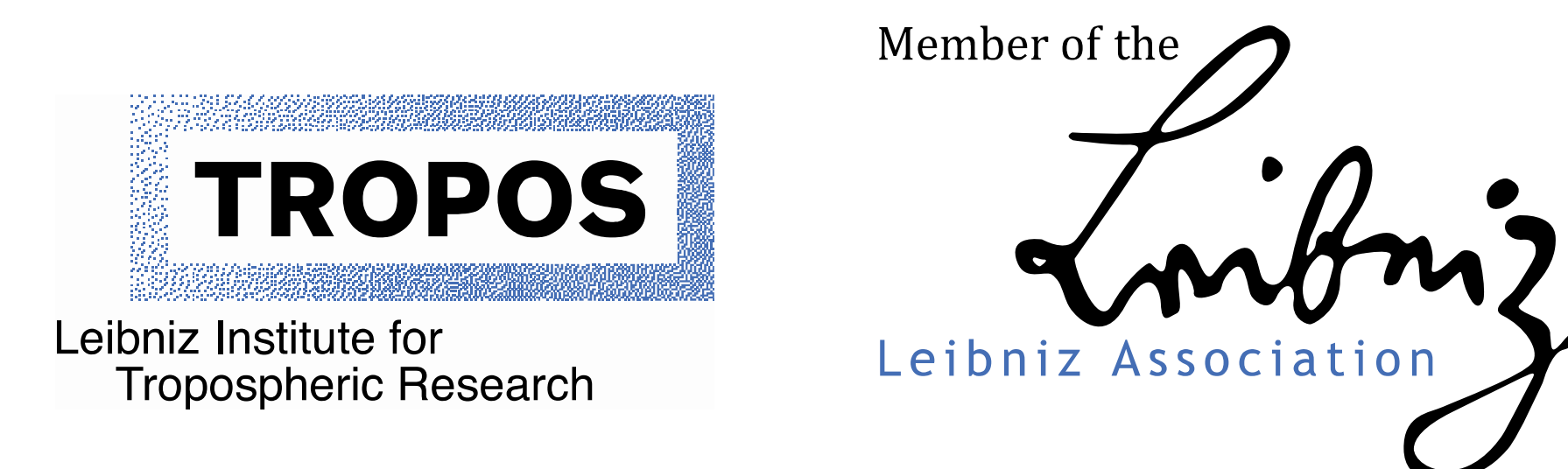


Reactions of important VOCs with hydrogen peroxide and ozone in the tropospheric aqueous phase

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Introduction

Besides research on the microphysics of cloud droplets and similar aqueous systems in the troposphere, **the chemistry of volatile organic compounds (VOCs)** from anthropogenic and biogenic sources **cannot be neglected** for the understanding of tropospheric processes such as the organic particle mass formation. Emissions of biogenic volatile organic compounds (BVOCs) can exceed those of VOCs from anthropogenic sources by a factor of 10^{11} .

Oxidation products of BVOCs like **glyoxal, methylglyoxal, glycolate, glyoxylate and pyruvate, glycolaldehyde, and the unsaturated compounds methacrolein and methyl vinyl ketone** are known precursors for less volatile organic substances found in secondary organic aerosols [2,3]. Yet, the main decomposition of these substances is believed to occur via radical reactions. However, Tilgner and Herrmann [2] showed evidence that the **turnovers by non-radical reactions with H_2O_2 or ozone** and some non-oxidative organic accretion reactions **may even exceed those from the most reactive species** in the lower troposphere, **the hydroxyl radical OH** (see Fig. 1).

As there are only estimations or thermodynamical calculations available, measurements on non-radical reactions with hydrogen peroxide and ozone are conducted within this contribution to gain more input data for future modelling studies (e.g., in CAPRAM) in order to improve prediction tools.

