OH radical reactions with oxygenated organic compounds in aqueous solution: A laser flash photolysis investigation

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Motivation

- Degradation and conversion processes of organic compounds are often initiated by radical reactions.
- These can occur in the gas phase as well as in the aqueous phase of the troposphere, which is formed by cloud droplets, fog, haze, rain or hygroscopic particles containing 'aerosol liquid water (ALW)'.
- As a result of biogenic or anthropogenic sources oxygenated organic compounds are omnipresent in the troposphere.
- In the present study, the temperature-dependent rate constants of the OH radical reactions with oxygenated organic compounds in the aqueous phase have been investigated. (**Schaefer and Herrmann, 2018**)
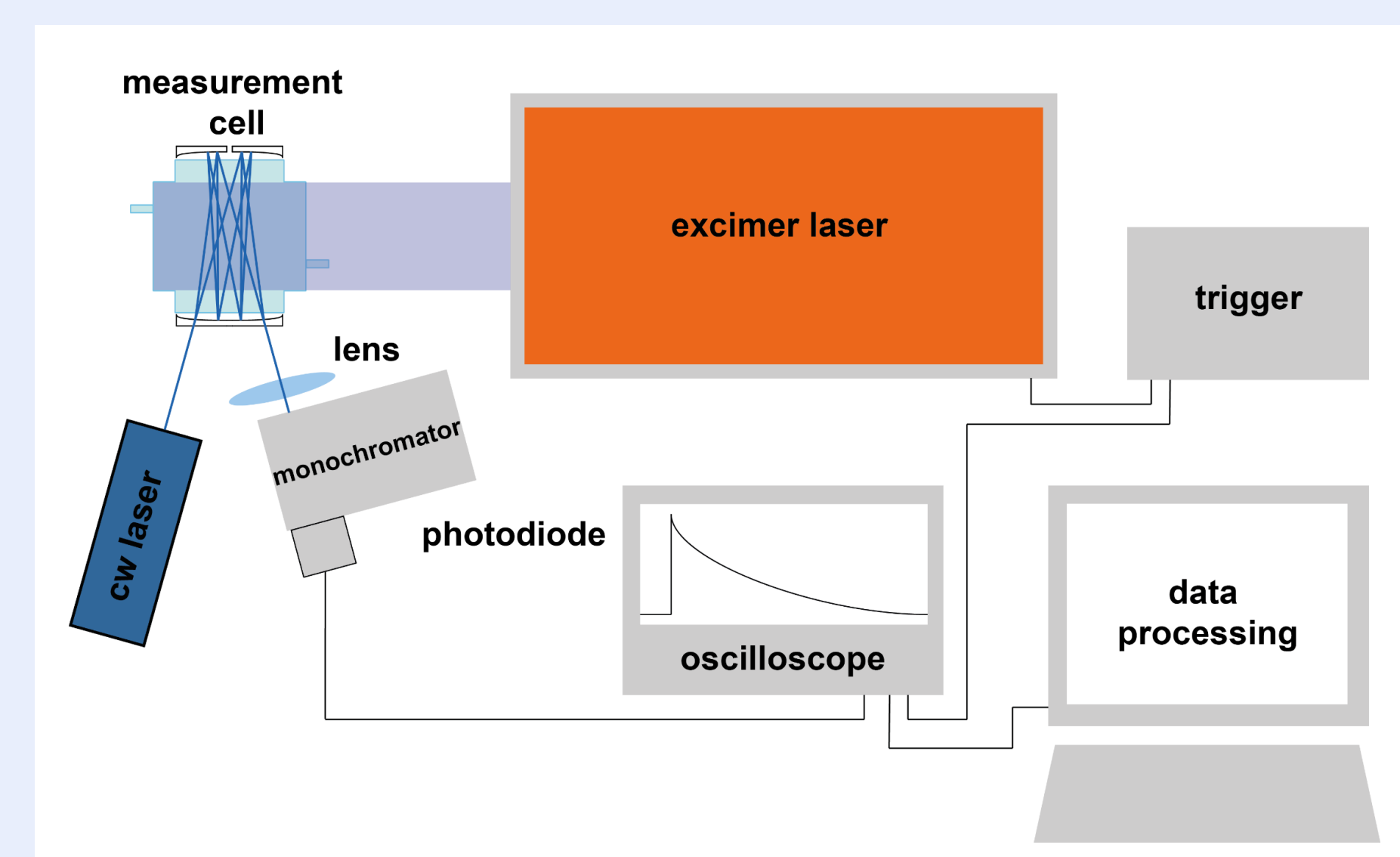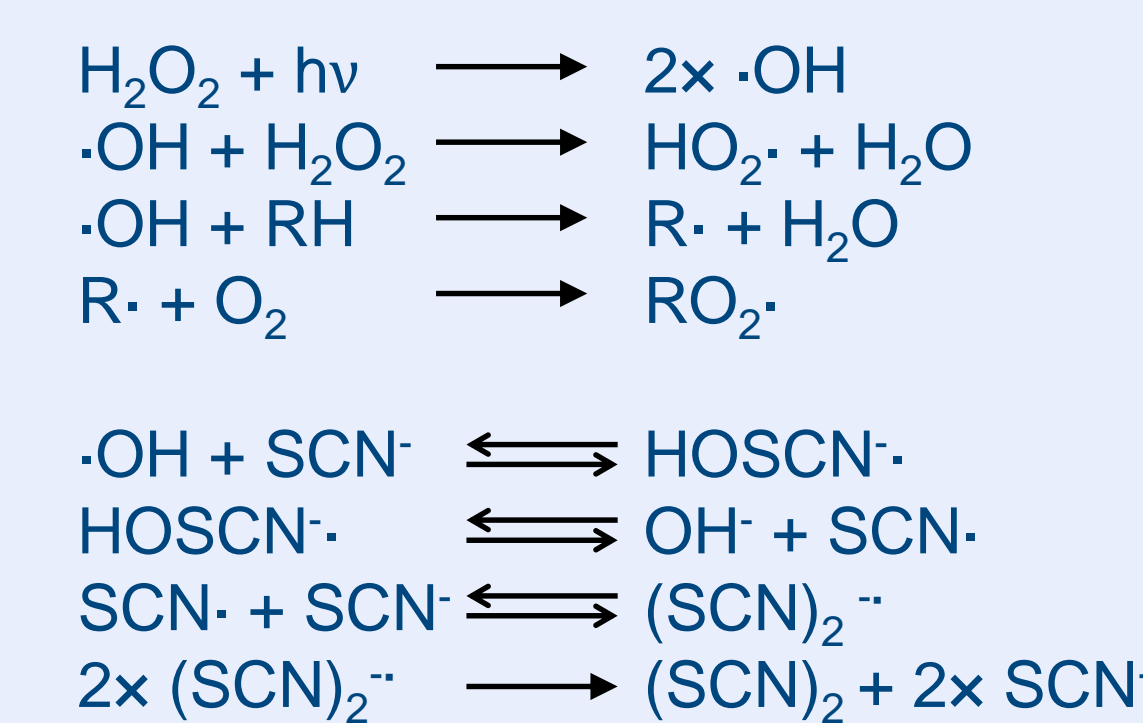
Experimental

