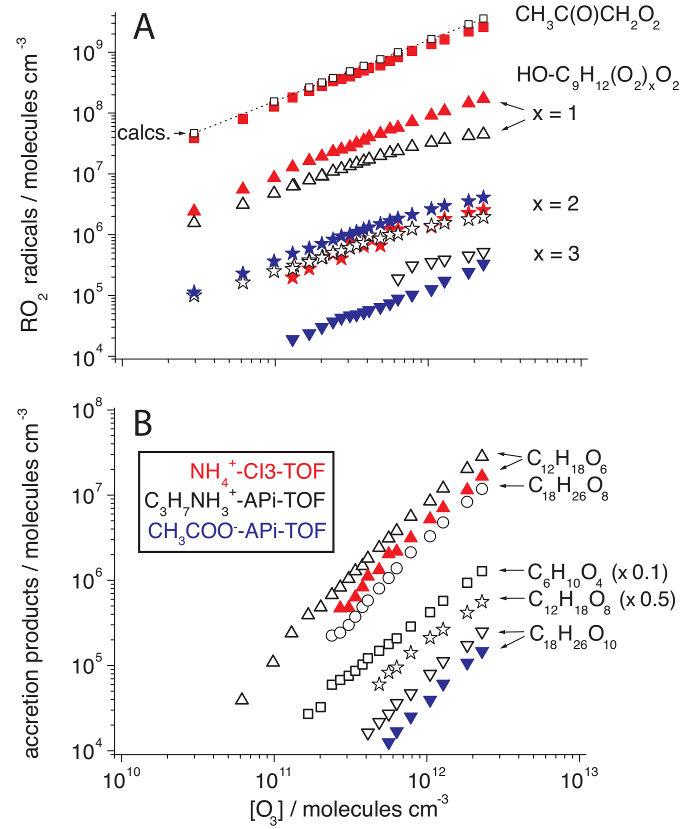
Accretion product formation via $RO_2 + RO_2$ -> $ROOR + O_2$ I

OH + mesitylene (1,3,5-trimethylbenzene), OH generation via TME ozonolysis





reacted mesitylene: (3.7 – 295) 10^7 molecules cm^{-3}

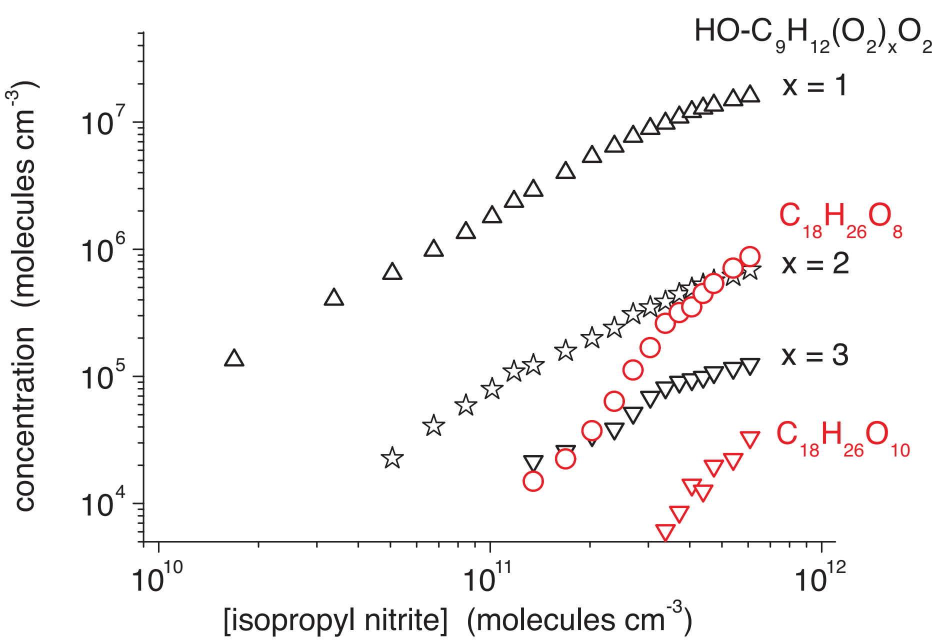
Berndt et al., *Angew.Chem.*(2018)

