Competitive reaction of CH_2OO with SO_2 and water vapour and the thermal lifetime of CH_2OO at 293 K

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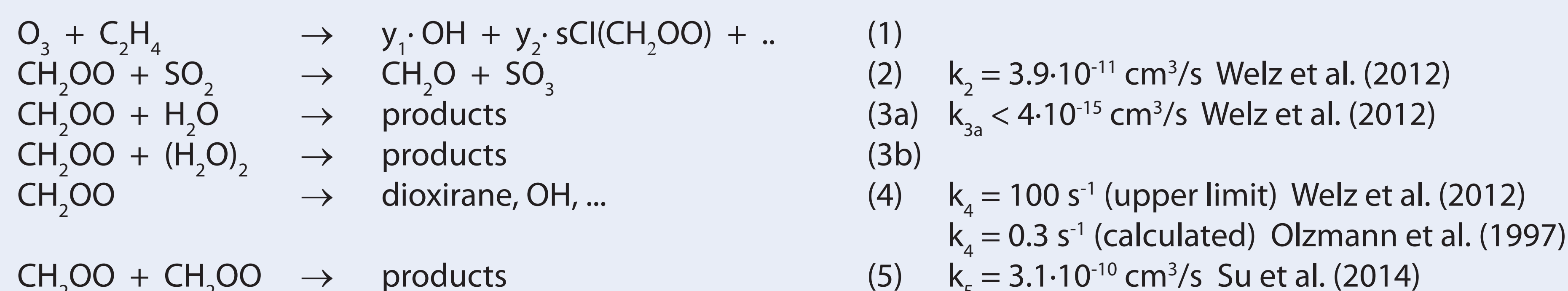TROPOS
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Motivation

H_2SO_4 represents a key substance in the process of atmospheric nucleation. The importance of gas-phase products from olefin ozonolysis other than OH radicals, most likely stabilized Criegee Intermediates (sCIs), for the process of atmospheric SO_2 oxidation to H_2SO_4 has recently been discovered.

Subject of this work are investigations on H_2SO_4 formation from $CH_2OO + SO_2$ as a function of the water vapour content and the measurement of the CH_2OO steady state concentration starting from the ozonolysis of ethylene used for formaldehyde oxide generation.

For the reaction with water vapour, up to now only upper limit estimates of k_{3a} are available from the diiodomethane photolysis technique differing by a factor of about 40, Welz et al. (2012) and Stone at al. (2014). Results from ethene ozonolysis experiments point to a much more effective reaction of CH_2OO with water vapour, e.g. Suto et al. (1985). Quantum chemistry favours reaction (3b) over (3a) for atmospheric conditions, Ryzhkov and Ariya (2004).

$O_3 + C_2H_4$	$\rightarrow$	$y_1 \cdot OH + y_2 \cdot sCI(CH_2OO) + ..$	(1)	
$CH_2OO + SO_2$	$\rightarrow$	$CH_2O + SO_3$	(2)	$k_2 = 3.9 \cdot 10^{-11}$ cm³/s Welz et al. (2012)
$CH_2OO + H_2O$	$\rightarrow$	products	(3a)	$k_{3a} < 4 \cdot 10^{-15}$ cm³/s Welz et al. (2012)
$CH_2OO + (H_2O)_2$	$\rightarrow$	products	(3b)	
CH_2OO	$\rightarrow$	dioxirane, OH, ...	(4)	$k_4 = 100$ s⁻¹ (upper limit) Welz et al. (2012)
				$k_4 = 0.3$ s⁻¹ (calculated) Olzmann et al. (1997)
$CH_2OO + CH_2OO$	$\rightarrow$	products	(5)	$k_5 = 3.1 \cdot 10^{-10}$ cm³/s Su et al. (2014)

Experiment

Institute for Tropospheric Research -
Laminar Flow Tube, IfT-LFT:
- length: 505 cm, 8 cm i.d.
- carrier gas: purified air (99.9999999 vol%)
- atmospheric pressure
- temperature: 293 K
- flow: 30 l min⁻¹ (STP), residence time: 39.5 s
- relative humidity: ca.2 - 50 %
- reactant concentrations:
    [ethene] = $1.5 \cdot 10^{13}$ cm⁻³
    $[O_3] = 2.2 \cdot 10^{11}$ cm⁻³
    $[SO_2] = (5.6 - 1600) \cdot 10^{11}$ cm⁻³
    $[C_3H_8] = (1.6 - 8.2) \cdot 10^{15}$ cm⁻³
    (OH scavenger)
- ethene conversion: 0.0014%

