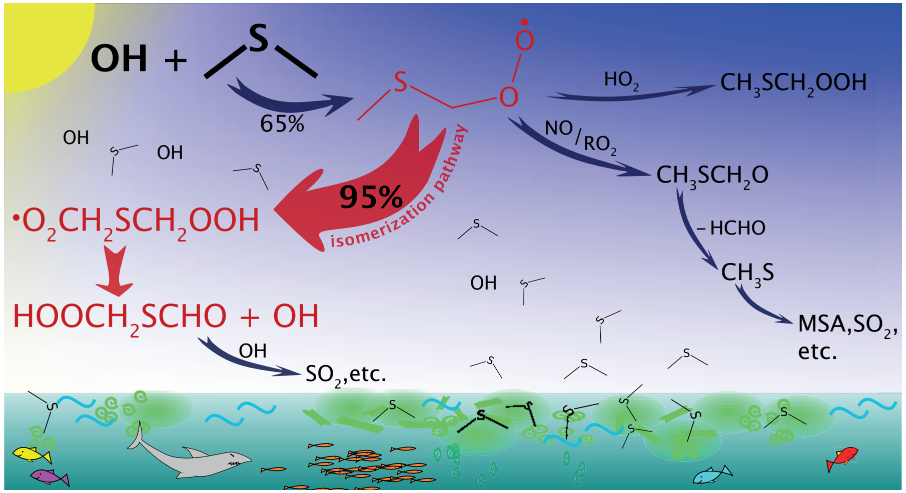
New pathways of the reaction of OH radicals with dimethyl sulfide based on CH_3SCH_2OO isomerization

T. Berndt,[1] W. Scholz,[2] B. Mentler,[2] L. Fischer,[2] E. H. Hoffmann,[1] A. Tilgner,[1] N. Hyttinen,[3] N. L. Prisle,[3] A. Hansel,[2] H. Herrmann[1]

[1] Leibniz Institute for Tropospheric Research (TROPOS), 04318 Leipzig, Germany.
[2] University of Innsbruck, 6020 Innsbruck, Austria.
[3] University of Oulu, 90014 Oulu, Finland.



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Motivation

DMS

- Largest natural sulfur source to the Earth´s atmosphere
- Estimated emission rate: (10 - 35) × 10^6 metric tons of sulfur per year over the oceans

  Lana *et al.*, *Global Biochem. Cy.*(2011)
- Gas-phase oxidation mainly initiated by the reaction with OH radicals

  -> formation of sulfuric acid (H_2SO_4) and methane sulfonic acid (MSA)
- Concentration over the oceans: a few 10^9 molecules cm^{-3}

- Also emission from soil/vegetation over the continents
- Biomass burning in Australia: DMS: 9 x 10^{11} molecules cm^{-3} (max.)

  DMDS: 3 x 10^{12} molecules cm^{-3} (max.)

  Meinardi *et al.*, *GRL*(2003)

Reduced sulfur compounds

- H_2S, OCS, CS_2, CH_3SH, CH_3SCH_3, CH_3SSCH_3

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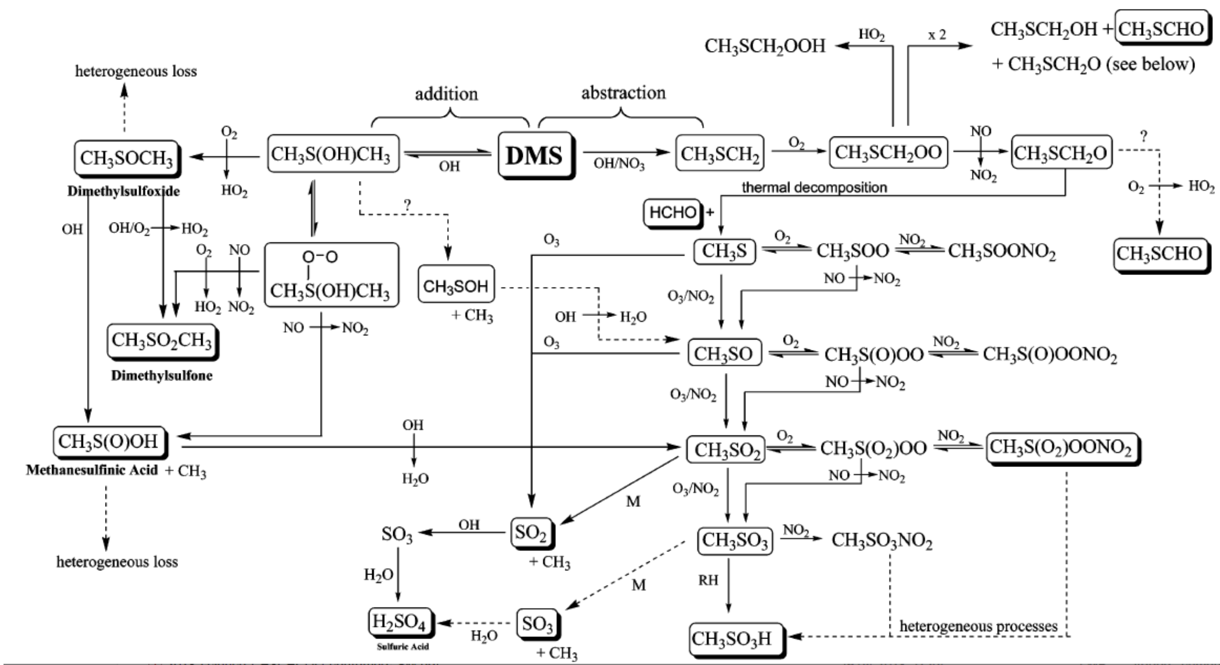
DMS degradation - knowledge in literature (beginning of 2019)



