

T- and pH-dependent OH Radical Kinetics of Lactic Acid, Glyceric Acid and Methylmalonic Acid in the Aqueous Phase

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Introduction

- Volatile organic compounds (VOCs) are omnipresent in the atmosphere and are emitted from biological and anthropogenic sources.
- Oxidative degradation and conversion processes of volatile organic compounds are often initiated by free radical reactions that take place in the multiphase system of the troposphere both in the gas phase and in the aqueous phase (e.g. clouds, fog and hygroscopic aerosols). [1]
- As oxidation products, carboxylic acids are a common class of compounds that occur in atmospheric particles and cloud droplets and thus also contribute to the formation of secondary aerosols (SOA). [1]
- Many processes, such as reactivity and the nature of chemical reactions, can be influenced by the different acidity (pH) of the aqueous phase and aerosols. [2]
- In the present study, the T- and pH-dependent rate constants of the $\cdot\text{OH}$ radical reactions with carboxylic acids in the aqueous phase were investigated.

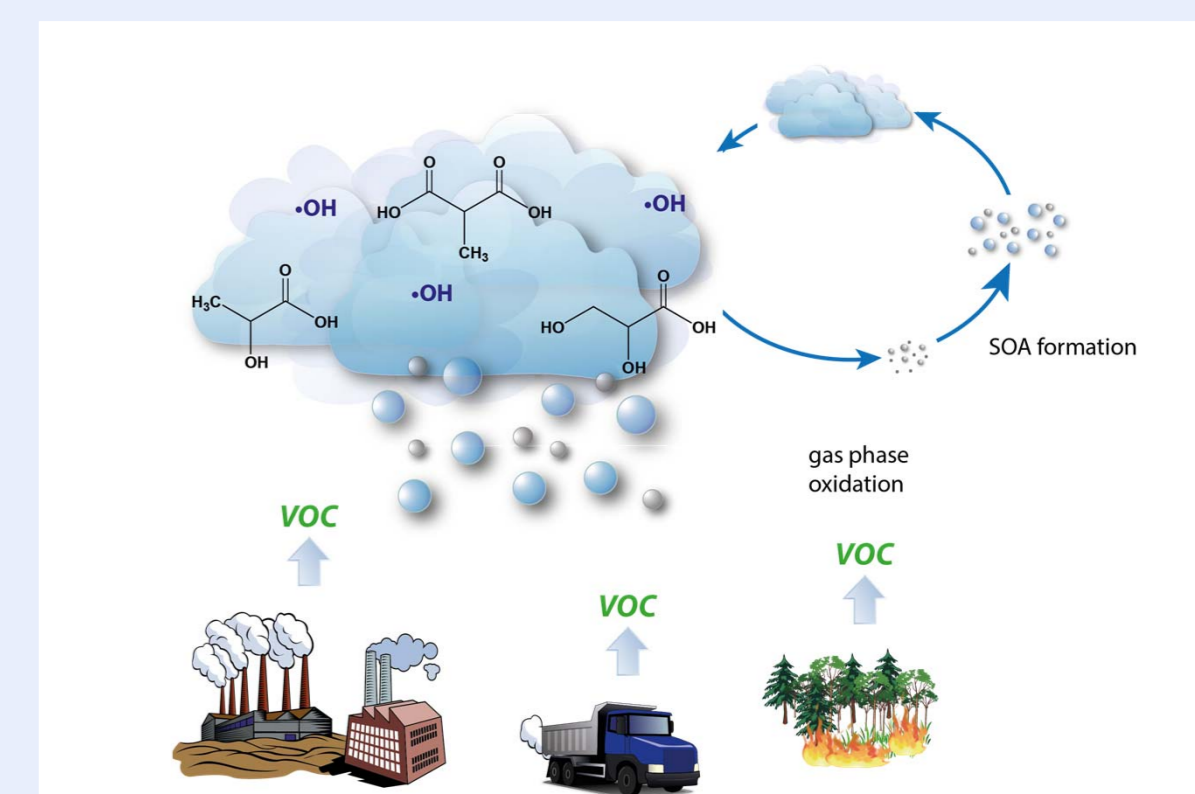


Fig. 1: Carboxylic acid formation by VOC oxidation in the atmosphere.