Setup

Fig. 1: Laser Photolysis Long Path Absorption setup.

Competition kinetics

$$H_2O_2 + h\nu \longrightarrow 2\times \cdot OH$$
$$\cdot OH + H_2O_2 \longrightarrow HO_2\cdot + H_2O$$
$$\cdot OH + RH \longrightarrow R\cdot + H_2O$$
$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

$$\cdot OH + SCN^- \rightleftharpoons HOSCN\cdot^-$$
$$HOSCN\cdot^- \rightleftharpoons OH^- + SCN\cdot$$
$$SCN\cdot + SCN^- \rightleftharpoons (SCN)_2\cdot^-$$
$$2\times (SCN)_2\cdot^- \longrightarrow (SCN)_2 + 2\times SCN^-$$

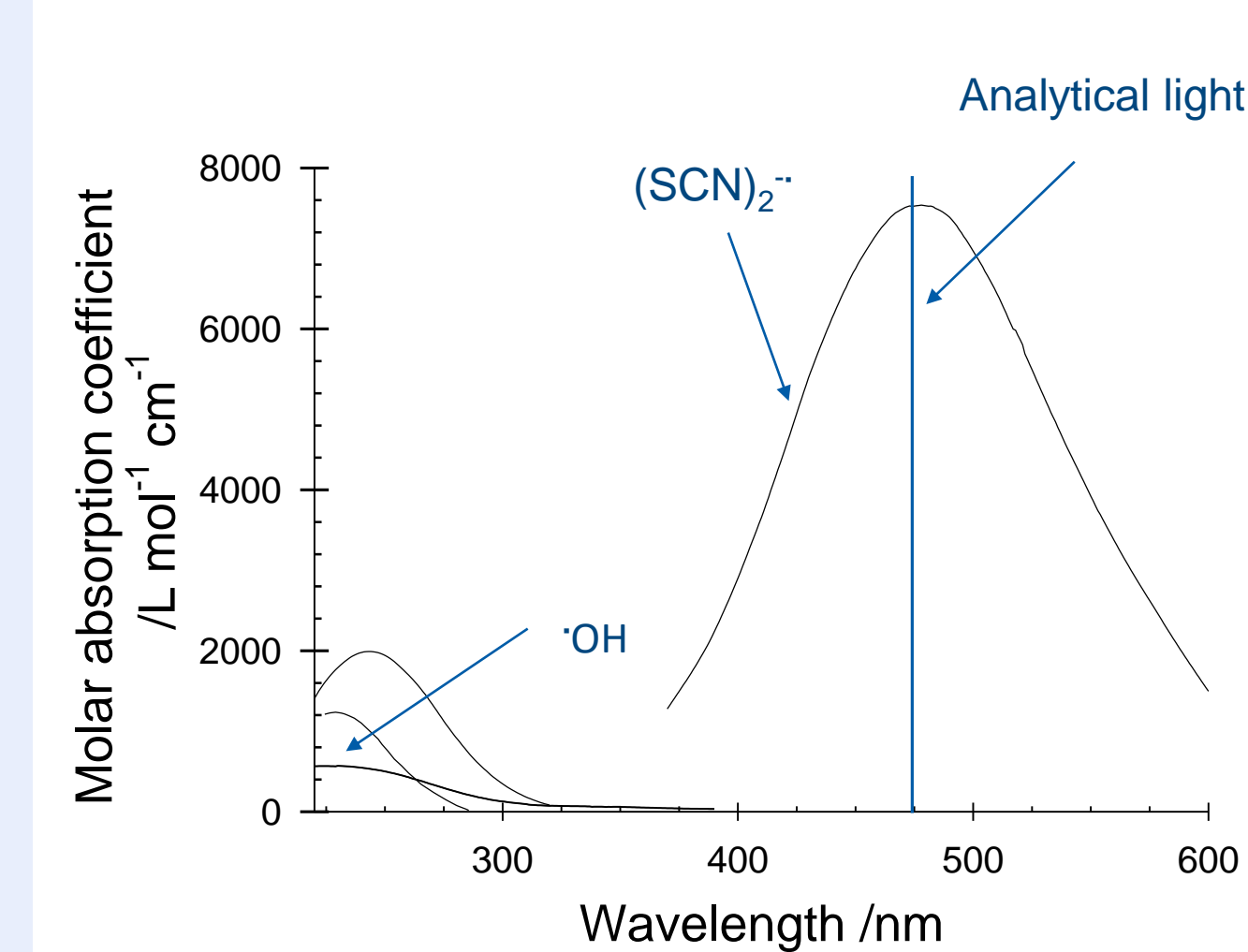| radical	λ_{Photo} /nm	λ_{Obs} /nm	precursors
hydroxyl radical	248	473	$[H_2O_2] = 2\times10^{-4}$ M $[SCN^-] = 2\times10^{-5}$ M

