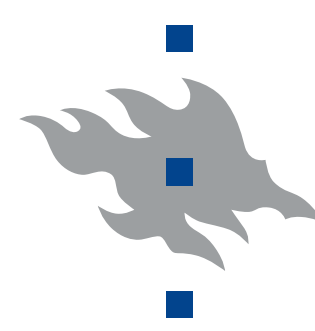# Kinetics of the unimolecular reaction of CH_2OO and its reactions with the water monomer, acetaldehyde and acetone at atmospheric conditions

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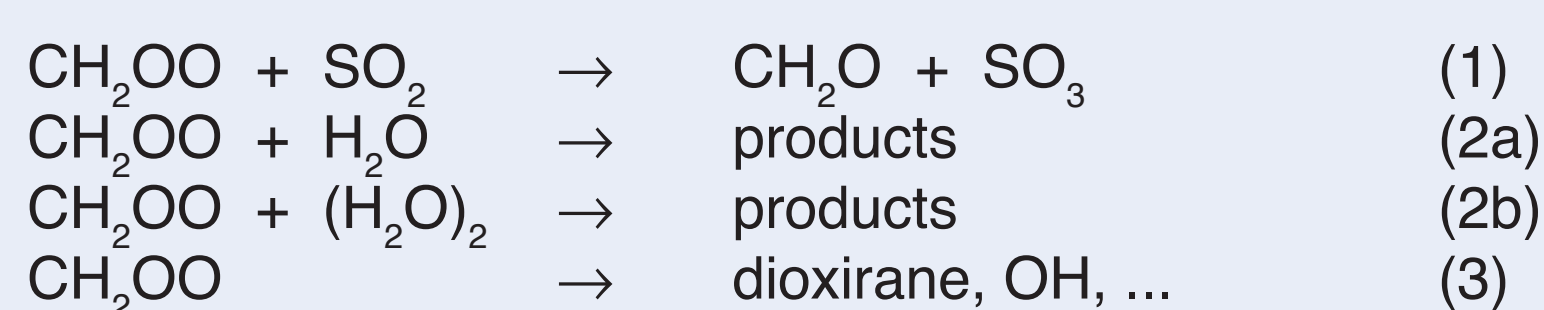3 Department of Physics, University of Helsinki, Helsinki 00014, Finland.

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Motivation

Stabilized Criegee Intermediates (sCI) have been identified as oxidants of atmospheric trace gases such as SO_2, NO_2, carboxylic acids or carbonyls. The atmospheric sCI concentrations, and accordingly their importance for trace gas oxidation, are controlled by the rate of the most important loss processes, very likely the unimolecular reactions and the reaction with water vapour (monomer and dimer) ubiquitously present in high concentrations in the troposphere.
For a reliable assessment of the importance of sCI reactions with SO_2, reaction (1), or other trace gases, the main loss processes in the atmosphere that control atmospheric sCI levels, must be accurately characterized. Most important loss paths are assumed to be the reaction with water vapour (monomer and/or dimer), reactions (2a) and (2b), and the unimolecular sCI reaction (decomposition forming dioxirane, OH and others), reaction (3):

$$CH_2OO + SO_2 \rightarrow CH_2O + SO_3 \quad (1)$$
$$CH_2OO + H_2O \rightarrow products \quad (2a)$$
$$CH_2OO + (H_2O)_2 \rightarrow products \quad (2b)$$
$$CH_2OO \rightarrow dioxirane, OH, ... \quad (3)$$