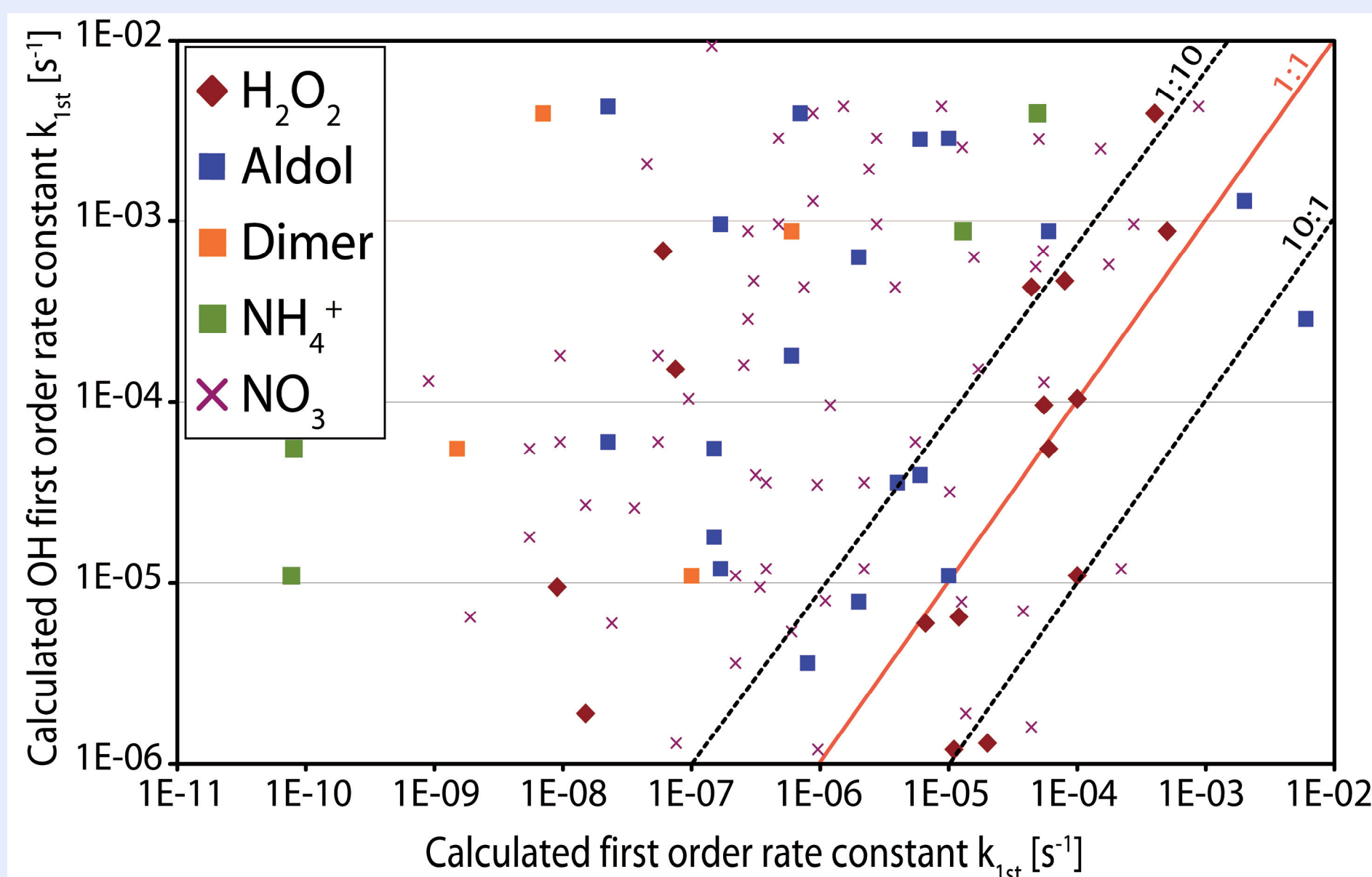


Fig. 1: Calculated turnovers of different reaction types (see legend) compared to OH-radical reactions (y-axis). Reaction partners are similar to this work's.

Experimental

Methods used for kinetic investigation:

- **UV/Vis spectroscopy** with dual beam spectrometer (Perkin Elmer, Lambda 900)
 - For slow reactions with hydrogen peroxide and ozone
- **Stopped Flow** (SF-61DX2, HI-TECH Scientific, also UV/Vis, Fig. 2)
 - For fast reactions of ozone with unsaturated compounds
- **Capillary electrophoresis** (CE, Agilent 7100, Agilent Technologies, Fig. 3)
 - For reactions of hydrogen peroxide with pyruvic acid/ pyruvate and glyoxylic acid/glyoxylate