Fig. 2: Spectra of different radical species. (Behar et al., 1970; Herrmann et al., 2010)

- The OH radical rate constant was determined by using a competition kinetic method.
- Thiocyanate anion was used as reference reactant. (**Behar et al., 1972**)

Results

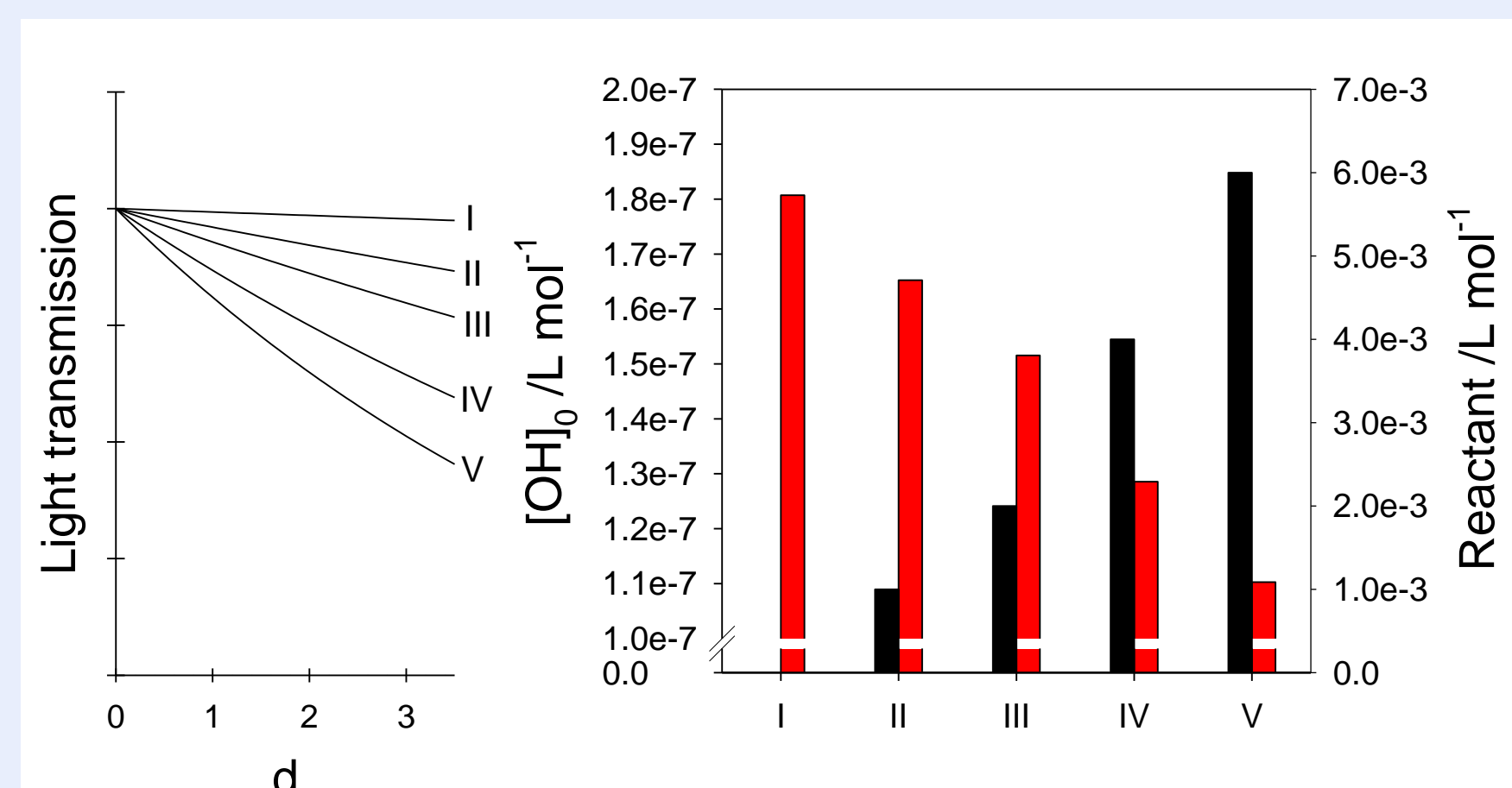### Competition kinetic method - Internal absorption effects