H_2SO_4 detection: NO_3^--CI-APi-TOF
detection limit: a few 10^4 cm⁻³

ozone →
← ethene, (SO_2) propane

TOF-MS | NO_3^- - APi | PTR-MS
RH
O_3 analyzer
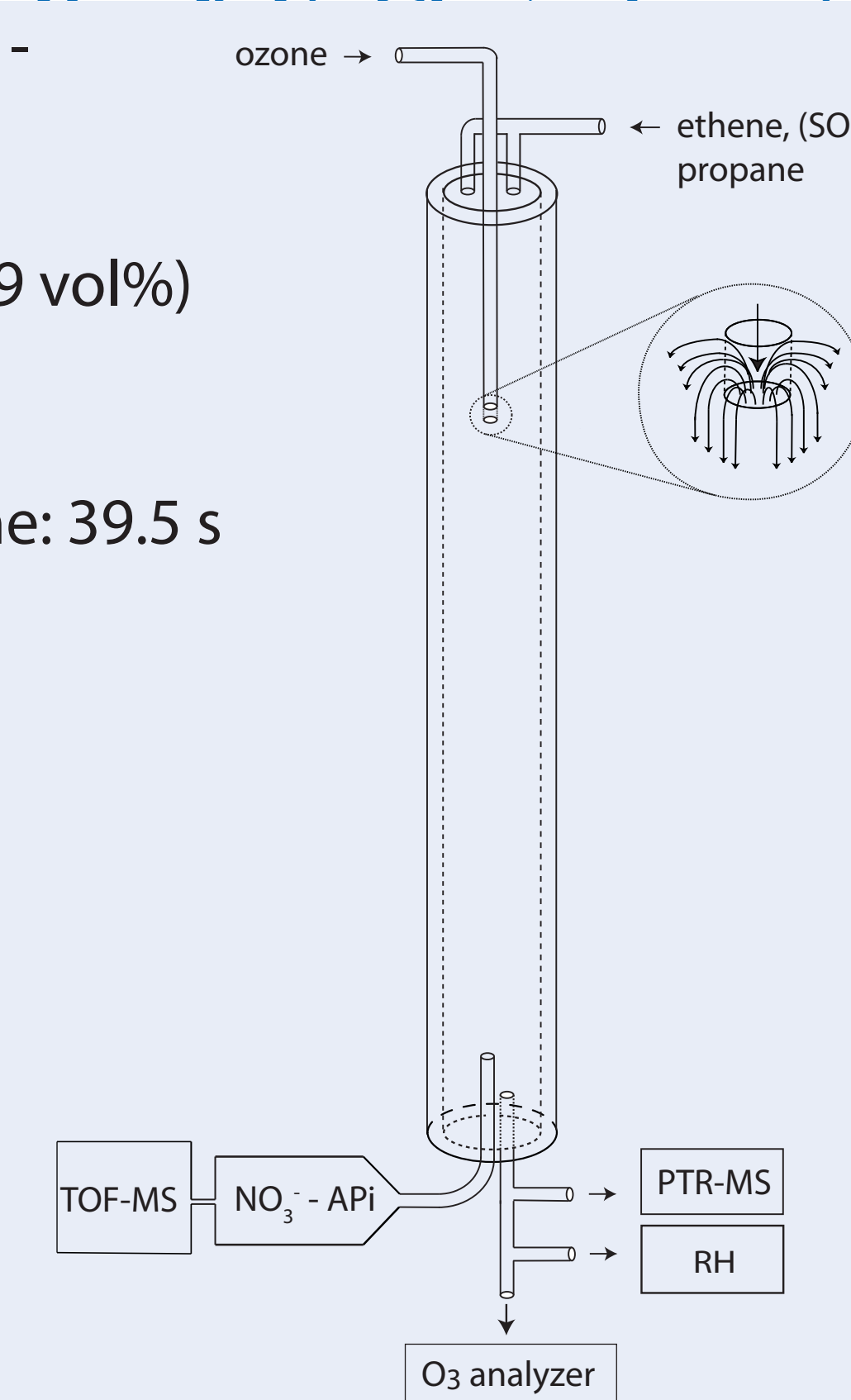
Results and Discussion