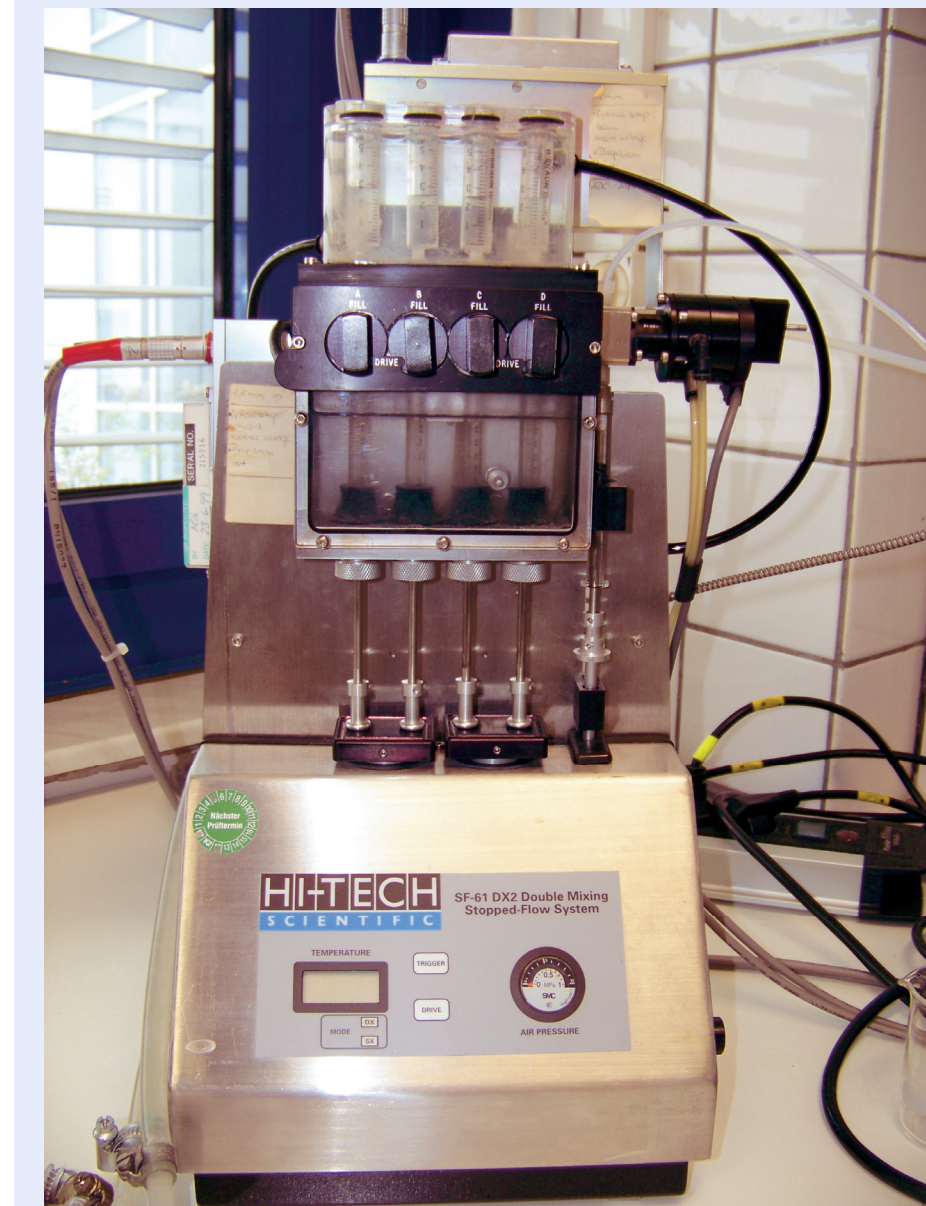


Fig. 2: Sample handling unit of the Stopped Flow system.

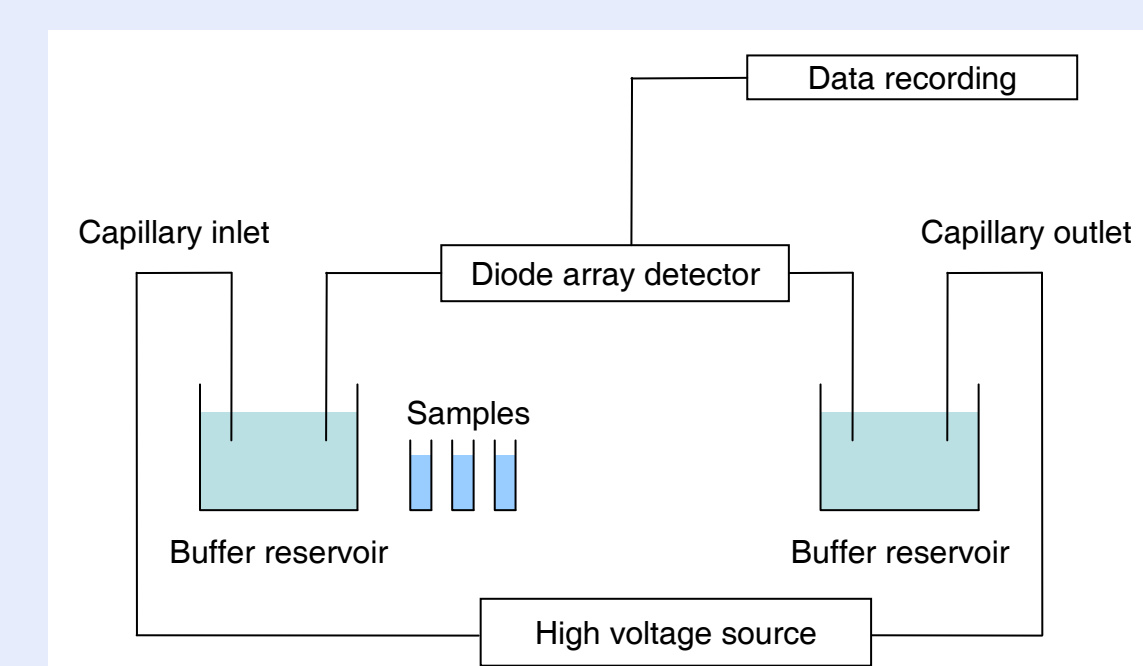


Fig. 3: Working scheme of a capillary electrophoresis system (based on Engelhardt et al., 1994 [4]).

Kinetics investigated under pseudo-first order conditions

- Reactions with ozone: reactant in excess
 - Absorbance of ozone monitored at $\lambda = 260 \text{ nm}$, $\epsilon_{O_3, 260 \text{ nm}} = 3300 \text{ M}^{-1} \text{ cm}^{-1}$ [5]
- Reactions with hydrogen peroxide: usually hydrogen peroxide in excess
 - Absorbance of the reactant monitored at an appropriate wavelength
 - Concentration of the acid monitored by CE
- Variation of the compound in excess to obtain the second order rate constant
- CE measurements: Reaction stopped by adding catalase to destroy H_2O_2 in the samples
- Indication of possible products via CE