Recently, the reaction of CH_2OO with the water dimer has been identified as an important atmospheric sink of CH_2OO.[1,2]
It is the subject of this work to investigate the kinetics of the unimolecular reaction of CH_2OO and the bimolecular reaction with the water monomer under atmospheric conditions. CH_2OO is produced via the reaction of ozone with ethene:

$$O_3 + C_2H_4 \rightarrow y\, CH_2OO + ... \quad (4)$$
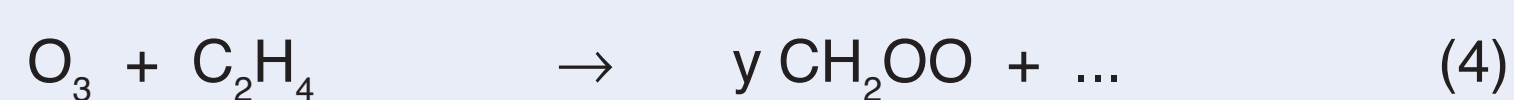
By performing kinetic measurements of the reaction of CH_2OO with acetaldehyde and acetone, the suitability of the chosen experimental approach (free-jet flow system) for the determination of absolute rate coefficients of sCI reactions is demonstrated.

Experiment

Free-jet flow system
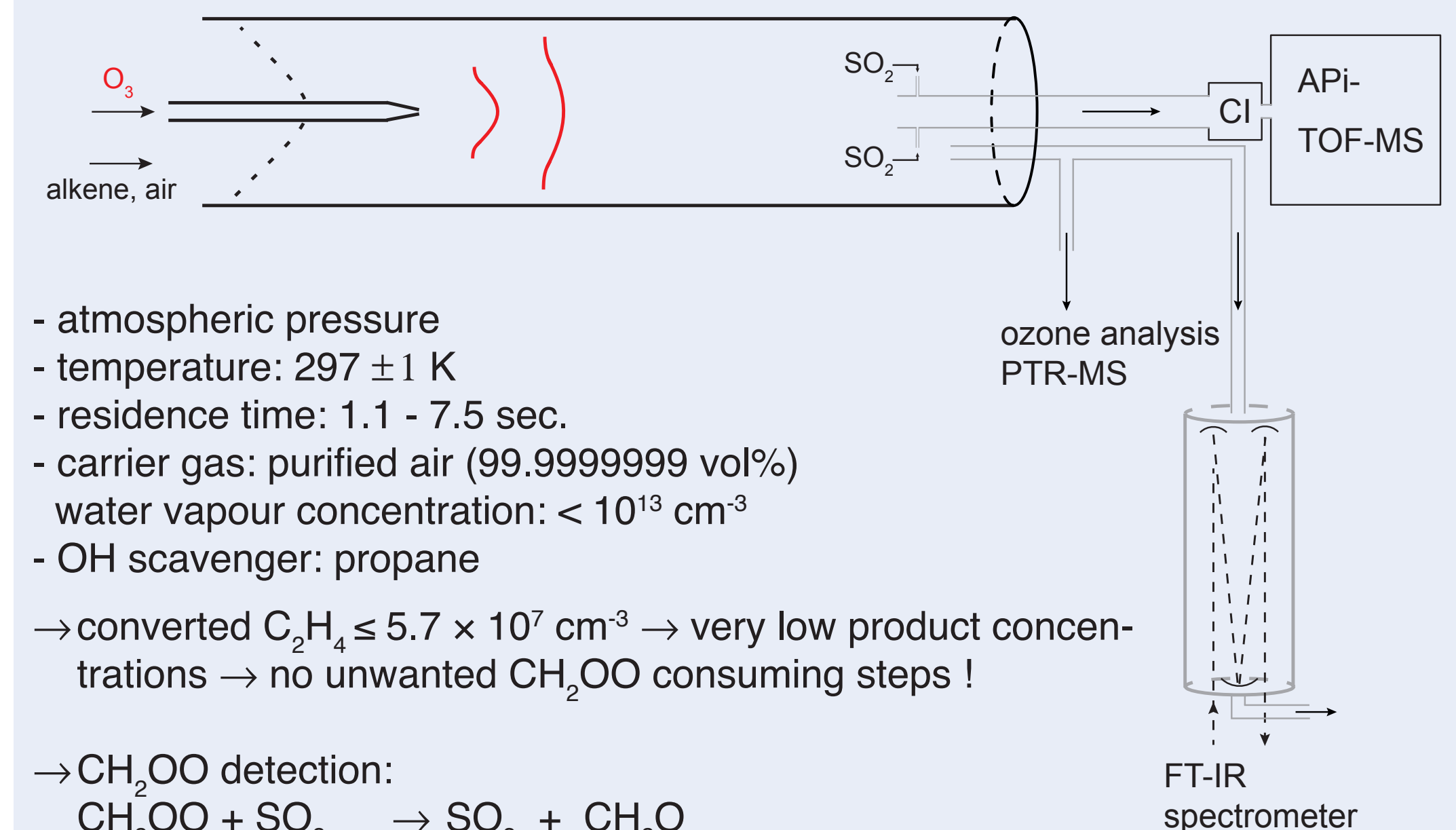
- atmospheric pressure
- temperature: 297 ± 1 K
- residence time: 1.1 - 7.5 sec.
- carrier gas: purified air (99.9999999 vol%)
  water vapour concentration: $< 10^{13}$ cm^{-3}
- OH scavenger: propane