Experimental setup

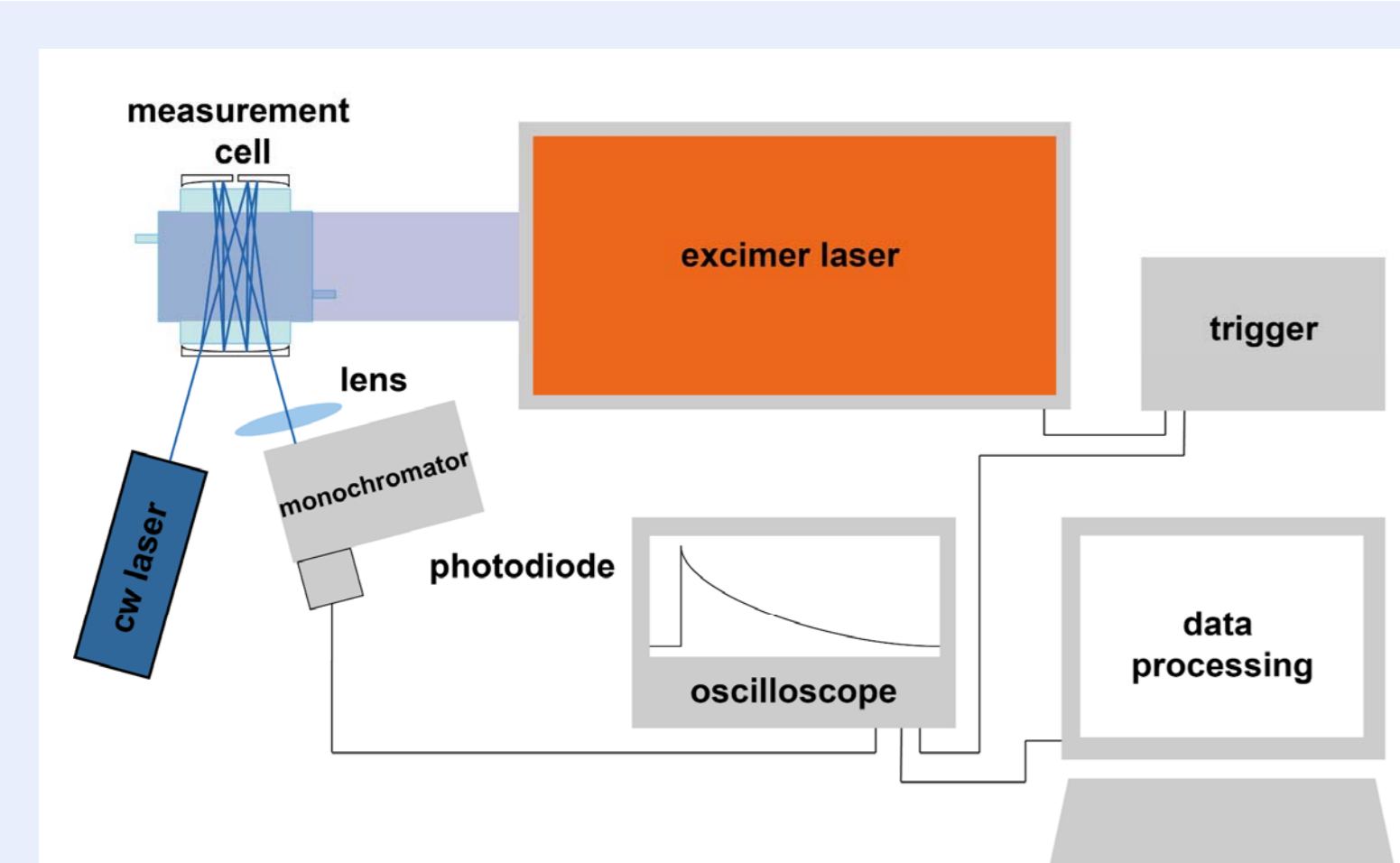


Fig. 2: Laser Photolysis Long Path Absorption setup. [3]

- Photolysis wavelength
➢ $\lambda = 248 \text{ nm}$
- Observation wavelength
➢ $\lambda = 407 \text{ nm}$
- Reaction cell volume
➢ $V = 28 \text{ ml}$
- Temperature range
➢ $278 \text{ K} \leq T \leq 318 \text{ K}$
- pH range
➢ $0 \leq \text{pH} \leq 9$

Competition kinetics method

- The $\cdot\text{OH}$ radical rate constant was determined by using a competition kinetic method.
- Thiocyanate was used as reference reactant. [4, 5]
- Precursors : $[\text{H}_2\text{O}_2] = 2 \times 10^{-4} \text{ M}$ and $[\text{SCN}^-] = 2 \times 10^{-5} \text{ M}$