Barnes *et al.*, *Chem. Rev.*(2006)

But: results from QC calculations point to rapid CH_3SCH_2OO isomerization

$$CH_3SCH_2O_2\ (+\ O_2) \rightarrow O_2CH_2SCH_2OOH \quad (1)$$

$$O_2CH_2SCH_2OOH \rightarrow \{HOOCH_2SCHOOH\} \rightarrow HOOCH_2SCHO + OH \quad (2)$$

Wu *et al.*, *JPC A*(2015)

$k_1(293\ K) = 2.1\ s^{-1}$; $k_2(293\ K) = 73\ s^{-1}$

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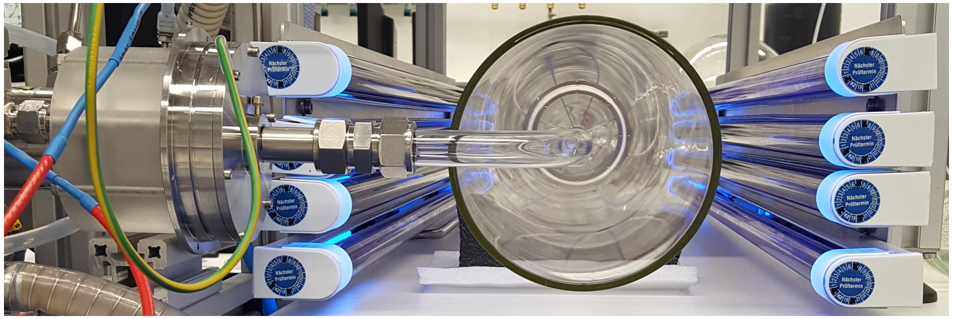
Experiment

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

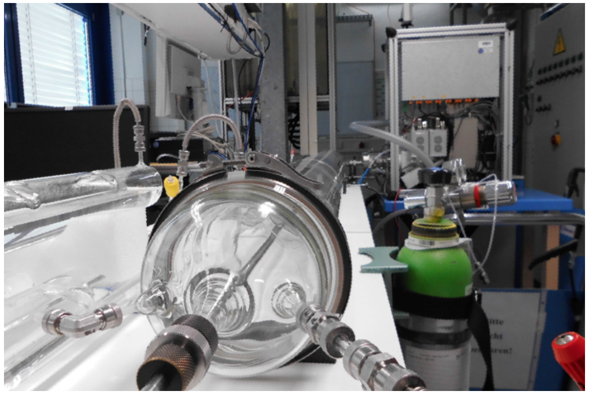
- Boulder-Typ inlet system
- Detection limit: 10^3 - 10^4 molecules cm^{-3}
- Different ionisation schemes:

  Iodide (I^-) / CH_3COO^- -> clustering with S-species

  RNH_3^+ -> clustering with SO_3 (indirect OH)

  $(CH_3C(O)CH_3)H^+$ -> proton transfer reaction

NH_4^+-CI3-TOF (Innsbruck)