Fig. 3: Internal absorption effect and the consequent initial OH radical concentration change
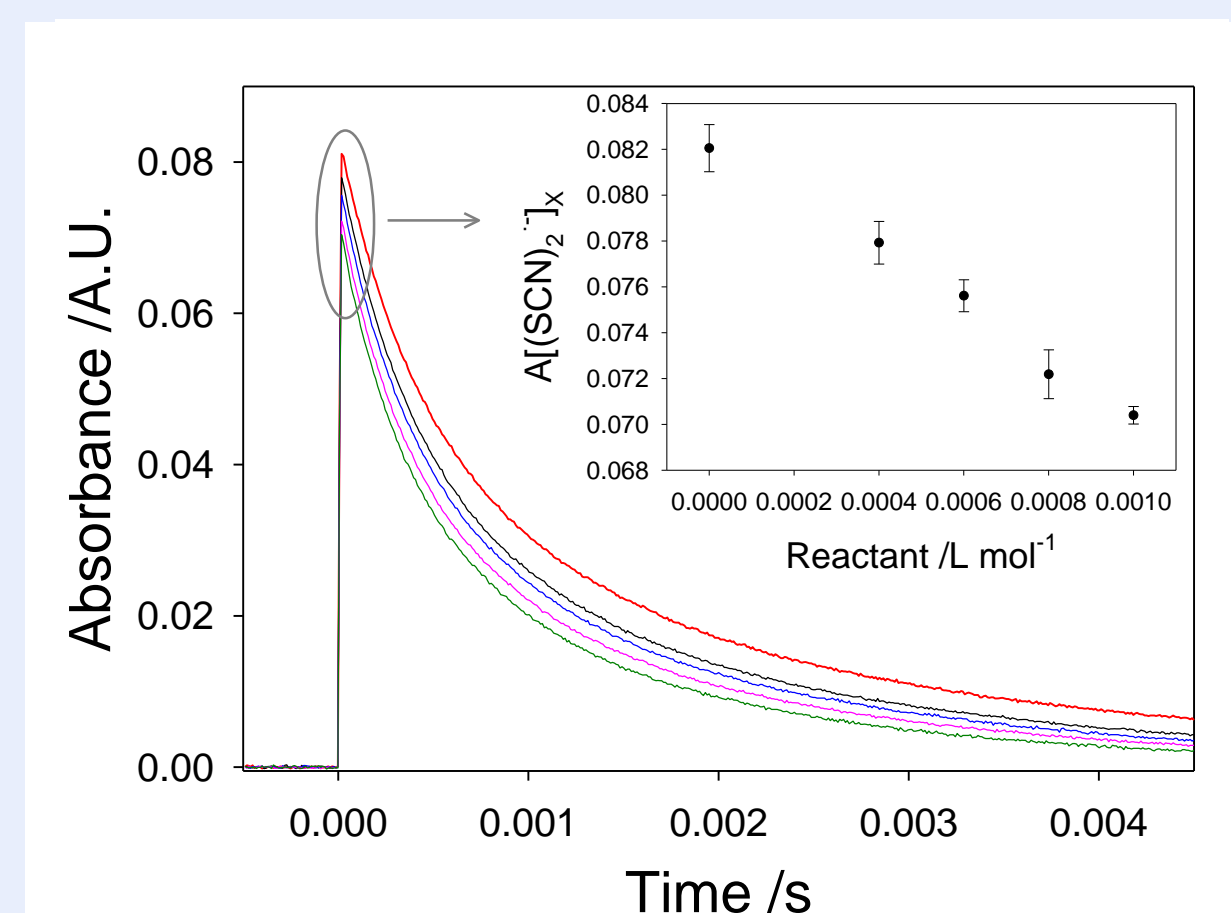

Fig. 4: Absorbance time profile of $(SCN)_2\cdot^-$.

- Once, the organic reactant absorbs at the excitation wavelength λ = 248 nm the OH radical concentration decrease.
- The dataset from **Ervens et al., 2003** was recalculated to characterize the influence of the internal absorption effect of 2-Propanone (Acetone) ($\varepsilon_{248\,nm}$ = 11.5 L mol^{-1} cm^{-1})