$\rightarrow$ converted $C_2H_4 \leq 5.7 \times 10^7$ cm^{-3} $\rightarrow$ very low product concentrations $\rightarrow$ no unwanted CH_2OO consuming steps !

$\rightarrow$ CH_2OO detection:
$$CH_2OO + SO_2 \rightarrow SO_3 + CH_2O$$
$$SO_3 + 2\, H_2O \rightarrow H_2SO_4 + H_2O$$

H_2SO_4 detection: NO_3^--CI-APi-TOF; detection limit: $\sim 10^4$ cm^{-3}

Results and Discussion
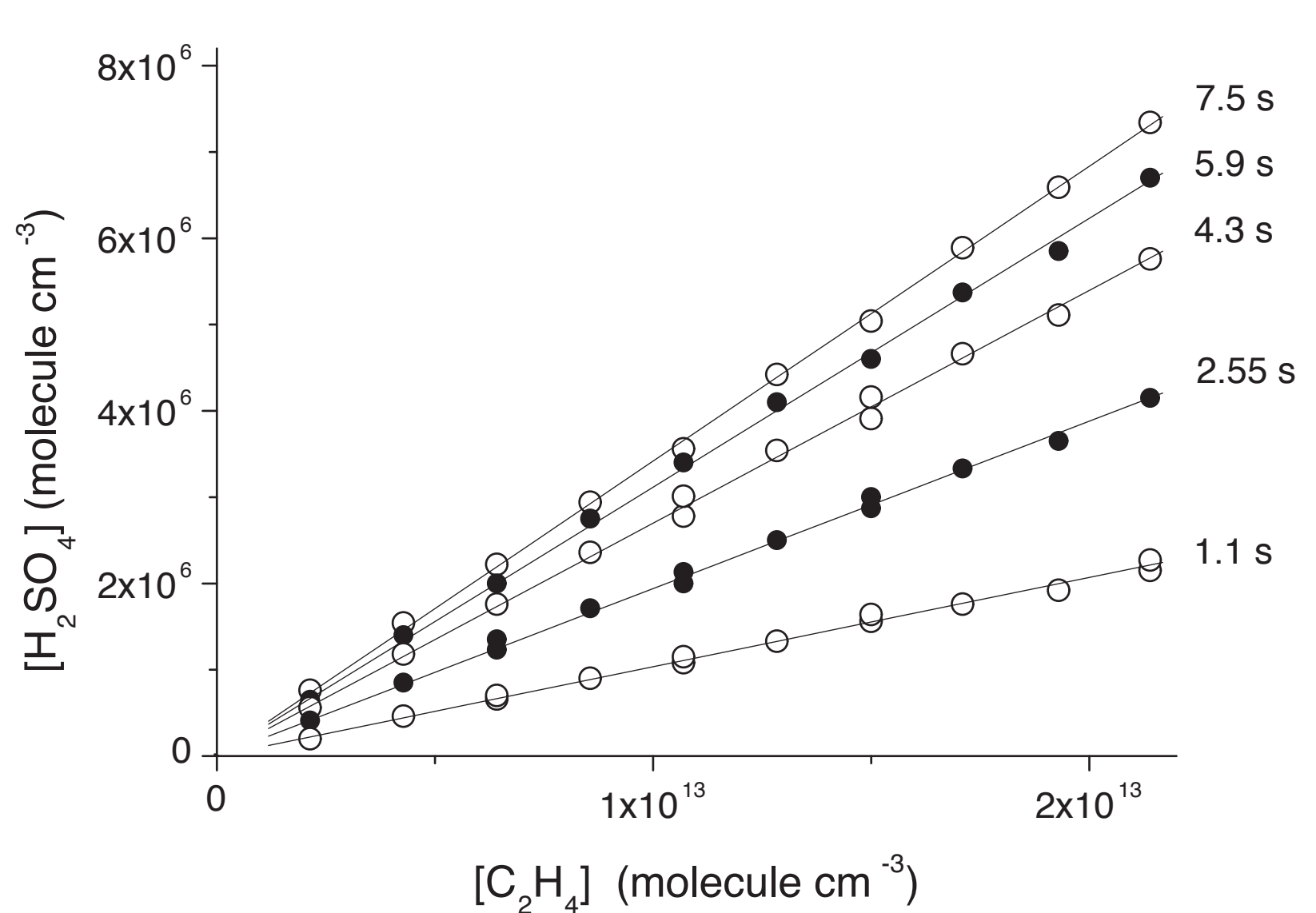
Unimolecular reaction of CH_2OO