Results and discussion

Kinetic investigations

- Experimental conditions: $T = 298 \text{ K}$, ambient air pressure, pH as given in Table 1
- Some reactions too slow to be measured
- Rather small rate constants observed, $k_{2nd} \leq 2.3 \text{ M}^{-1} \text{ s}^{-1}$
- Larger rate constants for reactions of ozone with unsaturated compounds (methacrolein, methyl vinyl ketone, Fig. 5)
- Deliberately omitted scavenger leads to highly overestimated rate constants during the reaction of glyoxylic acid with ozone (Fig. 4)
 - OH scavengers are essential for the investigation of ozone reactions
- Good agreement with values from Hoigné and Bader (1983)
 - Adoption of the method to similar reactions

Substance	Oxidant	$k_{2nd} / \text{M}^{-1} \text{s}^{-1}$	
		H_2O_2	O_3
Glycolic acid pH = 1	-	-	0.055 ± 0.015
Glycolate pH = 7	-	-	0.71 ± 0.05
Glyoxylic acid pH = 1	-	0.004 ± 0.001	0.14 ± 0.06
Glyoxylic acid/Glyoxylate pH = 3	-	-	0.53 ± 0.12
Glyoxylate pH = 7	-	0.11 ± 0.01	2.3 ± 0.6
Pyruvic acid pH = 1	-	0.12 ± 0.04	0.13 ± 0.04
Pyruvate pH = 7	-	0.75 ± 0.16	0.98 ± 0.35
Glycolaldehyde	-	0.04 ± 0.02	0.56 ± 0.15
Glyoxal	-	$(1.7 \pm 0.8) \cdot 10^4$	0.9 ± 0.17
Methylglyoxal	-	-	2.9 ± 0.7
Methacrolein	-	0.07 ± 0.03	$(2.1 \pm 0.9) \cdot 10^6$
Methyl vinyl ketone	-	-	$(9.6 \pm 0.9) \cdot 10^4$

Table 1: Second order rate constants for the investigated systems.

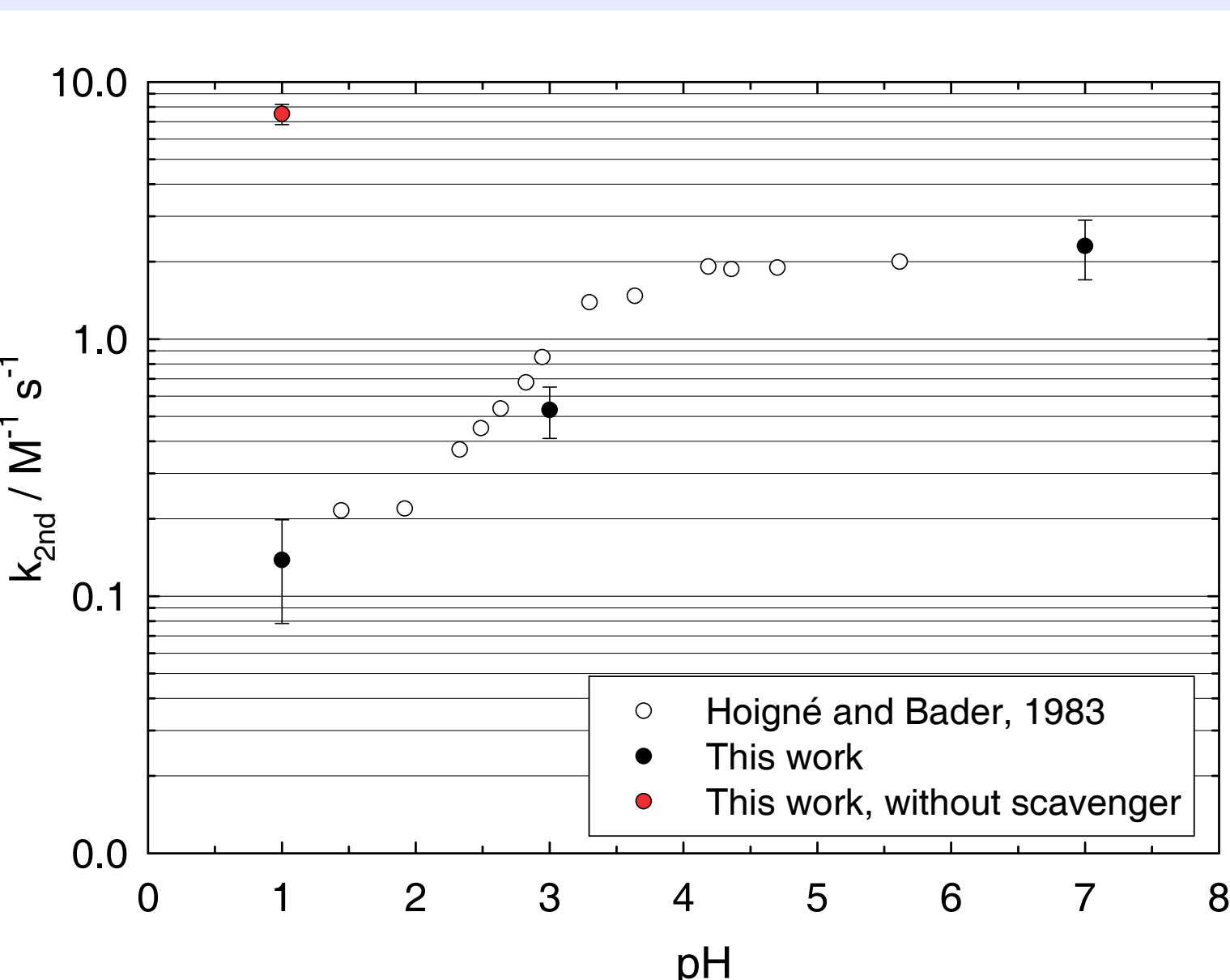


Fig. 4: Reaction of glyoxylic acid/glyoxylate with ozone: pH-dependence and comparison of this work's results (black dots) to literature values from Hoigné and Bader (1983) (white dots). The red dot labels the highly overestimated rate constant if no OH-scavenger is added to the solution.