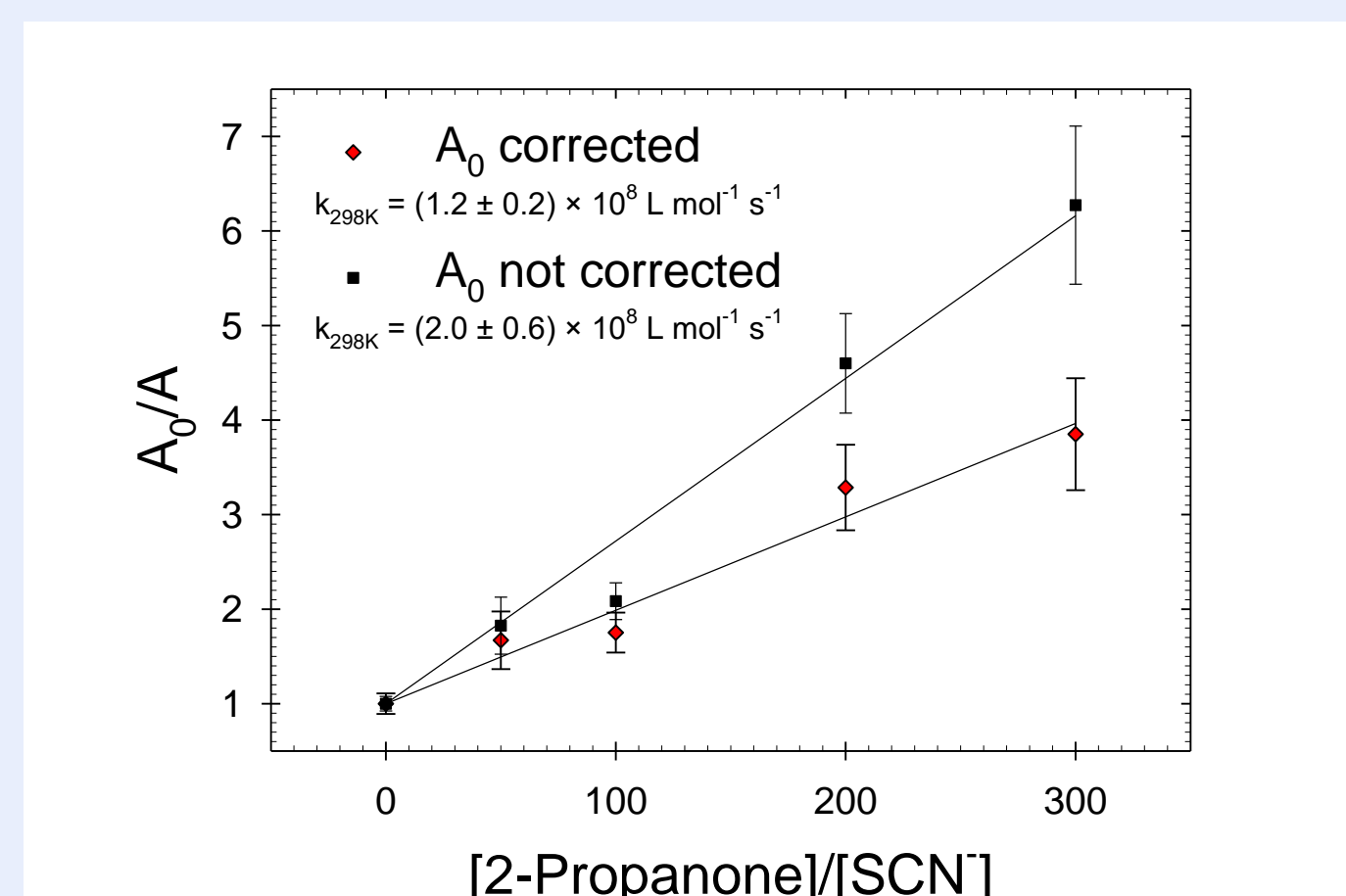**Fig. 5: Ratios of $A_{0,x}/A_x$ vs. [2-propanone]/[SCN$^-$] considering and omitting the internal absorption of Acetone.**
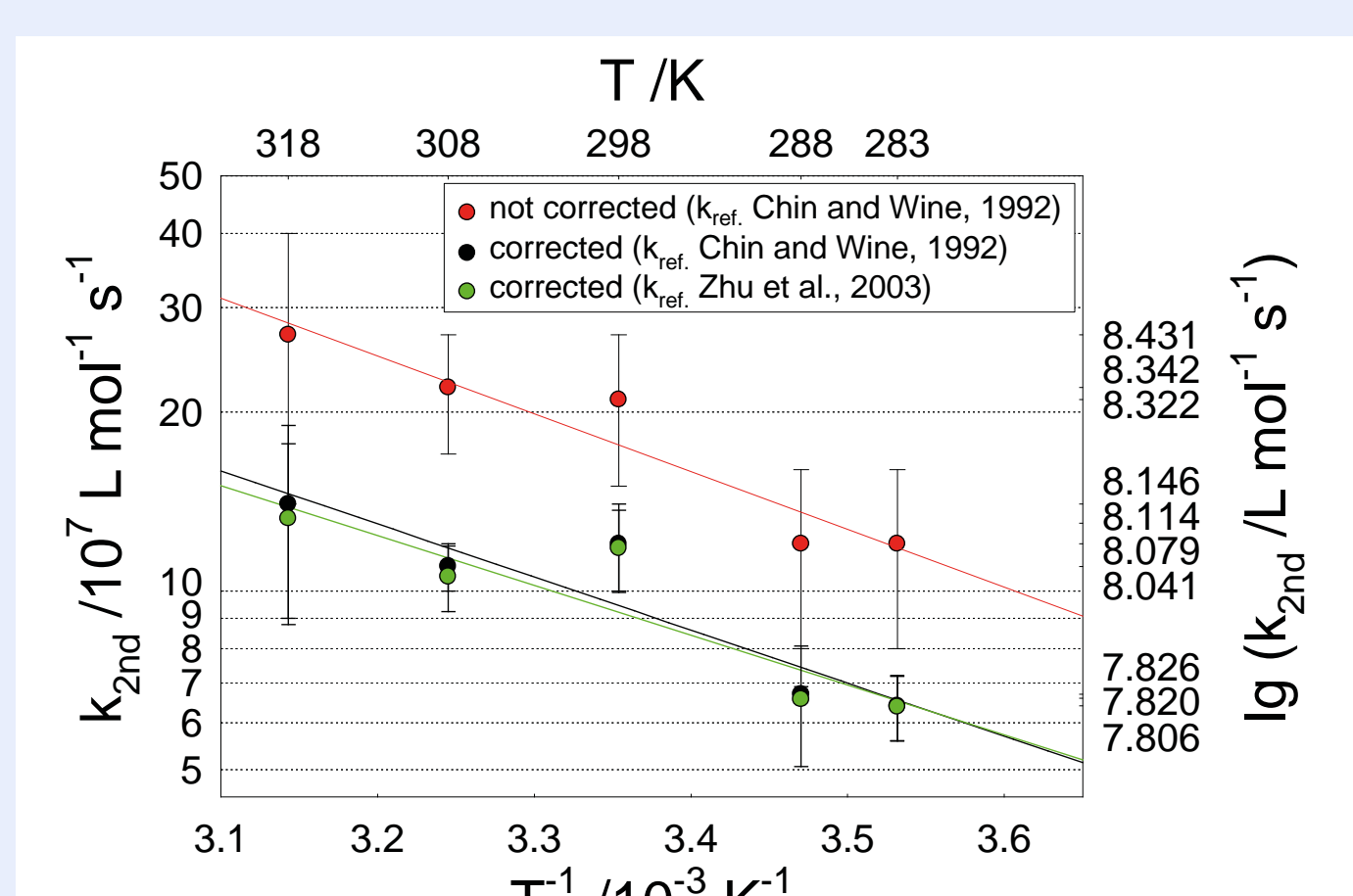