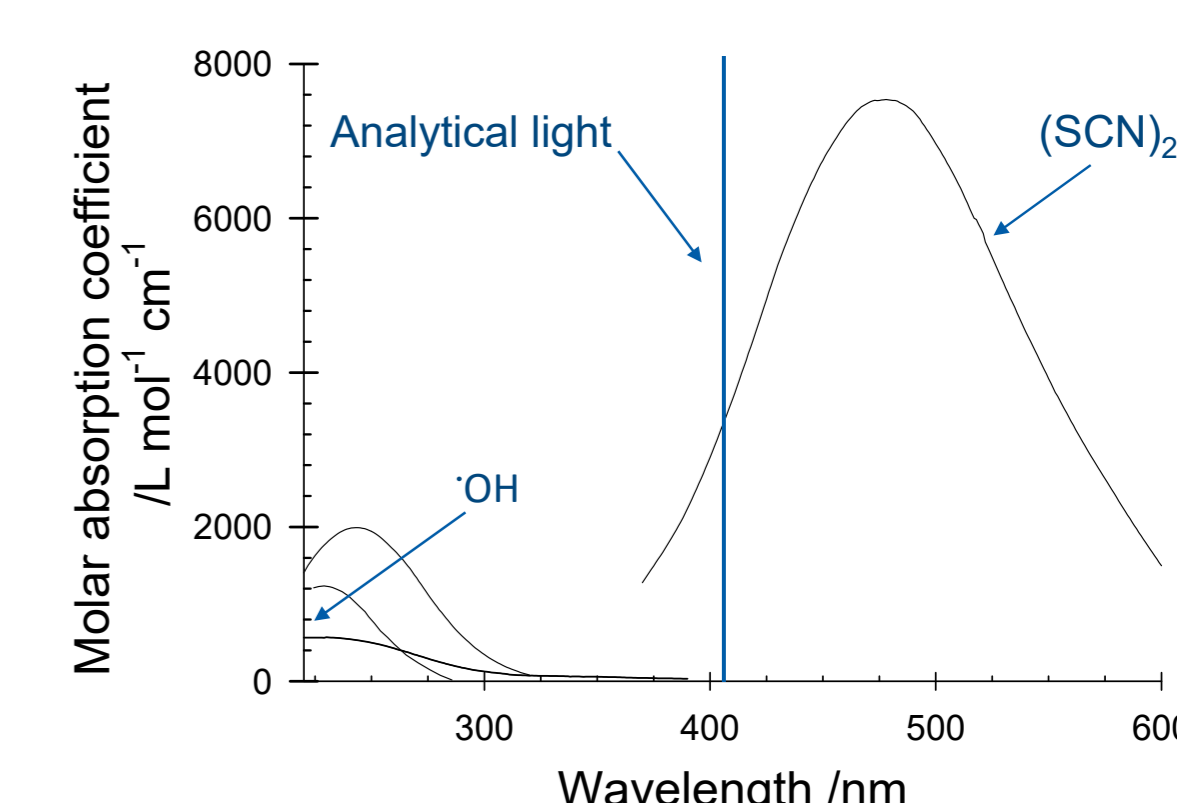
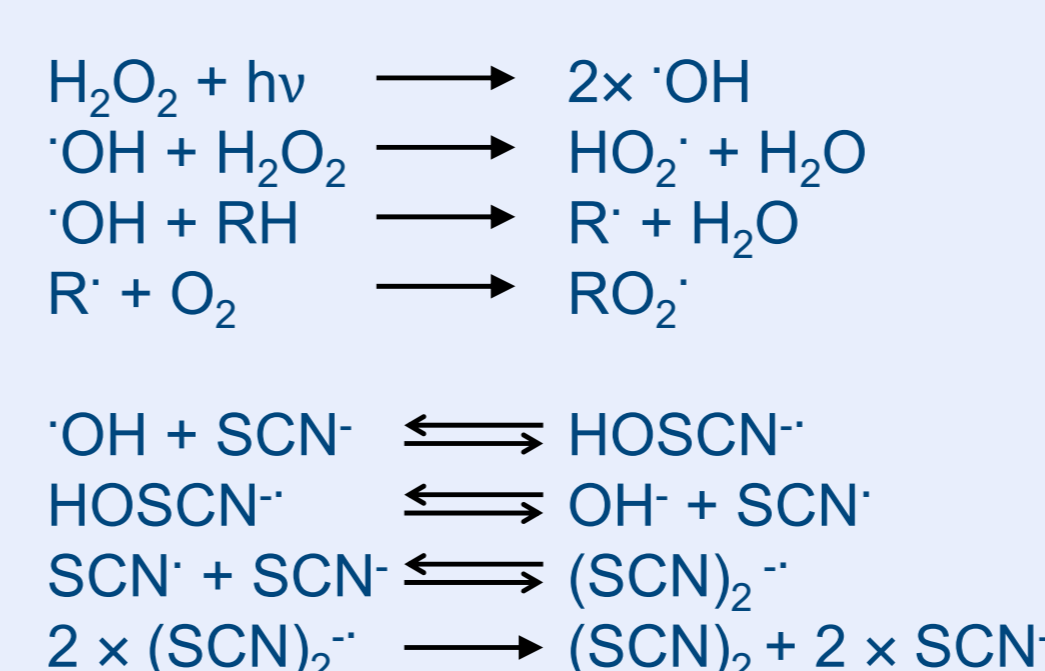