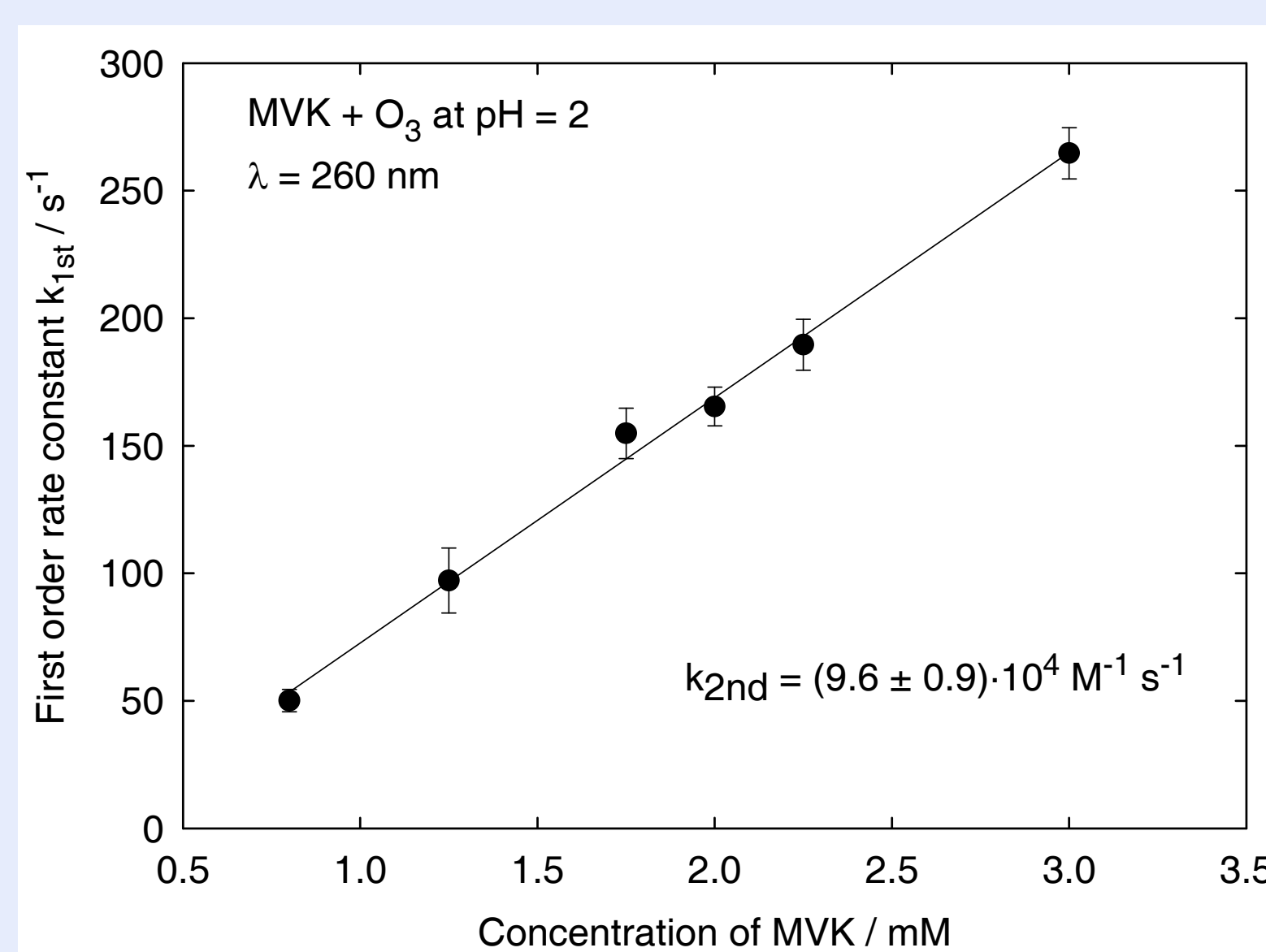


Fig. 5: Reaction of methyl vinyl ketone with ozone: Determination of the second order rate constant.