Experiments with variable H_2O vapour content
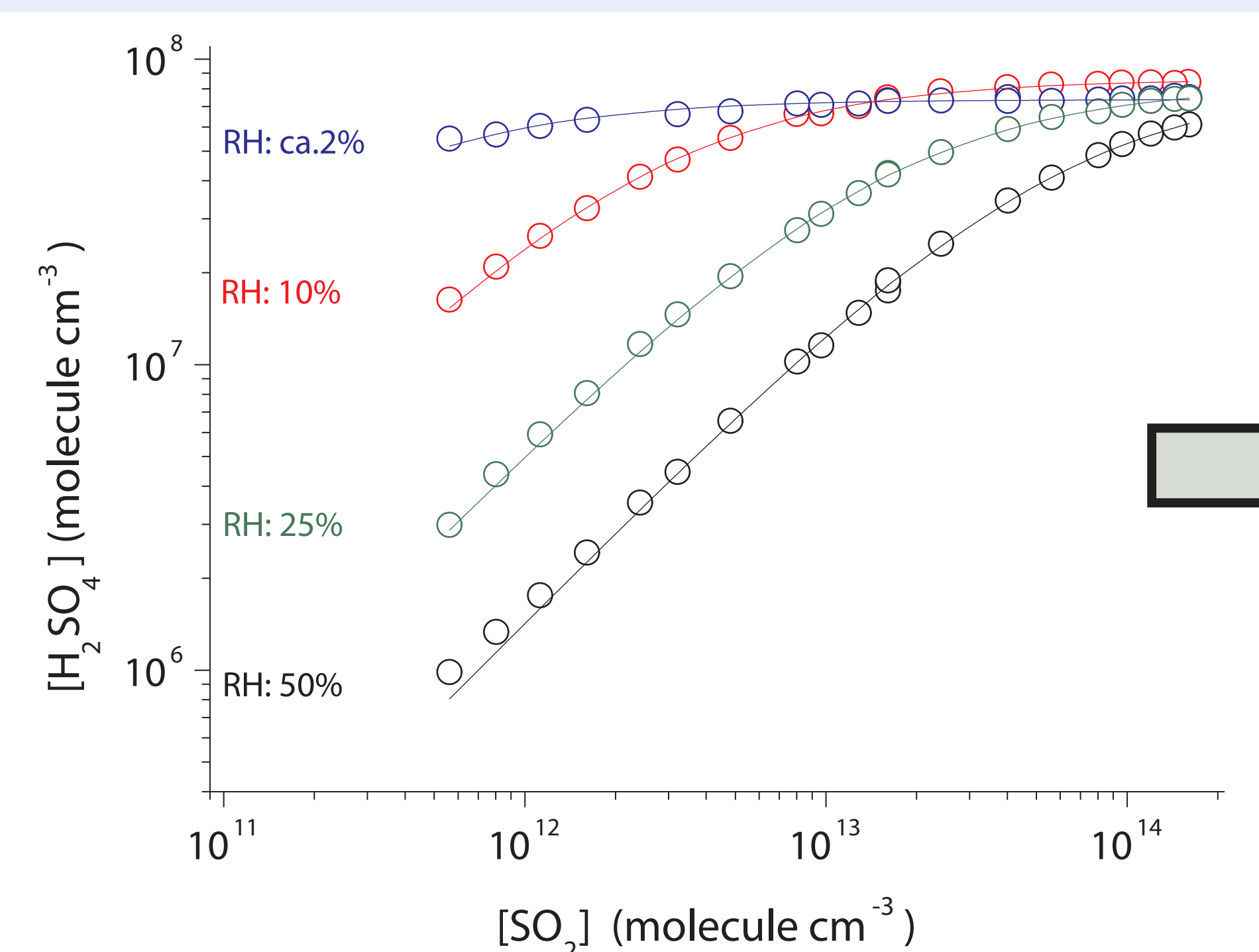
Figure 1: H_2SO_4 formation as a function of SO_2 and RH; $[O_3] = 2.2 \cdot 10^{11}$ and $[C_2H_4] = 1.5 \cdot 10^{13}$ cm⁻³. Lines are the results from regression analysis according to equation (II).