TROPOS

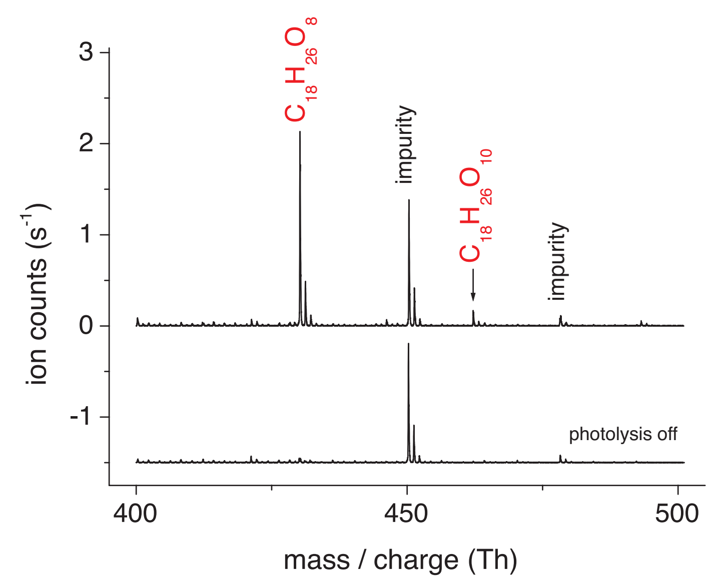
Accretion product formation via $RO_2 + RO_2$ -> $ROOR + O_2$ II

OH + mesitylene (1,3,5-trimethylbenzene), OH generation via $HO_2 + NO \rightarrow OH + NO_2$
isopropyl nitrite photolysis

Photolysis experiment
(free of ozonolysis products)
mesitylene: constant, ionization via $C_3H_7NH_3^+$-APi-TOF



Mass spectrum (example)



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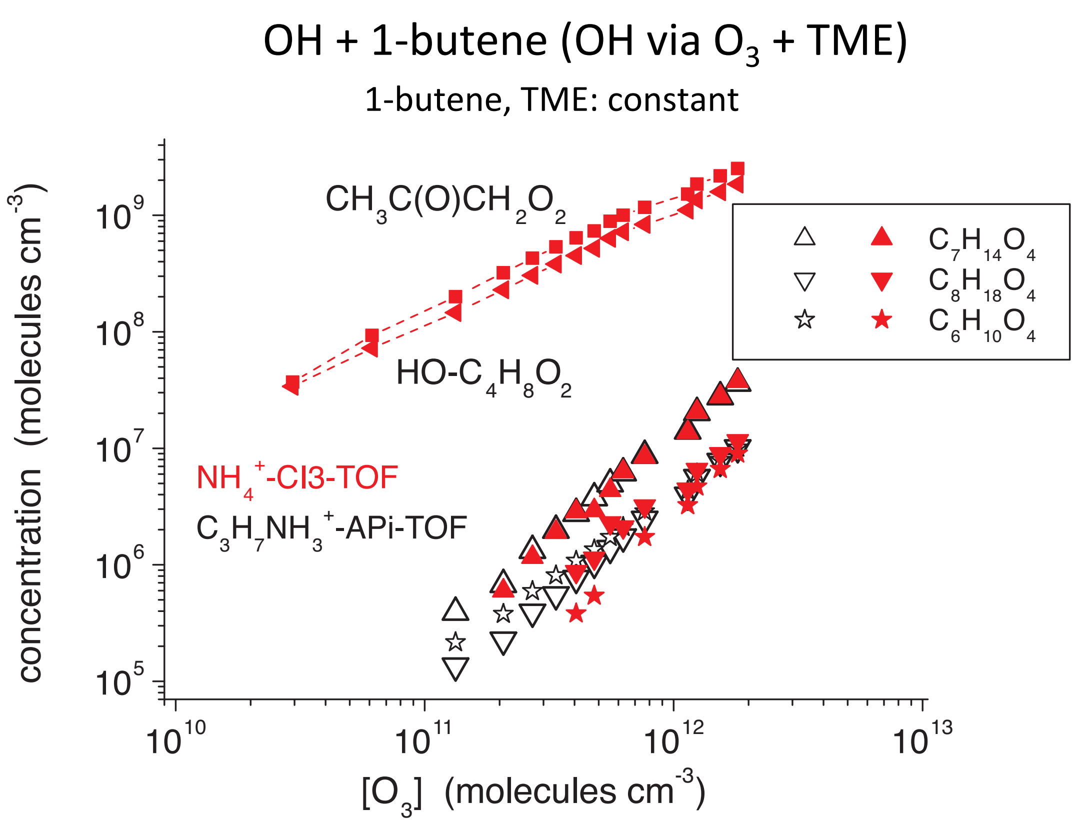
Accretion product formation via $RO_2 + RO_2 \rightarrow ROOR + O_2$ III