Fig.1: H_2SO_4 (CH_2OO) concentrations as a function of the ethene concentration for different reaction times. Distinct time dependence indicates $k_3 < 1$ s^{-1}. For comparison, a few experiments with CH_3CHOO (syn and anti) show no time dependence in this time range pointing to $k_3 > 3$ s^{-1}.
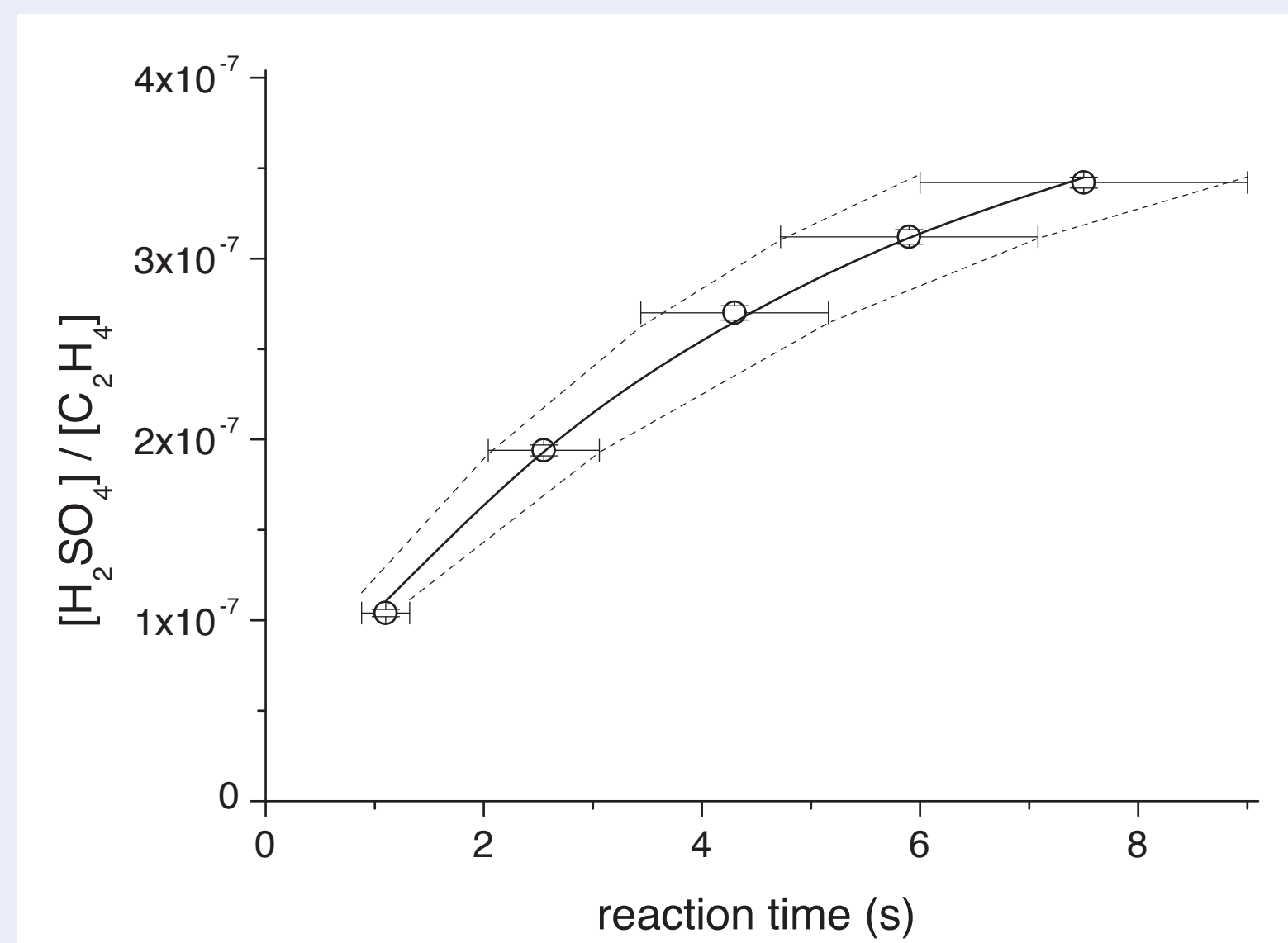