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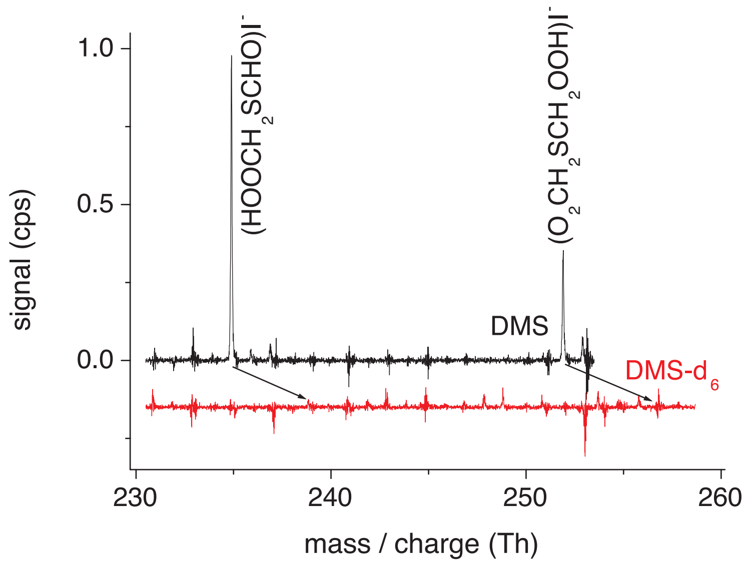
Observed products from CH_3SCH_2OO isomerization

$CH_3SCH_2O_2$ (+ O_2)	$\rightarrow$ $O_2CH_2SCH_2OOH$		(1)	Wu *et al.*,
$O_2CH_2SCH_2OOH$	$\rightarrow$ {$HOOCH_2SCHOOH$}	$\rightarrow$ $HOOCH_2SCHO$ + OH	(2)	*JPC A*(2015)

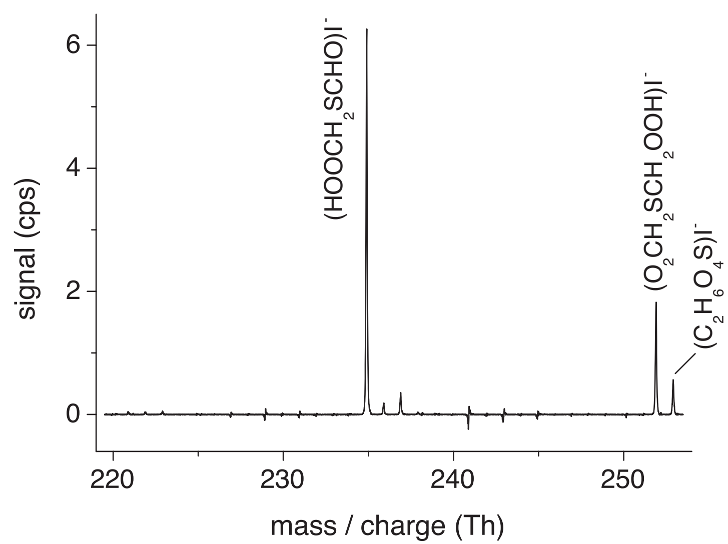
OH via O_3 + TME



- I⁻-CI-APi-TOF analysis
- reacted DMS: 4.5×10^7 molecules cm^{-3} and reacted DMS-d_6: about 2.8×10^7 molecules cm^{-3}

-> k(H-shift) / k(D-shift) about 15

OH via i-C_3H_7ONO photolysis



- I⁻-CI-APi-TOF analysis
- reacted DMS: 2.5×10^8 molecules cm^{-3}
- $C_2H_6O_4S$: $HOOCH_2SCH_2OOH$ formed via HO_2 + $O_2CH_2SCH_2OOH$?