OH + 1-butene / isoprene / n-hexane / methane



O_3 + TME ($+O_2$) -> OH + $CH_3C(O)CH_2O_2$ + ...

OH + 1-butene ($+O_2$) -> $HO\text{-}C_4H_8O_2$

$HO\text{-}C_4H_8O_2 + CH_3C(O)CH_2O_2$ -> $C_7H_{14}O_4 + O_2$

2 $HO\text{-}C_4H_8O_2$ -> $C_8H_{18}O_4 + O_2$

2 $CH_3C(O)CH_2O_2$ -> $C_6H_{10}O_4 + O_2$

-> ROOR formation seems to be generally valid!

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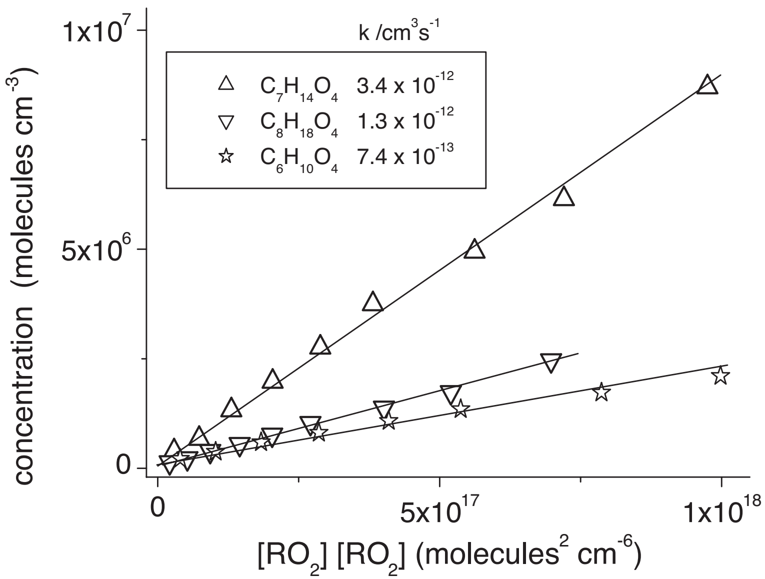
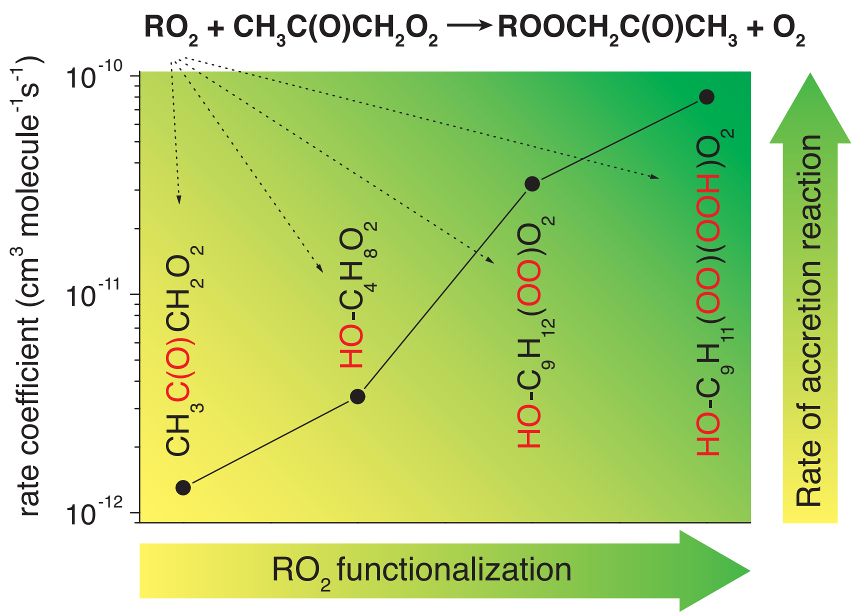
Accretion product formation via $RO_2 + RO_2 \rightarrow ROOR + O_2$ - Kinetics