Fig.2: Experimentally obtained ratios $[H_2SO_4] / [C_2H_4]$ as a function of time from the data given in Fig.1. Data analysis according to equ.(III) yields $k_3 = (0.19 \pm 0.04)$ s^{-1} (full line). Sensitivity study (dashed lines, uncertainty of reaction time) leads to extended error limits, $k_3 = (0.19 \pm 0.07)$ s^{-1}.

Kinetic analysis:
$\rightarrow$ CH_2OO is only consumed by the unimolecular reaction (3):
solution of the resulting differential equation from reactions (4) and (3) for very small conversion of O_3 and C_2H_4 ($< 0.025\%$ in the experiments) gives:

$$[CH_2OO] = \frac{1 - \exp(-k_3 t)}{k_3}\, y\, k_4 [O_3][C_2H_4] \qquad eq.(I)$$

$\rightarrow$ CH_2OO is converted to H_2SO_4 by SO_2 titration with a yield of 85%, additional H_2SO_4 formation in the inlet after SO_2 addition with $t^{add} = 0.4$ s (ozonolysis is still running):

$$[H_2SO_4] = \left\{ 0.85 \frac{1 - \exp(-k_3 t)}{k_3} + t^{add} \right\} y\, k_4 [O_3][C_2H_4] \qquad eq.(II)$$

$\rightarrow$ for the experimentally obtained ratio $[H_2SO_4] / [C_2H_4]$ and setting $y\, k_4 [O_3] = k_4'$ for constant $[O_3]$, it follows:

$$\frac{[H_2SO_4]}{[C_2H_4]} = \left\{ 0.85 \frac{1 - \exp(-k_3 t)}{k_3} + t^{add} \right\} k_4' \qquad eq.(III)$$

Results:
$\rightarrow$ $k_3 = (0.19 \pm 0.07)$ s^{-1} (time dependent measurement)
$k_3 = (0.23 \pm 0.12)$ s^{-1} (steady-state CH_2OO conditions, t = 39 s)
$k_3 = 0.04 - 0.26$ s^{-1} (quantum-chemical and statistical rate theory calculations)

literature: $k_3 \leq 4.6$ s^{-1} (Newland et al.[3])
$k_3 \leq (11.6 \pm 8.0)$ s^{-1} (Chhantyal-Pun et al.[4])