Mechanistic considerations

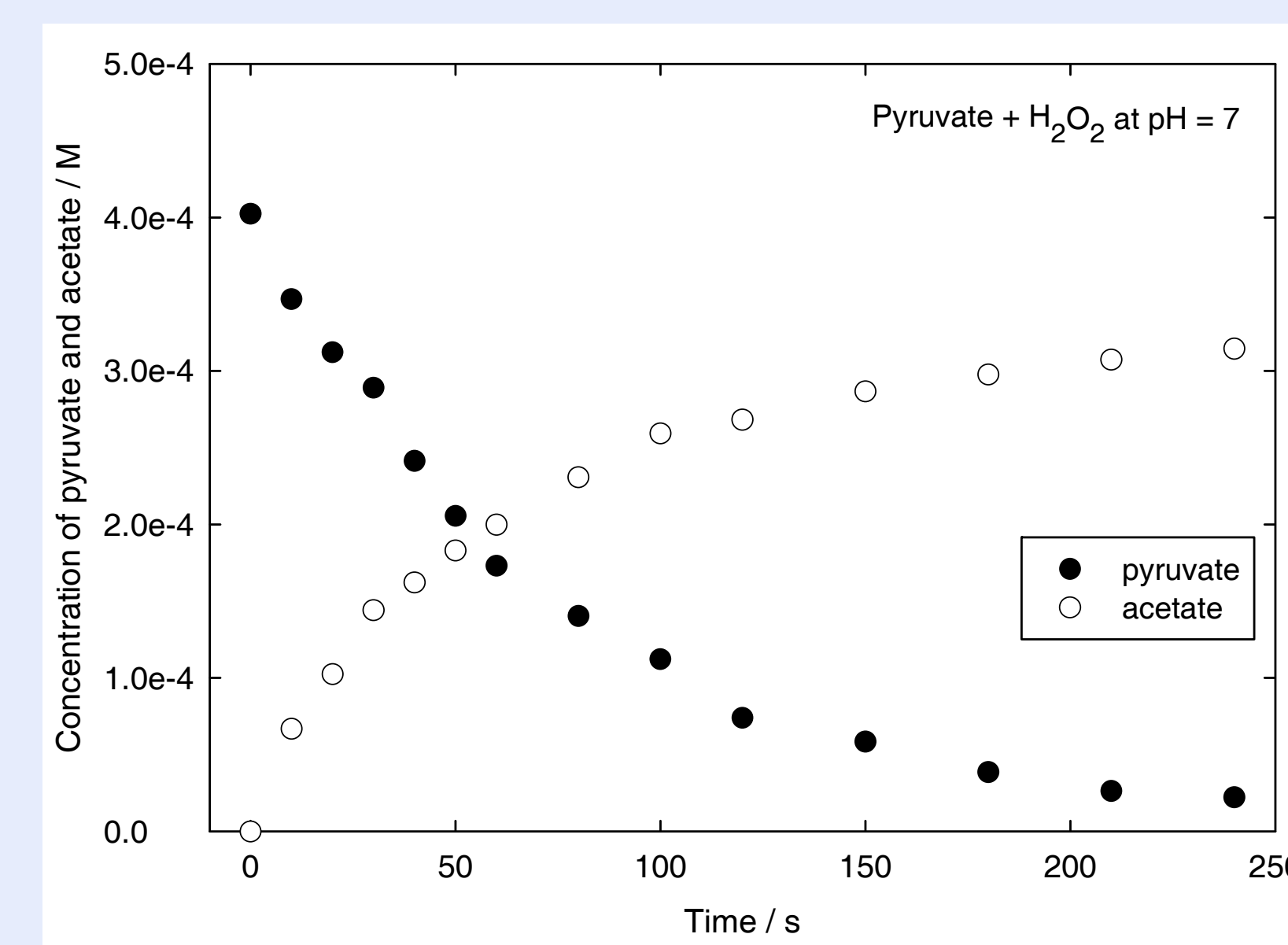
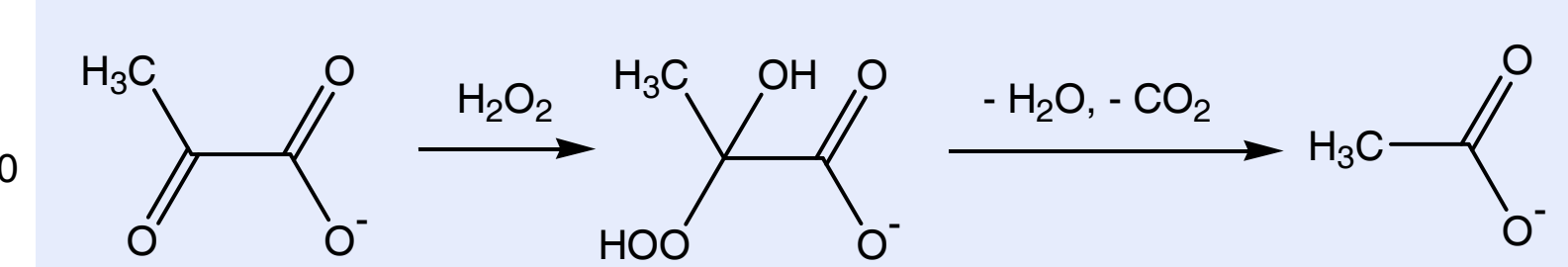


Fig. 6: Temporal evolution of pyruvate and acetate concentrations during the reaction of hydrogen peroxide with pyruvate.

- CE measurements indicate the formation of acetic acid during the reaction of hydrogen peroxide with pyruvate (Fig. 6)
- Scheme 1 according to Stefan and Bolton (1999) [6] suggests the addition of hydrogen peroxide to the double bond of the carbonyl group with subsequent C-C-bond cleavage leading to acetate, water and CO_2
- Same mechanism also postulated by von Sonntag and Schuchmann (1997) [7]
- Acetate end concentration smaller than initial pyruvate concentration indicates possibly further reactions of this reaction product



Scheme 1: Reaction mechanism of the reaction of pyruvate with hydrogen peroxide.