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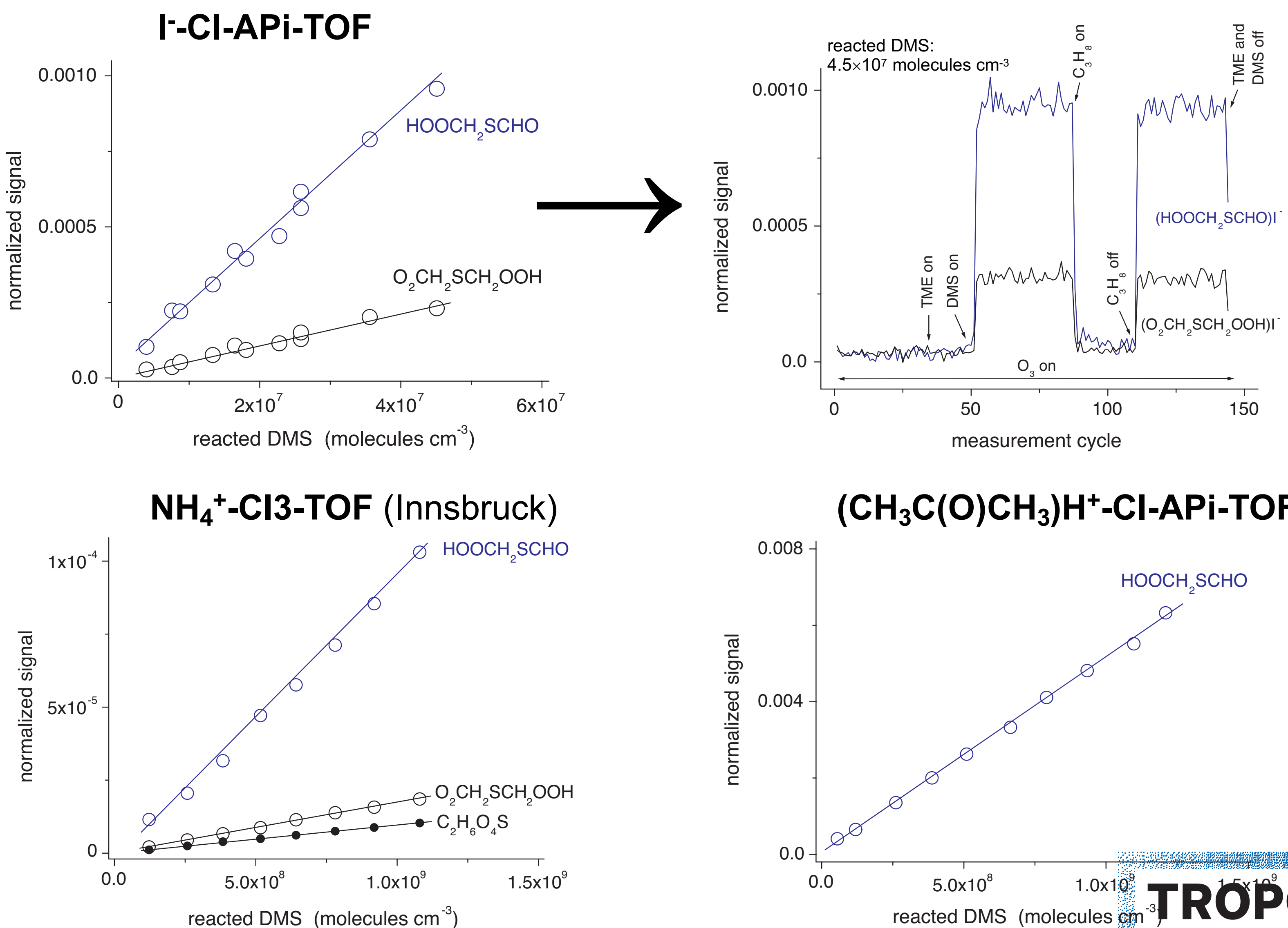
CH_3SCH_2OO isomerization products (OH via O_3 + TME)



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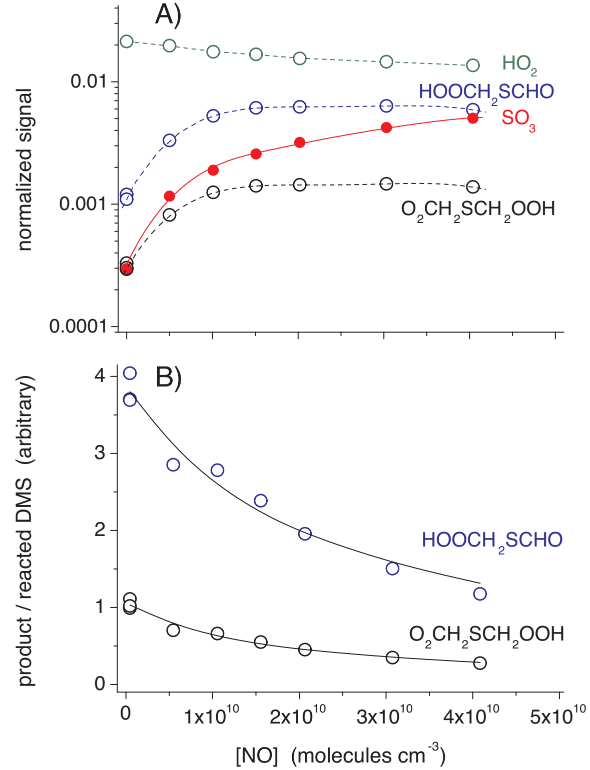
CH_3SCH_2OO isomerization rate