Fig. 6: Arrhenius plot of the OH radical reaction with Acetone (data taken from Ervens et al., 2003).

- The rate constants show no significant change due to the variation of the experimental conditions.

	H_2O_2 /mol L^{-1}	KSCN /mol L^{-1}	Reactant /mol L^{-1}	$[OH]_0$ change /%	$k_{not\ corrected}$ /L mol^{-1} s^{-1}	$k_{corrected}$ /L mol^{-1} s^{-1}	Change /%
A	2×10^{-4}	5.5×10^{-5}	$0 - 1\times10^{-3}$	$0 - 4.4$	$(1.1\pm0.1)\times10^8$	$(7.3\pm1.0)\times10^7$	30.9
B	2×10^{-4}	2×10^{-5}	$0 - 8\times10^{-4}$	$0 - 3.55$	$(9.3\pm1.1)\times10^7$	$(8.0\pm1.1)\times10^7$	14.4
C	1×10^{-3}	2.25×10^{-5}	$0 - 2\times10^{-3}$	$0 - 8.33$	$(1.1\pm0.1)\times10^8$	$(6.9\pm1.0)\times10^7$	34.5

Temperature dependencies

- The T-dependencies were calculated by using the updated reference rate constant from **Zhu et al., 2003**.
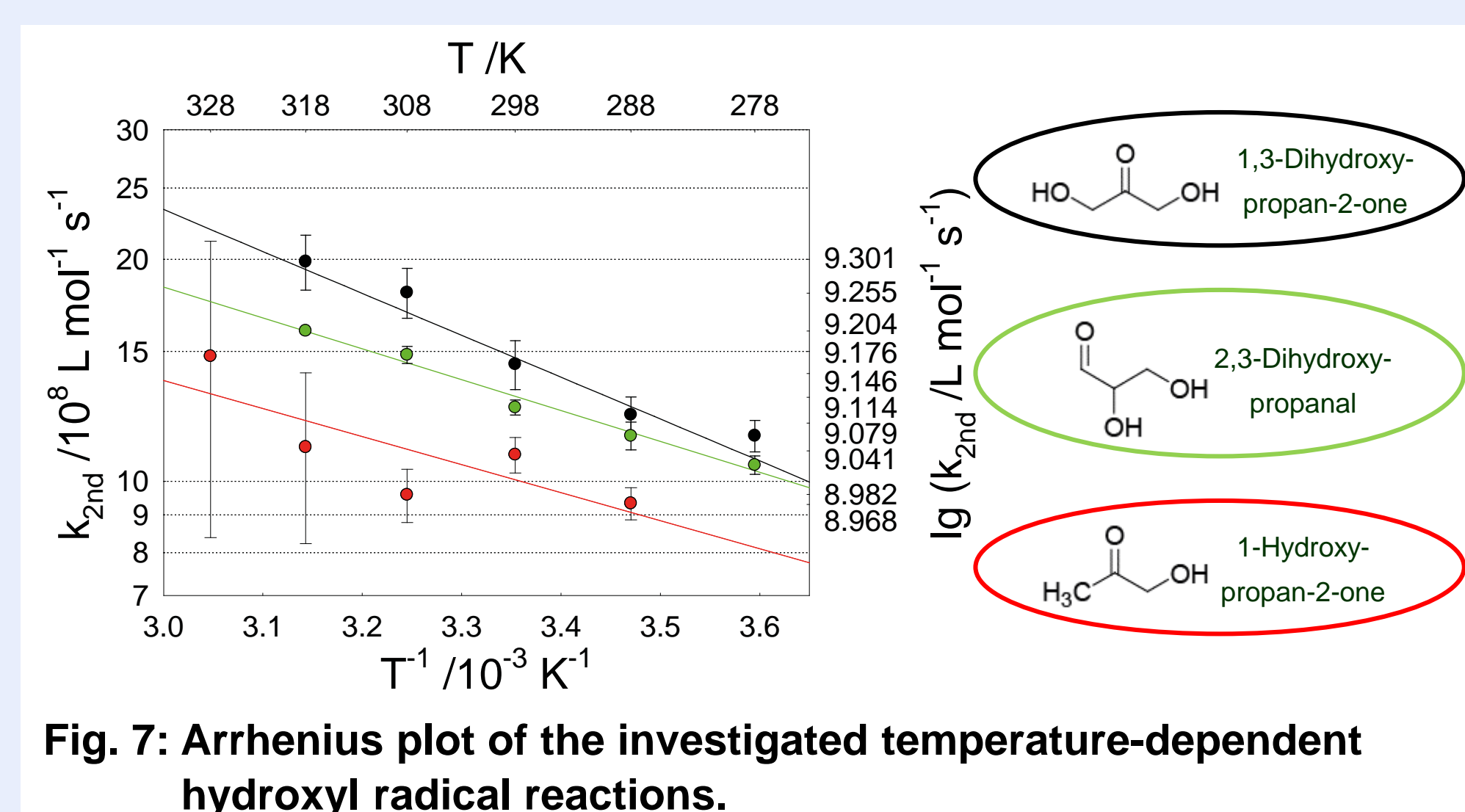

Fig. 7: Arrhenius plot of the investigated temperature-dependent hydroxyl radical reactions.