Comparison with model studies

- Concentrations of non-radical oxidants are much higher than radical concentrations in cloud droplets and aqueous particles (~10 orders of magnitude difference, Table 2)
 - Calculation of turnovers (s^{-1}) for an urban cloud droplet (Fig. 7)

$$k_{1st} = k_{2nd} \cdot c(\text{oxidant})$$
- Glyoxylate, pyruvic acid and pyruvate reactions with H_2O_2 show similar or higher turnovers than OH radical reaction turnovers
- Glycolaldehyde, glyoxylic acid, glyoxylate, pyruvic acid, pyruvate and methacrolein are competitive with NO_3 radical reaction turnovers
- Turnovers of ozone reactions only important for unsaturated compounds

Substance	Concentration / M			
	Urban		Remote	
	Cloud droplet	Aqueous particle	Cloud droplet	Aqueous particle
OH	$1.0E-14$	$8.0E-13$	$5.0E-14$	$3.6E-12$
NO_3	$2.0E-13$	$2.5E-13$	$5.0E-15$	$8.0E-13$
H_2O_2	$1.0E-04$	$4.0E-04$	$6.0E-05$	$4.0E-04$
O_3	$2.0E-09$	$3.0E-09$	$8.0E-10$	$8.0E-10$

Table 2: Concentration of some oxidants at different regimes. Values from CAPRAM3.0i, 20 - 44 h reaction time.

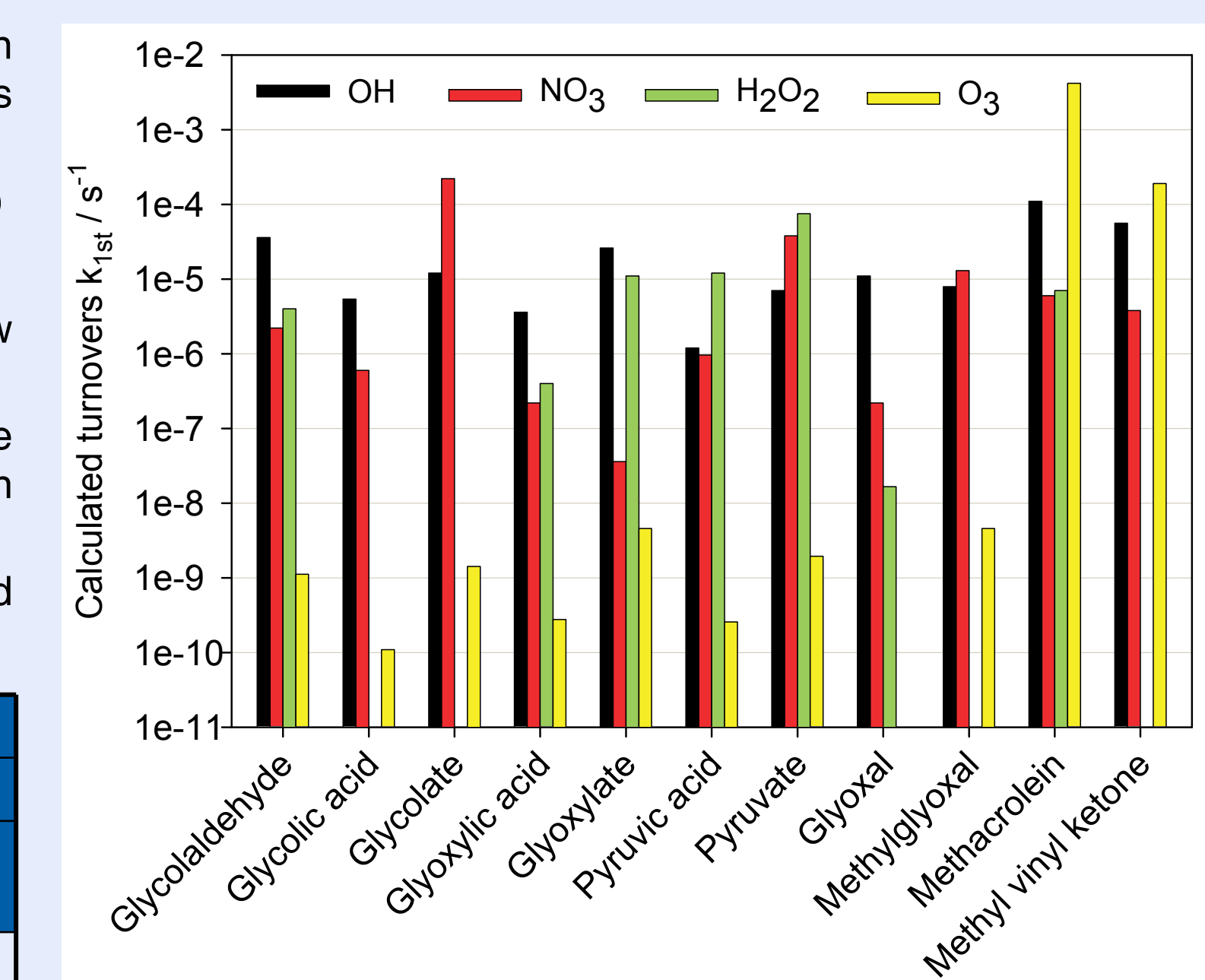


Fig. 7: Calculated turnovers (s^{-1}) for the investigated non-radical reactions from this work under urban cloud conditions. Rate constants (k_{2nd}) for the calculation of radical reaction turnovers taken from Tilgner and Herrmann (2010).