Fig. 3: Spectra of different radical species. [5]

Results

T- & pH-dependent $\cdot\text{OH}$ radical rate constants

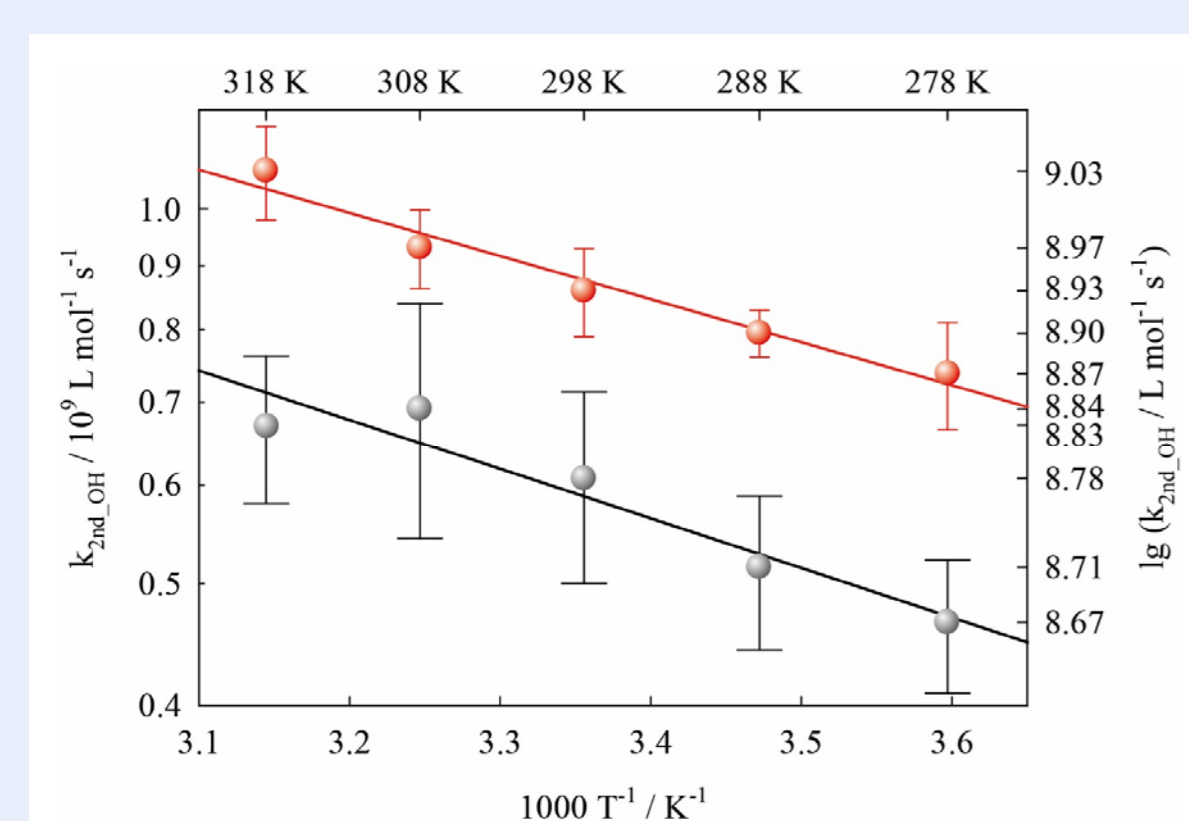


Fig. 4: Arrhenius plot of the $\cdot\text{OH}$ radical reaction with lactic acid.