$CH_3SCH_2O_2$ (+ O_2)	$\rightarrow$ $O_2CH_2SCH_2OOH$			(1)
$O_2CH_2SCH_2OOH$	$\rightarrow$ {$HOOCH_2SCHOOH$}	$\rightarrow$	$HOOCH_2SCHO$ + OH	(2)
$CH_3SCH_2O_2$ + NO	$\rightarrow$ products			(3)

Experiment

- OH via i-C_3H_7ONO photolysis



Competition kinetics:

- Signals of $O_2CH_2SCH_2OOH$ and $HOOCH_2SCHO$ = f(NO)

-> k_1 / k_3 if k_2 >(or better: >>) k_1

But: NO addition changes HO_x system

-> NO + HO_2 -> OH + NO_2

-> measurement of the integral OH conc.

via SO_3 formation from OH + SO_2

- low SO_2 addition: r(OH+SO_2) / r(OH+DMS) = 0.05
- SO_3 formation allows to account for rising OH conc.

-> k_1 / k_3 = $(2.1 \pm 0.4)\times10^{10}$ molecule cm^{-3} ($HOOCH_2SCHO$)

$(1.5 \pm 0.3)\times10^{10}$ molecule cm^{-3} ($O_2CH_2SCH_2OOH$)

-> $k_1 = 0.23 \pm 0.12$ s^{-1} at 295 ± 2 K (k_3 from literature)

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OH radical recycling

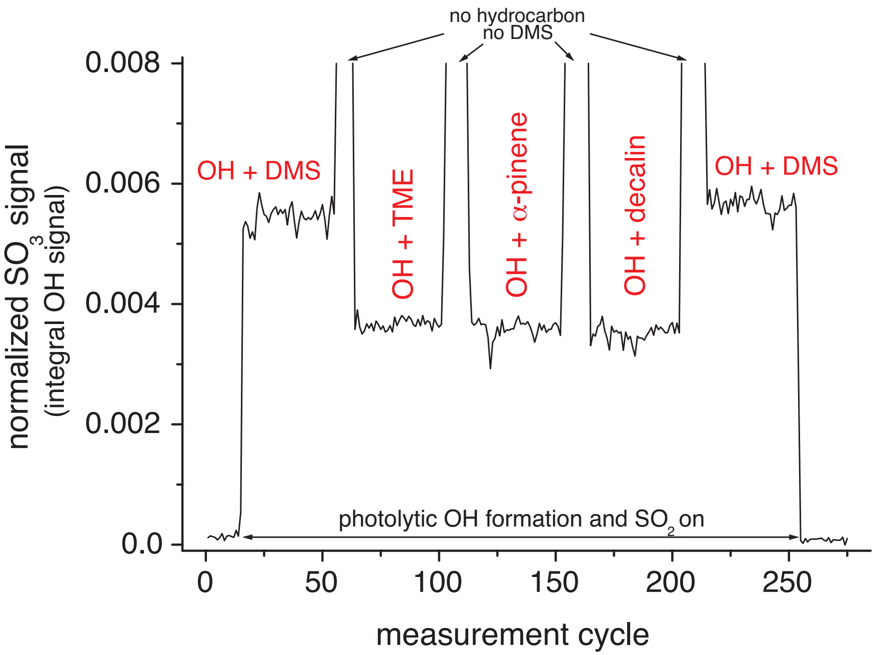
$CH_3SCH_2O_2$ (+ O_2) → $O_2CH_2SCH_2OOH$ (1)

$O_2CH_2SCH_2OOH$ → {$HOOCH_2SCHOOH$} → $HOOCH_2SCHO$ + OH (2)

-> constant OH formation rate via i-C_3H_7ONO photolysis
-> constant OH consumption rate via OH + DMS/organic