Conclusions

- Non-radical reactions of various carbonyl compounds with hydrogen peroxide and ozone were investigated via UV/Vis spectroscopy or capillary electrophoresis
- Kinetic measurements indicate that non-radical reaction rate constants ($M^{-1} s^{-1}$) are much smaller compared to radical reactions ($k_{OH} \sim 10^9 M^{-1} s^{-1}$, see Table 1)
- Calculated turnovers (s^{-1}) include urban cloud water concentrations of the different oxidants
 - In some cases turnovers of hydrogen peroxide reactions are similar or even larger than those for OH (see Fig. 8)
 - In further cases turnovers of hydrogen peroxide reactions are much larger than NO_3 reaction turnovers (see Fig. 7)
 - Turnovers of ozone reactions are only competitive when unsaturated compounds like methacrolein and methyl vinyl ketone are considered
- Owing to CE measurements proposed reaction mechanisms from literature could be validated

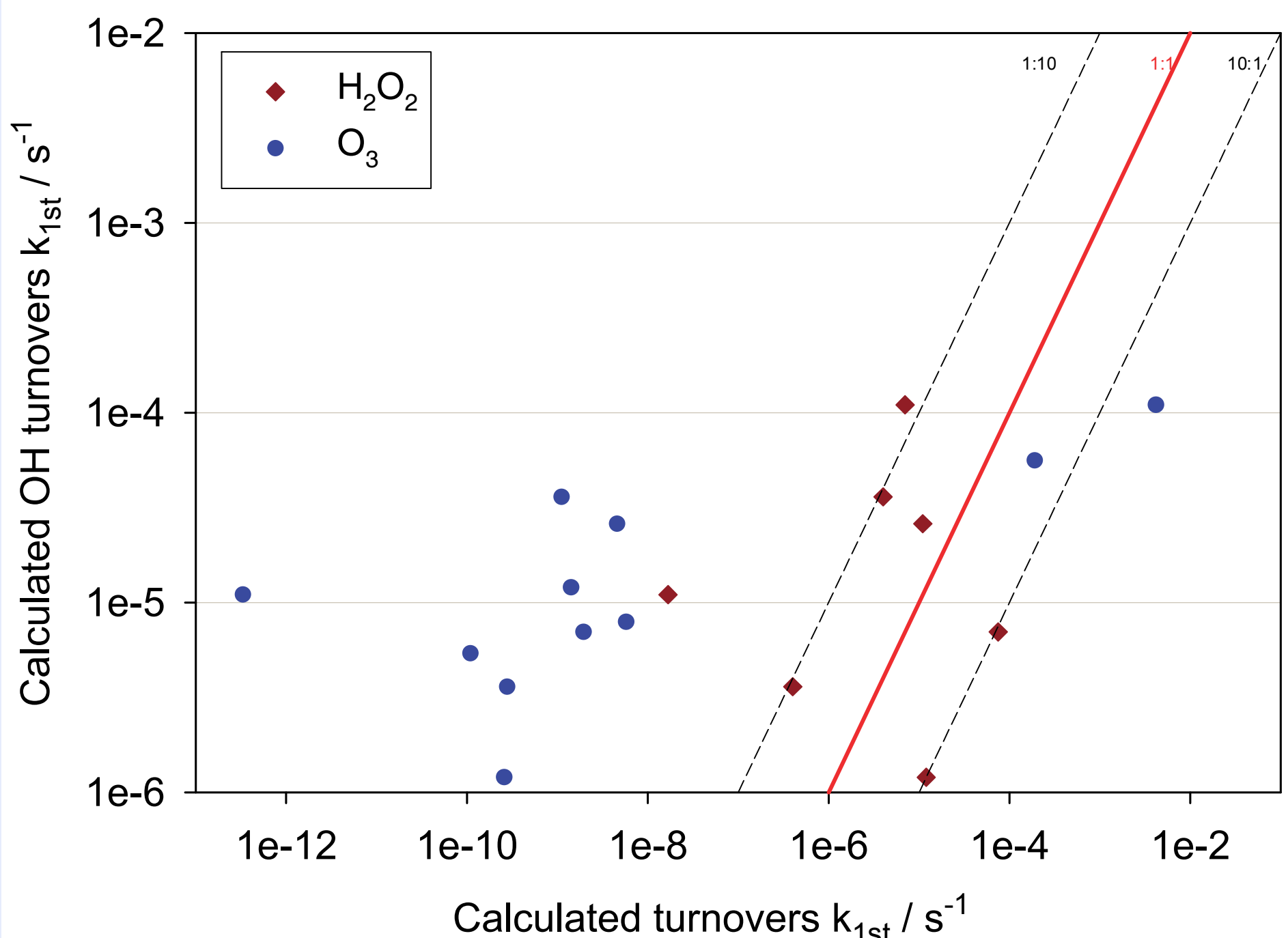


Fig. 8: Calculated turnovers of hydrogen peroxide and ozone reactions from this work (x-axis) compared to OH-radical reactions from literature (y-axis).

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