Reaction of CH_2OO with water monomer
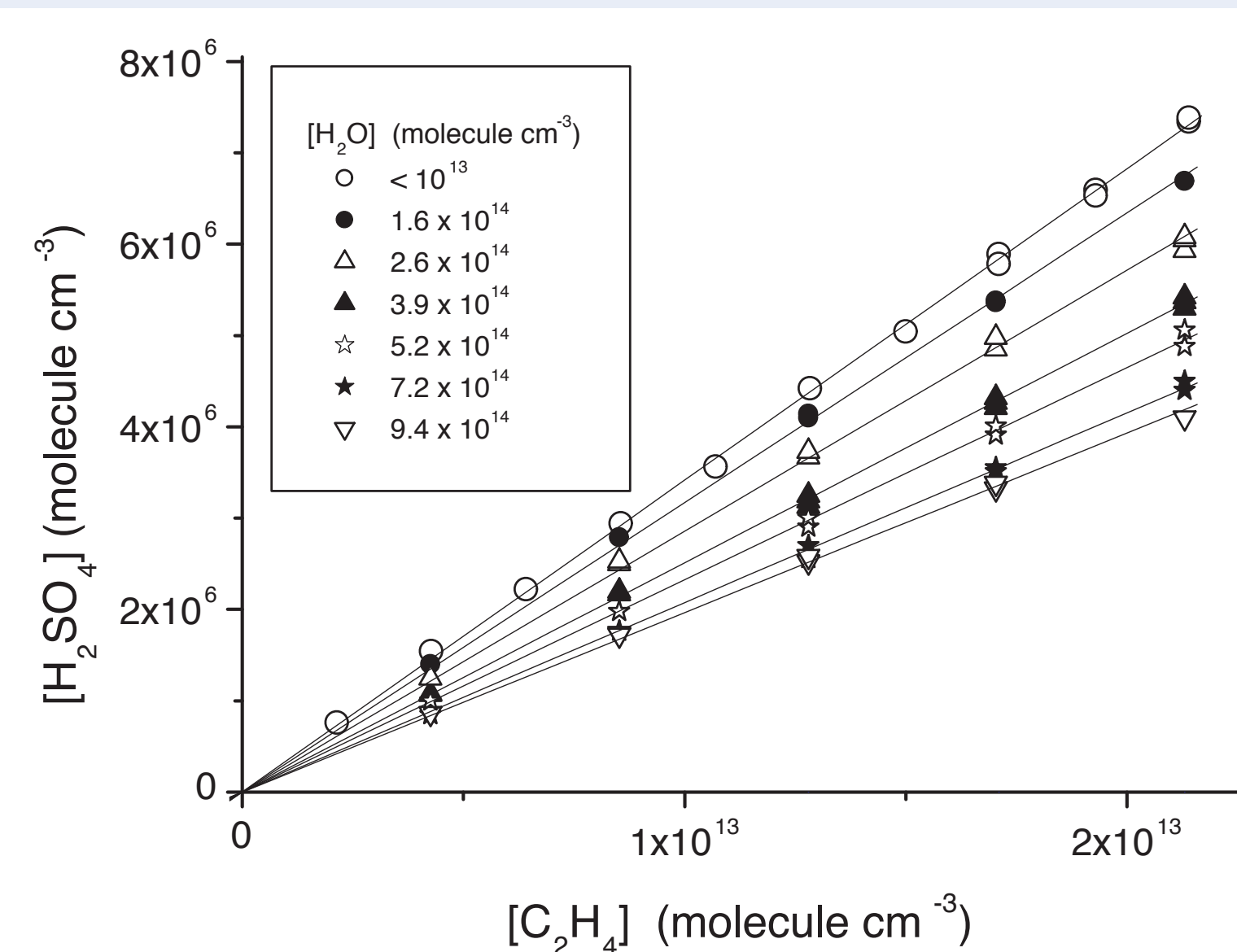
Fig.3: H_2SO_4 concentration as a function of ethene concentration for different H_2O concentrations, t = 7.5 s, $[O_3] = 2.3 \times 10^{11}$ cm^{-3}. Low water concentrations of $[H_2O] < 10^{15}$ cm^{-3} and, as a consequence, very low water dimer concentrations of $[(H_2O)_2] < 2.5 \times 10^9$ cm^{-3}, allow separation of reaction (2a) from reaction (2b).[1,2] $r_{2b} < 1/20\, r_{2a}$