-> measurement of the integral OH conc.
via SO_3 formation from OH + SO_2

-> enhanced integral OH signal for OH + DMS
-> OH recycling



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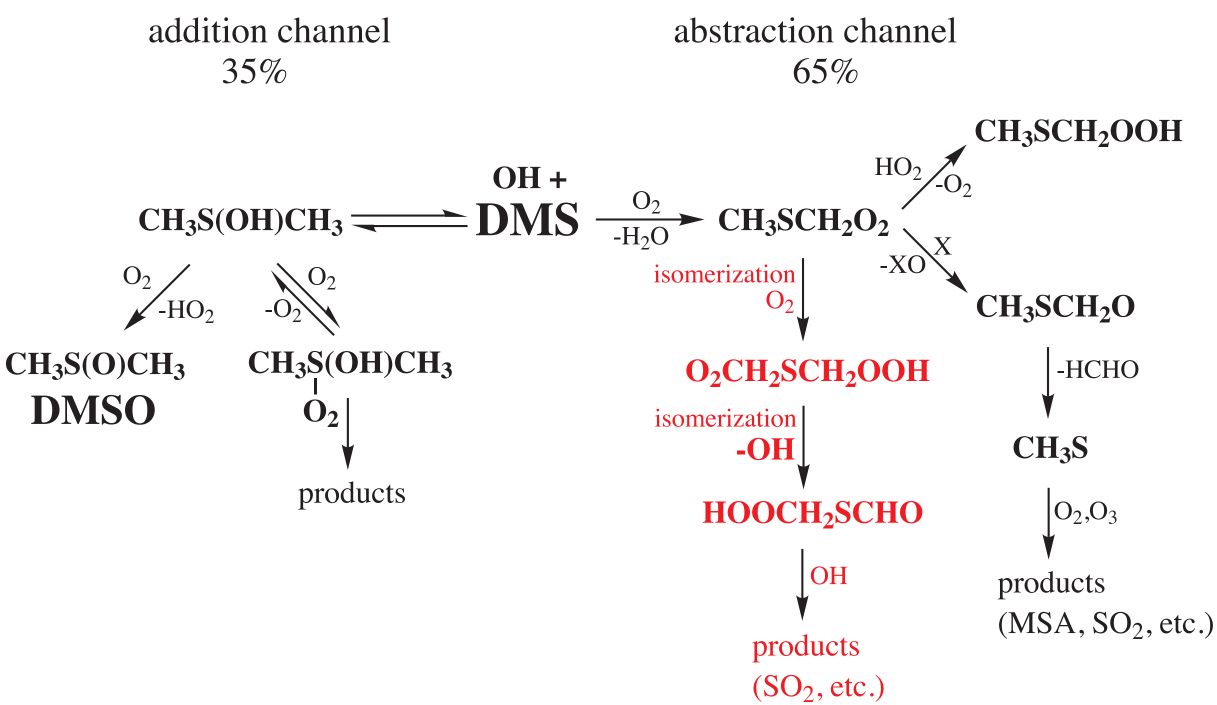
Updated scheme



Berndt *et al.*, *JPC Lett.*(2019)

-> Supported by measurements from field campaigns of U.S. and U.K. groups
see: Veres *et al.*,
P.N.A.S.(2020)

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Summary

- Rapid two-step CH_3SCH_2OO isomerization process forming finally $HOOCH_2SCHO$
- Isomerization rate outruns "traditional" bimolecular CH_3SCH_2OO reactions with HO_2, NO, RO_2
- Still open question: Formation of SO_2 and MSA
- A next example for a rapid unimolecular RO_2 pathway important for atmospheric conditions

-> Improved techniques allow a more direct insight into a reaction!

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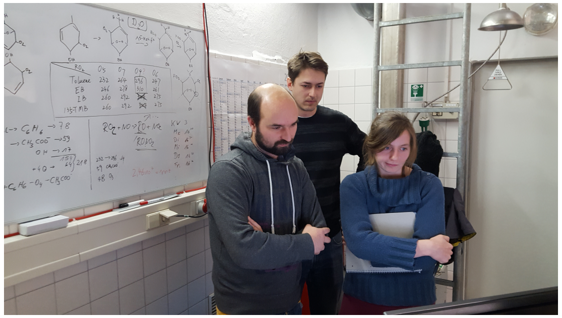
Thanks!



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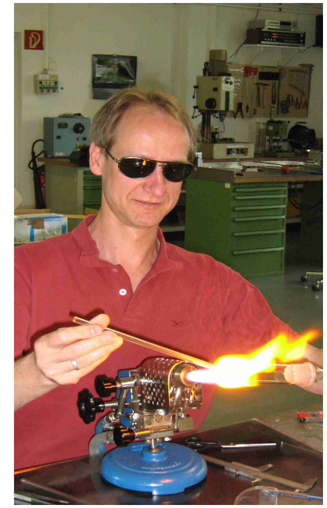

A. Rohmer

K. Pielok

ACD modeling group (TROPOS)

Thank you for your attention!

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