Kinetic analysis
OH + 1-butene



Reactivity trend



-> increasing RO_2 functionalization leads to increasing RO_2 reactivity

-> Hypothesis: attractive forces (donor-acceptor-relationships) form a longer-living reactive complex ROOOOR

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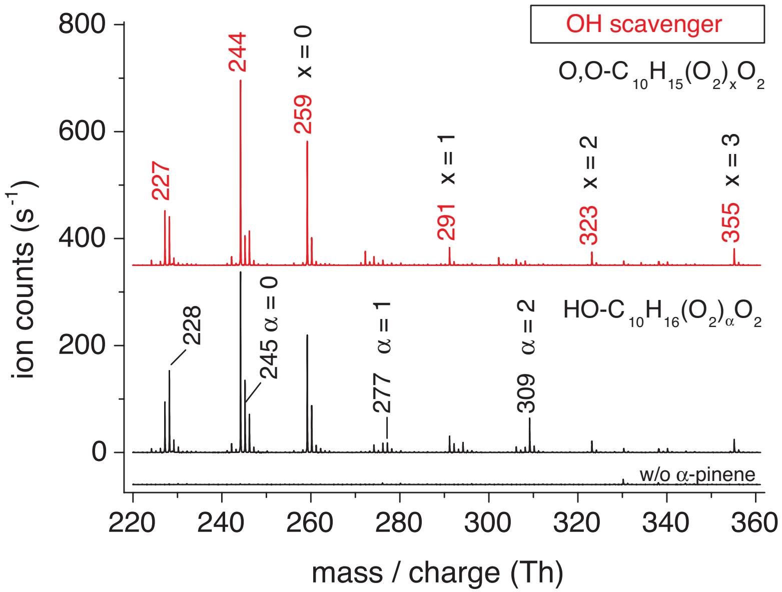
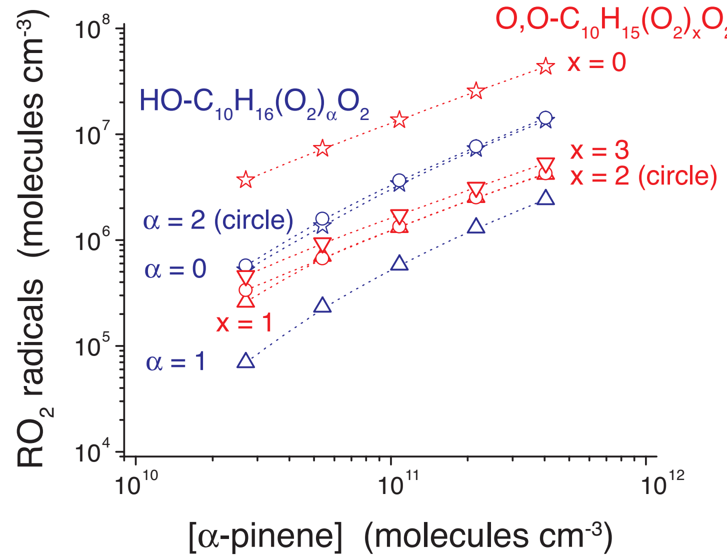
RO_2 radical formation from O_3/OH + α-pinene