Data analysis:
- path (5) is negligible for CH_2OO consumption, < 0.0002%
- fraction of stabilized CH_2OO producing H_2SO_4, $CH_2OO_{H2SO4} / CH_2OO_{total}$, is equal to the reaction rate of path (2) divided by the total reaction rate

$$\frac{CH_2OO_{H2SO4}}{CH_2OO_{total}} = \frac{k_2[SO_2]}{k_2[SO_2] + k_{3a}[H_2O] + k_{3b}[(H_2O)_2] + k_4} \quad (I)$$

- $k_{loss} = k_{3a}[H_2O] + k_{3b}[(H_2O)_2] + k_4$ for a given water concentration (or RH)

$$[H_2SO_4] = \frac{1}{1 + \frac{k_{loss}}{k_2[SO_2]}} \cdot [H_2SO_4]_{CH2OO} \quad (II)$$

- here $[H_2SO_4]_{CH2OO}$ stands for $[H_2SO_4]$ from CH_2OO titration by SO_2
- $[H_2SO_4]_{CH2OO}$ allows to determine the yield of stabilized CH_2OO, y_2

RH (%)	k_{loss} / k_2 (molecule cm³)	$[H_2SO_4]_{CH2OO}$ (molecule cm³)	y_2, stabilized CH_2OO yield
ca. 2	$(2.36 \pm 0.32) \cdot 10^{11}$	$(7.38 \pm 0.04) \cdot 10^7$	0.36 ± 0.16
10	$(2.59 \pm 0.10) \cdot 10^{12}$	$(8.58 \pm 0.03) \cdot 10^7$	0.42 ± 0.19
25	$(1.55 \pm 0.04) \cdot 10^{13}$	$(8.18 \pm 0.03) \cdot 10^7$	0.40 ± 0.18
50	$(5.79 \pm 0.20) \cdot 10^{13}$	$(8.36 \pm 0.07) \cdot 10^7$	0.41 ± 0.18

Figure 2: k_{loss} / k_2 as a function of the water dimer concentration

→ k_{loss} / k_2 is proportional to the water dimer concentration
→ $k_{3b} / k_2 = 0.29 \pm 0.01$
→ intercept: $k_4 / k_2 = (4.3 \pm 3.0) \cdot 10^{11}$ cm⁻³
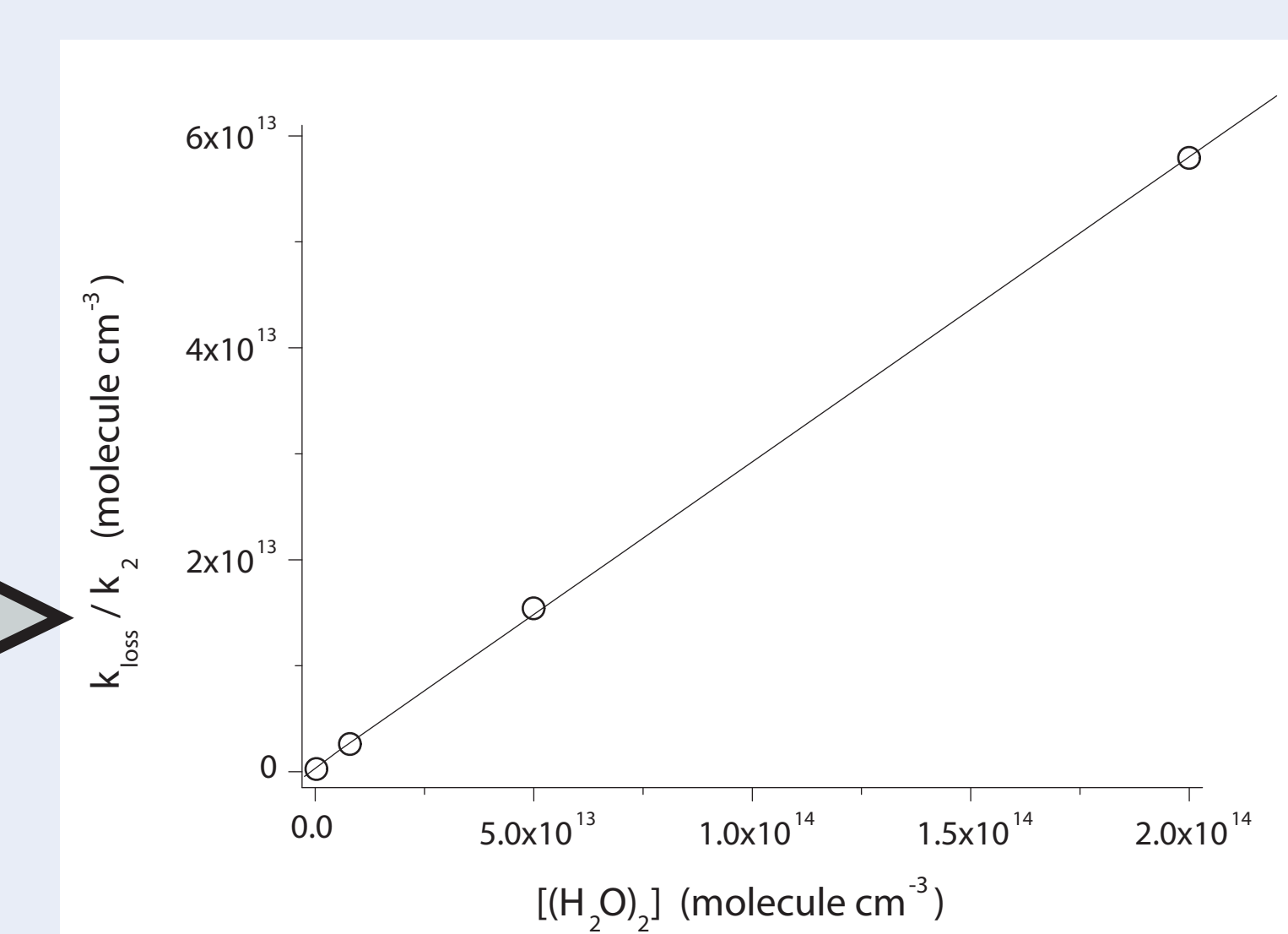
Experiments with variable CH_2OO production