- Derived pre-exponential factor (A) and activation energy (E_A) from the investigated reactions shown in Fig. 7 (left).

A /L mol^{-1} s^{-1}	E_A /kJ mol^{-1}
$(1.2\pm0.1)\times10^{11}$	11 ± 2
$(3.3\pm0.1)\times10^{10}$	8 ± 1
$(1.9\pm0.1)\times10^{10}$	7 ± 4

- Resulting pre-exponential factor (A) and activation energy (E_A) from the investigated reactions displayed in Fig. 8 (right).

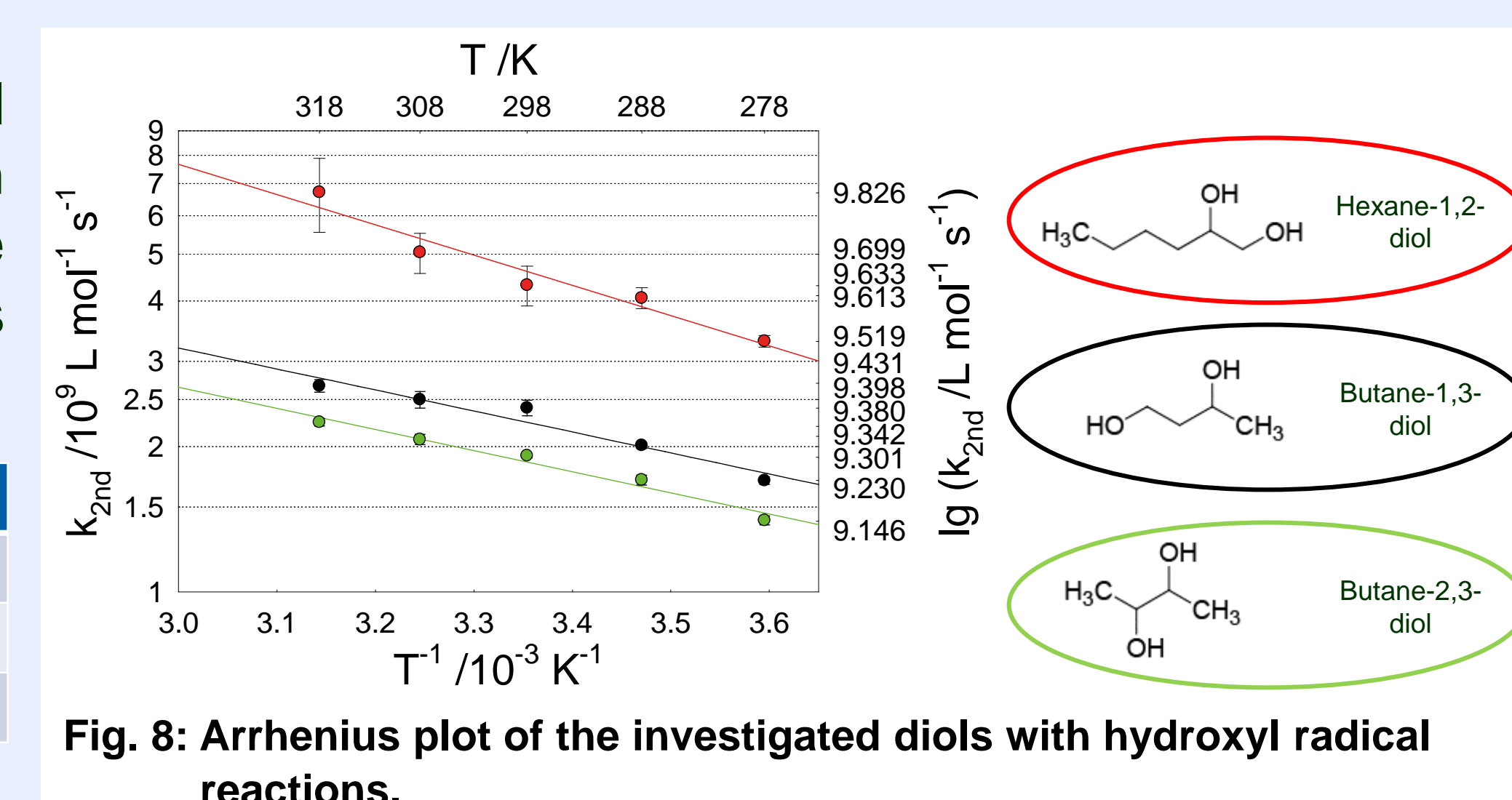| A /L mol^{-1} s^{-1}	E_A /kJ mol^{-1}
$(5.8\pm0.2)\times10^{11}$	12 ± 2
$(6.4\pm0.2)\times10^{10}$	8 ± 2
$(5.4\pm0.1)\times10^{10}$	8 ± 1

Fig. 8: Arrhenius plot of the investigated diols with hydroxyl radical reactions.