cluster formation via $C_3H_7NH_3^+$-APi-TOF



O_3: 6.8 x 10^{11} molecules cm^{-3}
α-pinene: (2.7 - 40.5) 10^{10} molecules cm^{-3}
reacted α-pinene: (2.9 - 43) 10^7 molecules cm^{-3}

-> ozonolysis derived RO_2 radicals $O,O\text{-}C_{10}H_{15}(O_2)_xO_2$
x = 0 - 3

-> OH reaction derived RO_2 radicals $HO\text{-}C_{10}H_{16}(O_2)_\alpha O_2$
α = 0 - 2

Berndt et al., *ES&T* (2018)

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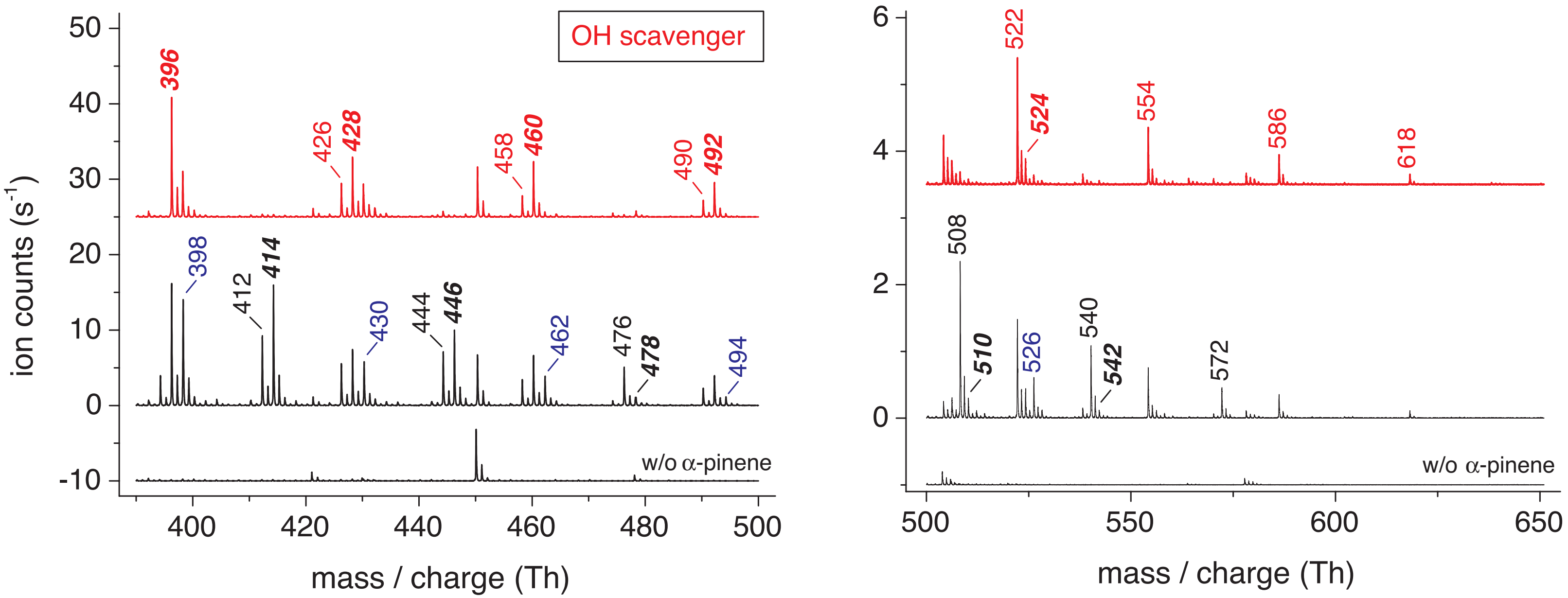
C_{19}/C_{20} accretion product formation from O_3/OH + α-pinene I