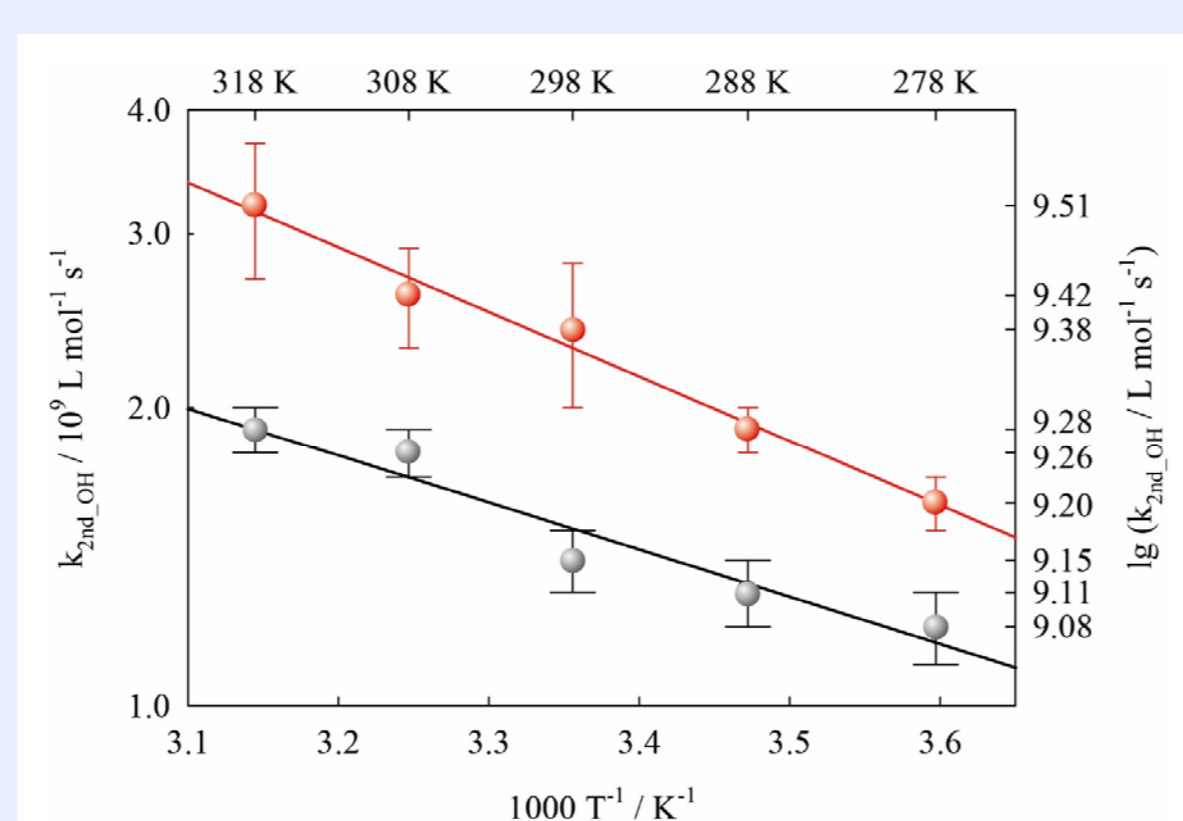


Fig. 5: Arrhenius plot of the $\cdot\text{OH}$ radical reaction with glyceric acid.