$\rightarrow$ CH_2OO is consumed by the unimolecular reaction (3) and by the reaction with the water monomer (2a) resulting in eq.(IV):

$$\frac{[H_2SO_4]}{[C_2H_4]} = \left\{ 0.85 \frac{1 - \exp(-\{k_3 + k_{2a}[H_2O]\}\, t)}{k_3 + k_{2a}[H_2O]} + t^{add} \right\} k_4'$$

$\rightarrow$ Data from Fig.3 gave $[H_2SO_4] / [C_2H_4]$ ratios as a function of $[H_2O]$ for fixed t = 7.5 s. Nonlinear regression analysis:
$k_{2a} = (3.2 \pm 0.5) \times 10^{-16}$ cm^3 s^{-1}

Results:
$\rightarrow$ $k_{2a} = (3.2 \pm 1.2) \times 10^{-16}$ cm^3 s^{-1} (incl. error propagation)

literature: $\rightarrow$ wide range of k_{2a} values !
$k_{2a} = 1.3 \times 10^{-15}$ cm^3 s^{-1} [3] - 5.4×10^{-18} cm^3 s^{-1} [5]

Consequences:
$\rightarrow$ Reaction of CH_2OO with water monomer (2a) cannot compete with the reaction of the water dimer (2b).

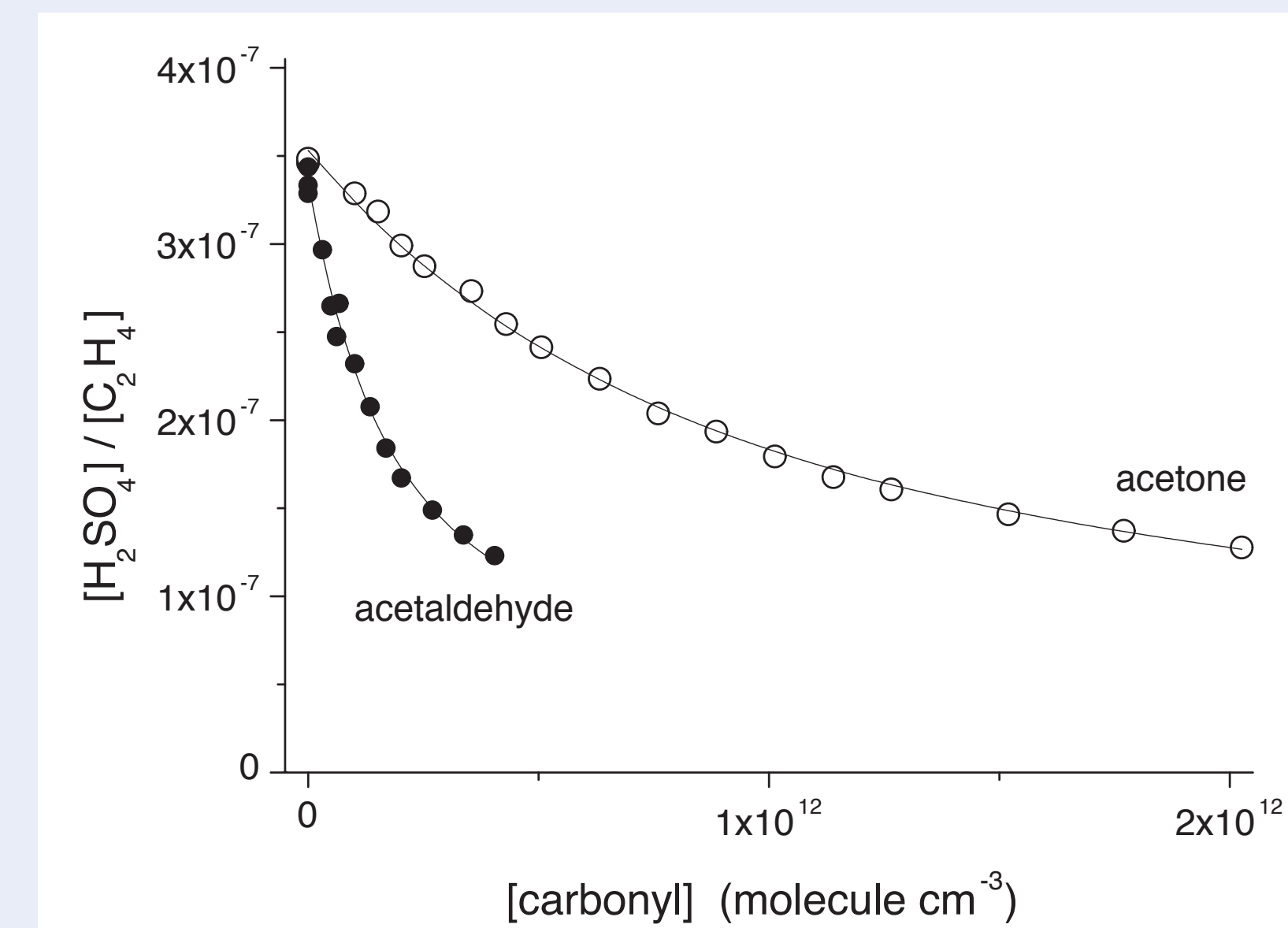### Reaction of CH_2OO with acetaldehyde and acetone