Figure 3: CH_2OO steady-state concentrations (H_2SO_4) as a function of different $[C_2H_4]$, $(7.8 - 26) \cdot 10^{12}$ cm⁻³; $[O_3] = 2.2 \cdot 10^{11}$ cm⁻³, OH scavenger, RH = 0%. CH_2OO titration with SO_2 ($1.05 \cdot 10^{14}$ cm⁻³) at the the flow tube outlet.

- reaction in absence of SO_2 and water ($[H_2O] < 10^{14}$ cm⁻³)
- titration of $[CH_2OO]_{ss}$ at the tube outlet with SO_2 (presence of H_2O)

- $[CH_2OO]_{ss} = y_2 \cdot k_1 \cdot [O_3] \cdot [C_2H_4] / k_4$
- additional H_2SO_4 formation after SO_2 addition: $[H_2SO_4]_{additional} = y_2 \cdot k_1 \cdot [O_3] \cdot [C_2H_4] \cdot t$
- slope of $[H_2SO_4]_{total}$ vs. $k_1 \cdot [O_3] \cdot [C_2H_4]$: $y_2/k_4 + t$

- experimental: slope = 1.44 ± 0.05 s
- $y_2 = 0.4$, t ~ 0.4 s
→ $k_4 = 0.38 \pm 0.02$ s⁻¹ (only statistical error)
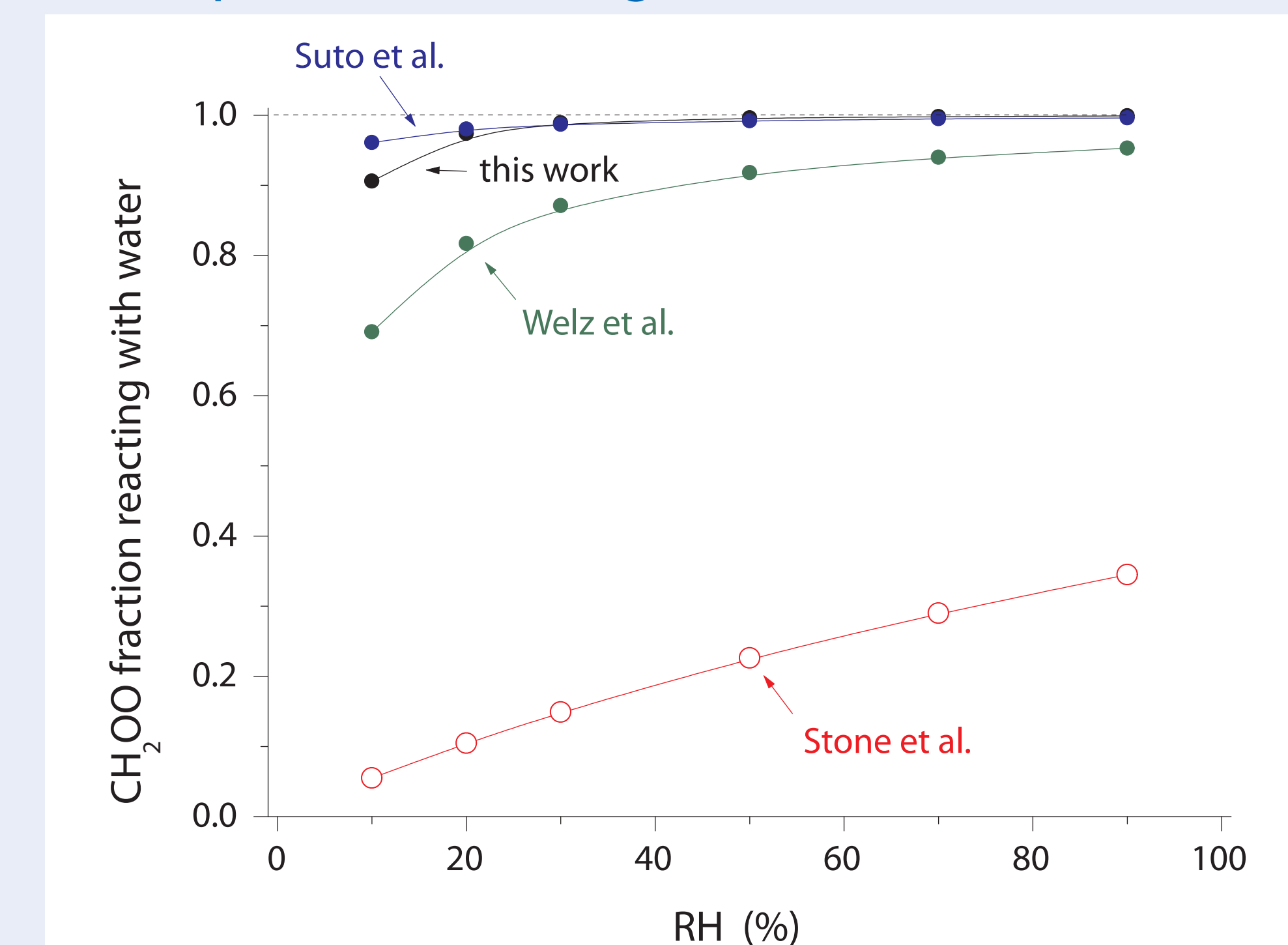
Atmospheric modelling

Figure 4: Modelling results of the CH_2OO fraction reacting with water vapour either via path (3a) or (3b), k-values from literature as stated, $[SO_2] = 10^{10}$ molecule cm⁻³.

References

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- Stone et al., PCCP, 16, 1193 (2014).
- Suto et al., Environ. Sci. Technol., 19, 815 (1985).
- Ryzhkov and Ariya, PCCP, 6, 5042 (2004).
- Olzmann et al., J. Phys. Chem. A, 101, 9421 (1997).
- Su et al., Nature Chem., doi10.1038/nchem.1890 (2014).
- Berndt et al., Atmos. Environ., 89, 603 (2014.

Summary and Conclusions

- The reaction of CH_2OO with water vapour is second order in $[H_2O]$ indicating a reaction of CH_2OO with the water dimer as favoured from quantum chemical calculations.

- The atmospheric fate of CH_2OO is governed by the reaction with water vapour. There are conflicting rate coefficients (or k-ratios) for k_{3a}/k_2 (k_{3b}/k_2) and k_4/k_2 in the literature.

- A comparison with the reactivity of CH_3CHOO and $(CH_3)_2COO$ (Berndt et al., 2014) shows a distinct sCI-structure dependent behaviour.

- A CH_2OO thermal lifetime at 293 K of about 3 s is deduced from CH_2OO steady-state measurements in agreement with theoretical calculations (Olzmann et al., 1997).