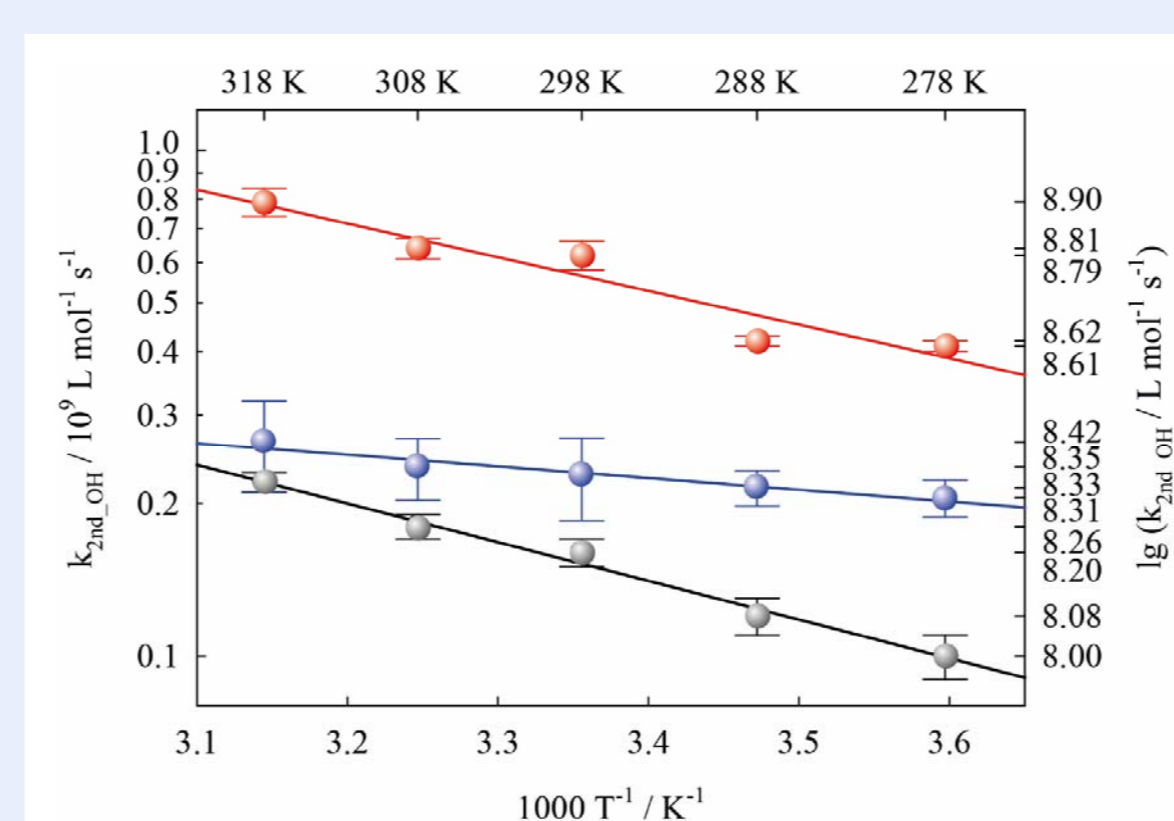


Fig. 6: Arrhenius plot of the $\cdot\text{OH}$ radical reaction with methylmalonic acid.

- T-dependencies were calculated using reference rate constant from Zhu et al., 2003. [6]
- Derived pre-exponential factors (A) and activation energies (E_A) from the investigated reactions, shown in Fig. 4, 5 and 6 are shown above.

Activation parameters

Tab. 2: Calculated pre-exponential factors and activation energies of the $\cdot\text{OH}$ radical reactions.

Reactant	A / $\text{L mol}^{-1} \text{ s}^{-1}$	E_A / kJ mol^{-1}
Lactic acid		
HA	$1.3 \pm 0.1 \times 10^{10}$	8 ± 1
A ⁻	$1.3 \pm 0.1 \times 10^{10}$	7 ± 1
Glyceric acid		
HA	$6.0 \pm 0.2 \times 10^{10}$	9 ± 1
A ⁻	$3.6 \pm 0.1 \times 10^{11}$	13 ± 1
Methylmalonic acid		
H ₂ A	$5.5 \pm 0.1 \times 10^{10}$	15 ± 1
HA ⁻	$1.4 \pm 0.1 \times 10^9$	4 ± 1
A ²⁻	$9.6 \pm 0.4 \times 10^{10}$	13 ± 1

SAR methods

- Methods for predicting the rate constants of $\cdot\text{OH}$ radicals in aqueous solution based on (SAR) structure-activity relationships. [7, 8, 9]
- Deviations of the rate constants from the calculated values reflect the precision level and its predictive capability, which is a factor of 0.5 to 2.