Fig.4: $[H_2SO_4] / [C_2H_4]$ as a function of carbonyl concentrations. The curves represent the best-fit results according to modified eq.(IV). t = 7.5 s, $[O_3] = 2.3 \times 10^{11}$, $[C_2H_4] = 2.14 \times 10^{13}$ cm^3 s^{-1}.

$\rightarrow$ CH_2OO is consumed by the unimolecular reaction (3) and by the reaction with the carbonyls (instead of the H_2O reaction):

Results:
$\rightarrow$ $k_{CH2OO+acetald} = (1.7 \pm 0.5) \times 10^{-12}$ cm^3 s^{-1} (incl. error propagation)
lit.:$k_{CH2OO+acetald} \sim 1.7 \times 10^{-12}$ cm^3 s^{-1} [5] (high-pressure limit)

$\rightarrow$ $k_{CH2OO+acetone} = (3.4 \pm 0.9) \times 10^{-13}$ cm^3 s^{-1} (incl. error propagation)
lit.:$k_{CH2OO+acetone} = (2.3 \pm 0.3) \times 10^{-13}$ cm^3 s^{-1} [6]

$\rightarrow$ good agreement of our results with literature data

Consequences:
$\rightarrow$ free-jet flow system is suitable for the determination of CH_2OO rate coefficients.

References

- (1) Chao, et al., Science, 2015, 347, 751-754.
- (2) Berndt et al., PCCP, 2014, 16, 19130-19136.
- (3) Newland et al., PCCP, 2015, 17, 4076-4088.
- (4) Chhantyal-Pun et al., PCCP, 2015, 17, 3617-3626.
- (5) Stone et al., PCCP, 2014, 16, 1139-1149.
- (6) Taatjes et al., PCCP, 2012, 14, 10391-10400.

Summary

$\Rightarrow$ The unimolecular reaction of CH_2OO, reaction (3), is very slow, $k_3 = (0.19 \pm 0.07)$ s^{-1}, and can be neglected in atmospheric modelling.

$\Rightarrow$ Reaction of CH_2OO with water monomer, reaction (2a), $k_{2a} = (3.2 \pm 1.2) \times 10^{-16}$ cm^3 s^{-1}, is less efficient compared with the reaction of the water dimer.

$\Rightarrow$ The good agreement of our results for $k_{CH2OO+acetald}$ and $k_{CH2OO+acetone}$ with literature data indicates that the free-jet flow system is suitable for the determination of rate coefficients of uni- and bimolecular reactions of CH_2OO.