Structure activity relationships (SAR)

- Prediction methods for OH radical rate constants in aqueous solution based on structure activity relationships (SAR) have been developed by **Minakata et al., 2009** and **Doussin and Monod, 2013**.
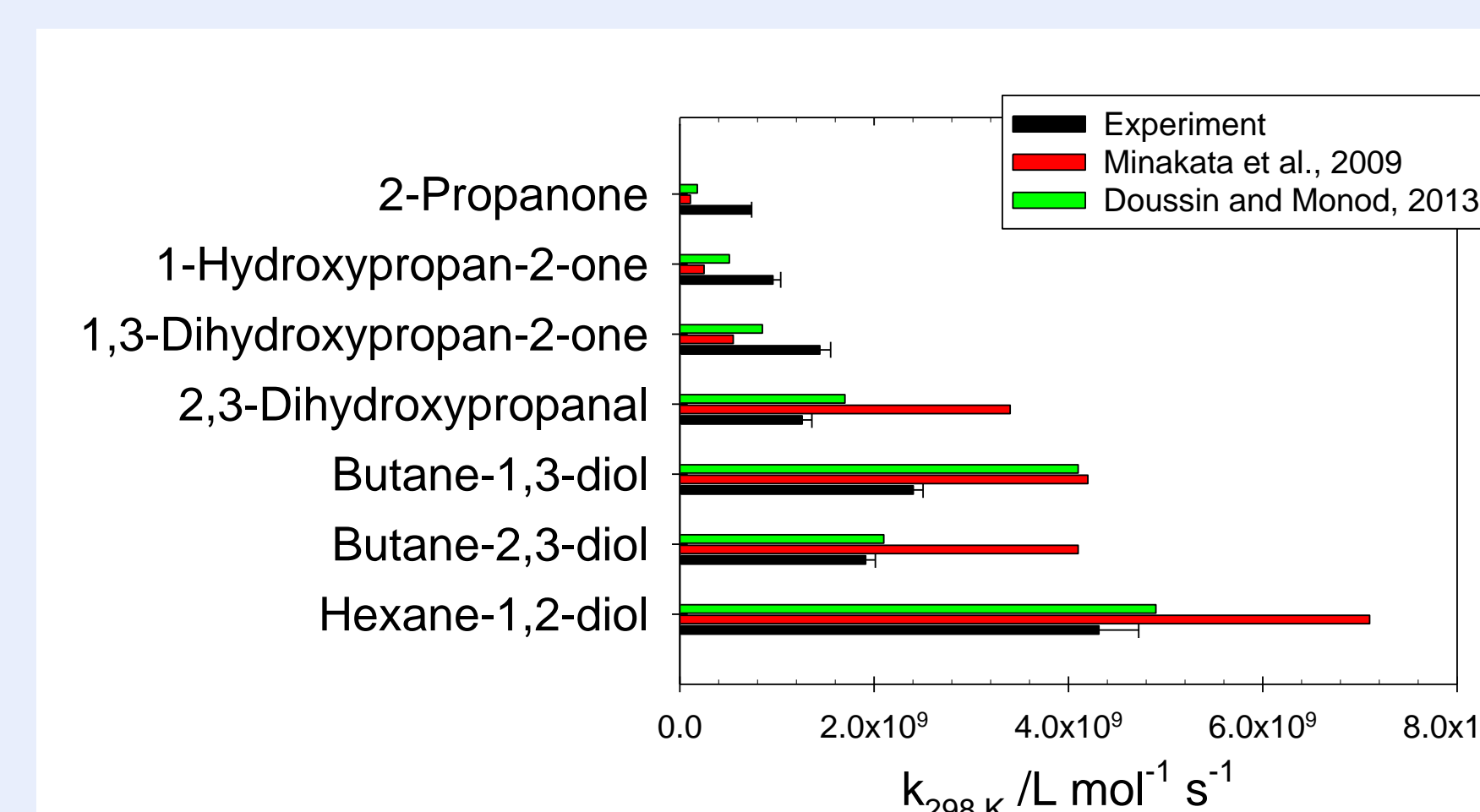

Fig. 9: Comparison of measured and calculated OH radical rate constants in the aqueous solution at T = 298 K.

- The comparison of the measured and the calculated OH radical rate constants by SAR methods results in a under- or over-estimation.
- For branched molecules with a variety of functional groups, the prediction is more difficult due to the uncertainties of the functional group parameters and group rates.

Summary

- Temperature-dependent reactions of oxygenated organic compounds with the OH radical in the aqueous phase have been studied.
- The contribution of the internal absorption effect caused by the absorption of the organic compound to the OH reaction rate constants was determined.
- This effect strongly depends on the molar absorption coefficient and the concentration of the investigated compound used.
- The change of the initial OH concentrations leads to overdetermined rate constants influencing the resulting Arrhenius activation parameters, especially the pre-exponential factor (A) and the entropy of activation $\Delta S^\ddagger$.
- Comparison with SAR prediction tools for OH radical rate constants in the aqueous phase, leads to underestimation or overestimation.

References

[1] Schaefer and Herrmann, Phys. Chem. Chem. Phys., **2018**, 20, 10939-10948. [2] Behar et al., J. Phys. Chem., **1970**, 74, 3209-3212. [3] Behar et al., J. Phys. Chem., 1972, 76, 1537-1542 [4] Hermann et al., ChemPhysChem, **2010**, 11, 9351-9363. [5] Ervens et al., Phys. Chem. Chem. Phys., **2003**, 5, 1811-1824. [6] L. Zhu, J. M. Nicovich and P. H. Wine, Aquatic Sciences, **2003**, 65, 425-435. [7] Minakata et al., Environ. Sci. Technol., **2009**, 43, 6220-6227. [8] Doussin and Monod, Atmos. Chem. Phys., **2013**, 13, 11625-11641.