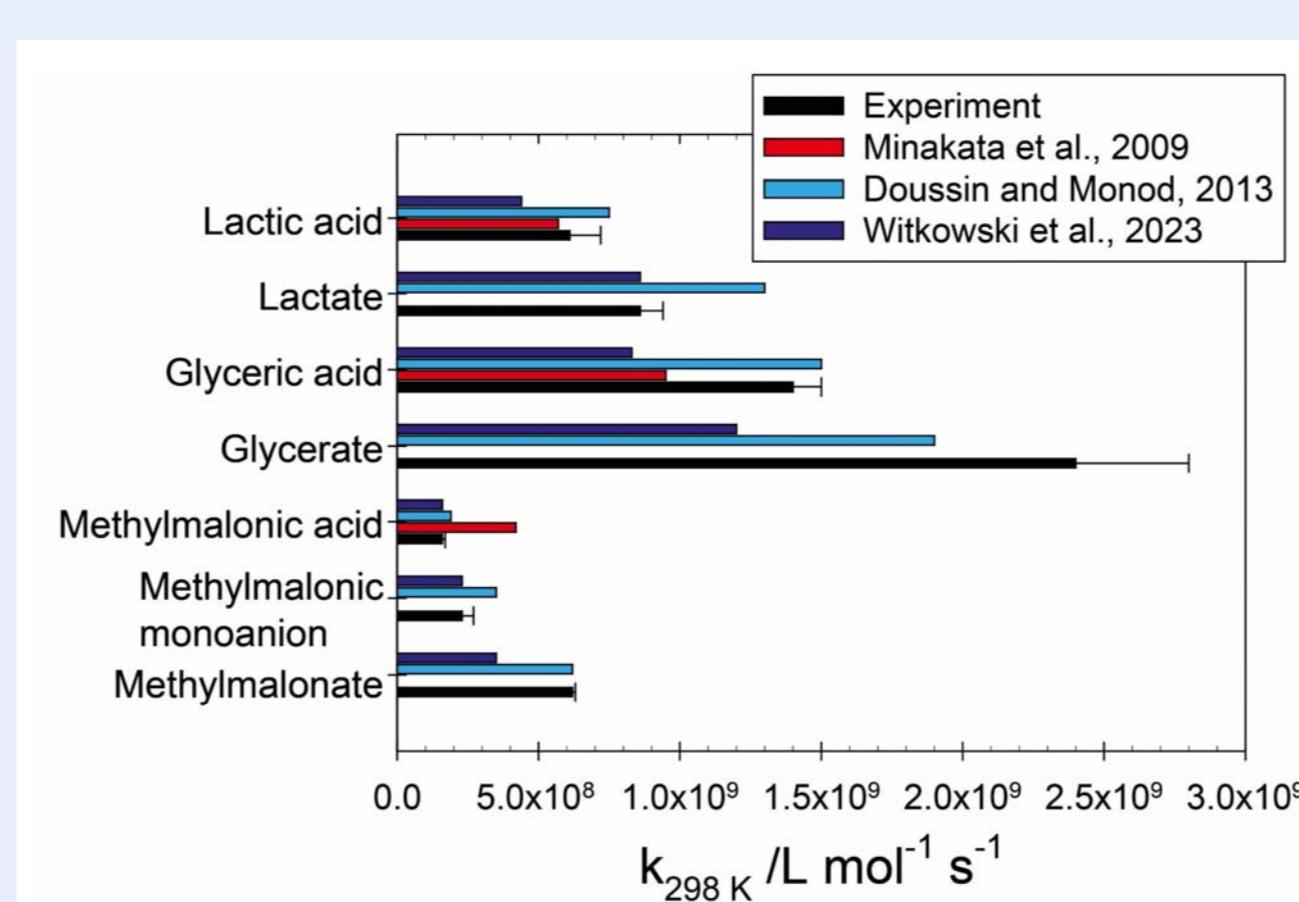


Fig. 7: Comparison of the OH radical rate constants with carboxylic acid.

- The obtained rate constants and activation parameters are comparable to the literature values for the H-atom abstraction reactions of short-chain carbon compounds.