cluster formation via $C_3H_7NH_3^+$-APi-TOF



-> $RO_2 + R'O_2 \rightarrow C_{20}\text{-}ROOR' + O_2$

$C_{20}H_{30}O_{6,8,10,12,14,16,18}$ via $O_3\text{-}RO_2 + O_3\text{-}RO_2$

$C_{20}H_{34}O_{4,6,8,10,12}$ via $OH\text{-}RO_2 + OH\text{-}RO_2$

$C_{20}H_{32}O_{5,7,9,11,13,15}$ via $O_3\text{-}RO_2 + OH\text{-}RO_2$

-> $RO_2 + R'O_2 \rightarrow C_{19}\text{-}ROOR' + O_2$ (+ CH_2O ?)

$C_{19}H_{28}O_{5,7,9,11,13}$ via $O_3\text{-}RO_2 + O_3\text{-}RO_2$

$C_{19}H_{30}O_{6,8,10,12,14}$ via $O_3\text{-}RO_2 + OH\text{-}RO_2$

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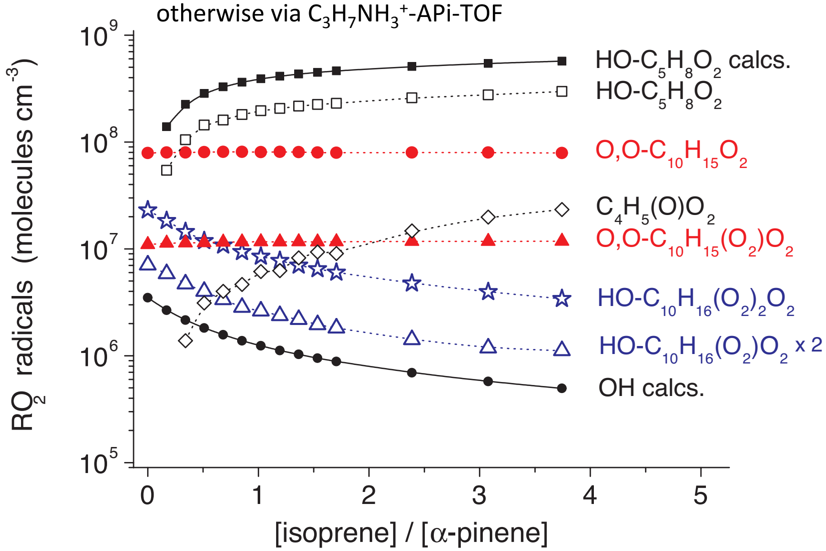
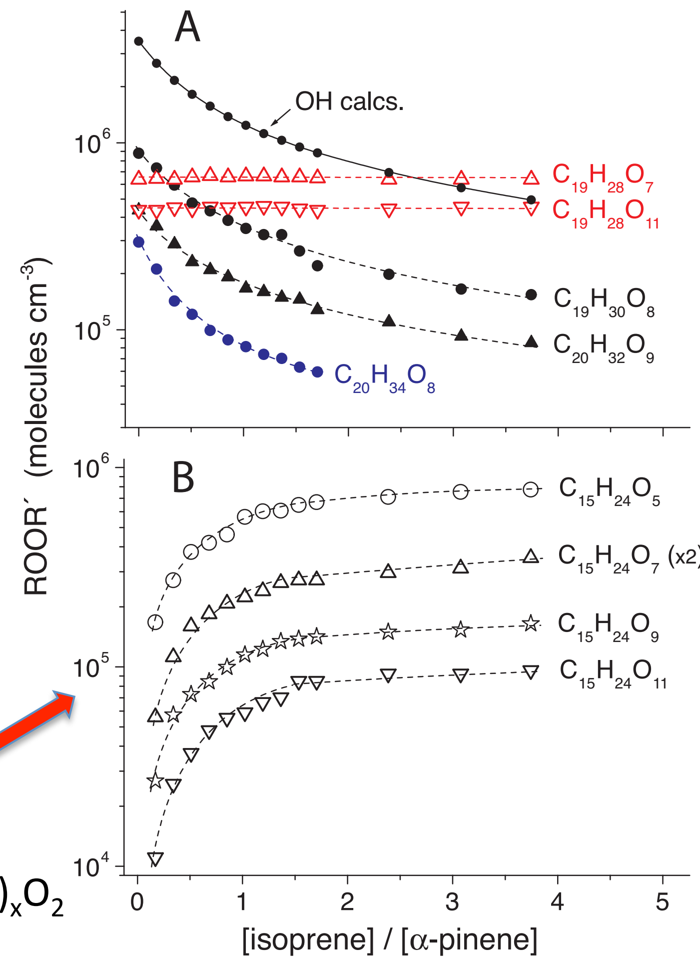
Accretion product formation from O_3/OH + α-pinene II