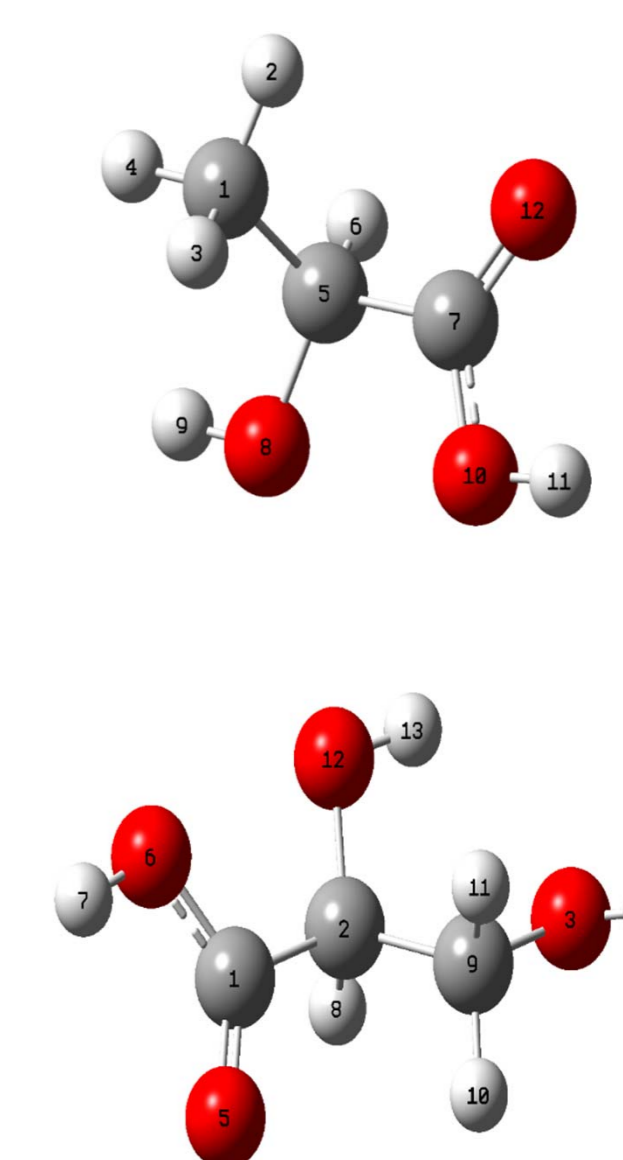
DFT calculations

Gibbs energy barriers

- DFT simulations in GAUSSIAN using the M06-2X method and the 6-311++G(3df,2p) basis set were used to calculate the energy barriers of the $\cdot\text{OH}$ radical reaction and the most probable position of H-atom abstraction.

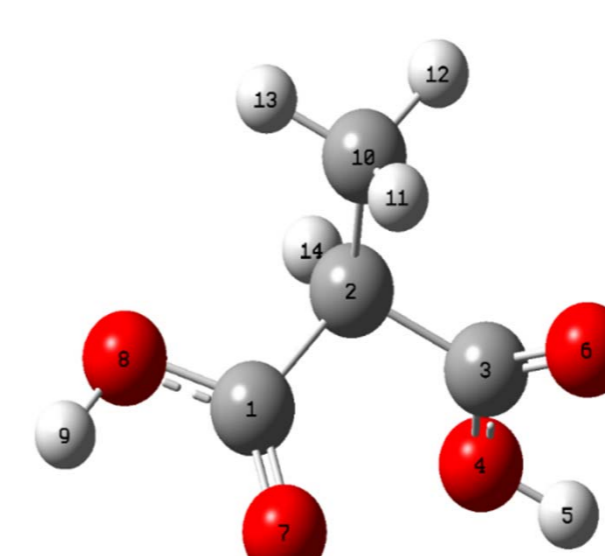
Tab. 1: Calc. Gibbs energies of the $\cdot\text{OH}$ reaction in the aqueous phase.

Group / (H position)	HA / kJ mol^{-1}	A ⁻ / kJ mol^{-1}
Lactic acid		
COOH / (11)	68.7	/
OH / (9)	58.5	46.6
CH ₃ / (2, 3, 4)	44.7	34.7
CH / (6)	35.5	23.4
Glyceric acid		
COOH / (7)	50.2	/
OH / (13)	60.9	55.4
OH / (4)	50.9	39.0
CH ₂ / (10, 11)	30.5	19.7
CH / (8)	33.5	30.0



Tab. 3: Calc. energies in kJ mol^{-1} of the $\cdot\text{OH}$ reaction with methylmalonic acid.

Reactant	COOH	CH	CH ₃	COOH
H ₂ A	69.3	45.9	43.1	70.2
HA ⁻	/	33.9	43.4	53.2
A ²⁻	/	26.0	30.2	/



- The deprotonation of the carboxylic acid group leads to a change in the energy barriers.
- Changes in the energy barriers can explain the different rate constants $k(\text{H}_2\text{A}) > k(\text{HA}^-) > k(\text{A}^{2-})$ of the carboxylic acids.

Summary & Outlook

- T-dependencies of the reactions of carboxylic acids with $\cdot\text{OH}$ radicals were investigated.
- Deprotonation of the carboxylic acid leads to an increase in the rate constants with following trend: $k(\text{H}_2\text{A}) > k(\text{HA}^-) > k(\text{A}^{2-})$.
- Energy barriers of the $\cdot\text{OH}$ radical reaction and the most probable position of the H-atom abstraction were calculated with DFT simulations
- Comparison with SAR prediction tools for $\cdot\text{OH}$ radical rate constants in the aqueous phase, leads to an under- or overestimation.

References

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