Isoprene addition

$HO\text{-}C_5H_8O_2$, $C_4H_5(O)O_2$ detection via NH_4^+-CI3-TOF
otherwise via $C_3H_7NH_3^+$-APi-TOF



O_3: 2.0 x 10^{12} molecules cm^{-3}
α-pinene: 3.9 x 10^{11} molecules cm^{-3}
isoprene: (0 – 1.46) 10^{12} molecules cm^{-3}



C_{15} products from
$HO\text{-}C_5H_8O_2 + O,O\text{-}C_{10}H_{15}(O_2)_xO_2$

-> Complex accretion product spectrum in atmosphere!

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Summary

New RO_2 pathways

- RO_2 isomerization
  -> higher oxidized RO_2 radicals
- Accretion product formation: $RO_2 + RO_2 \rightarrow ROOR + O_2$
  -> formation of large molecules as 1st generation products during VOC degradation
  -> ROOR formation seems to be generally valid
  -> Complex accretion product spectrum in atmosphere

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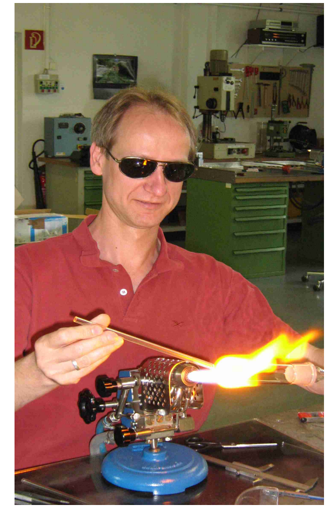
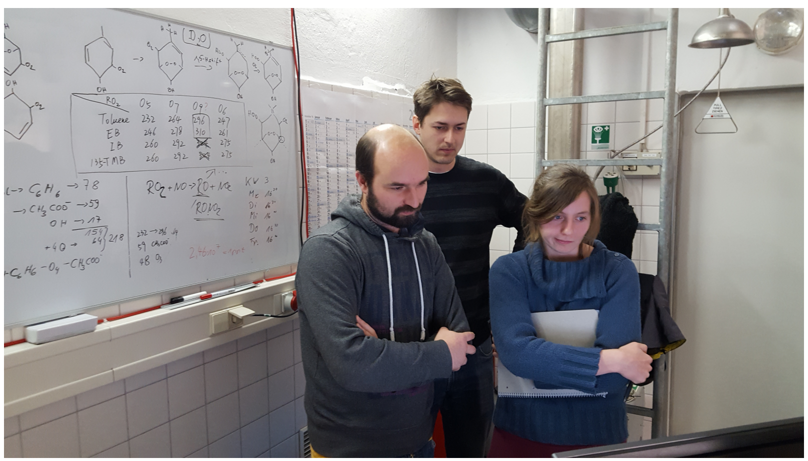
Thanks!

K. Pielok



A. Rohmer



A. Hansel´s group,
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Thank you for your attention!

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