

Motivation and background

OH-radical chemistry in the troposphere

- OH most important radical to initiate transformation and decomposition processes in the troposphere
- Oxidation of organic and inorganic compounds in the gas- and aqueous phase of the troposphere

Carboxylic acids in the troposphere

- Ubiquitary abundance in the troposphere
- Stable intermediates in secondary oxidation processes
- Possible influence on particle hygroscopicity
- Influence on oxidation potential and photochemistry of troposphere

- Tropospheric chemical modeling to understand sources and sinks
- Kinetic and thermodynamic data are necessary input parameters
- Reactivity correlations to quantify underlying reaction mechanism

Experimental

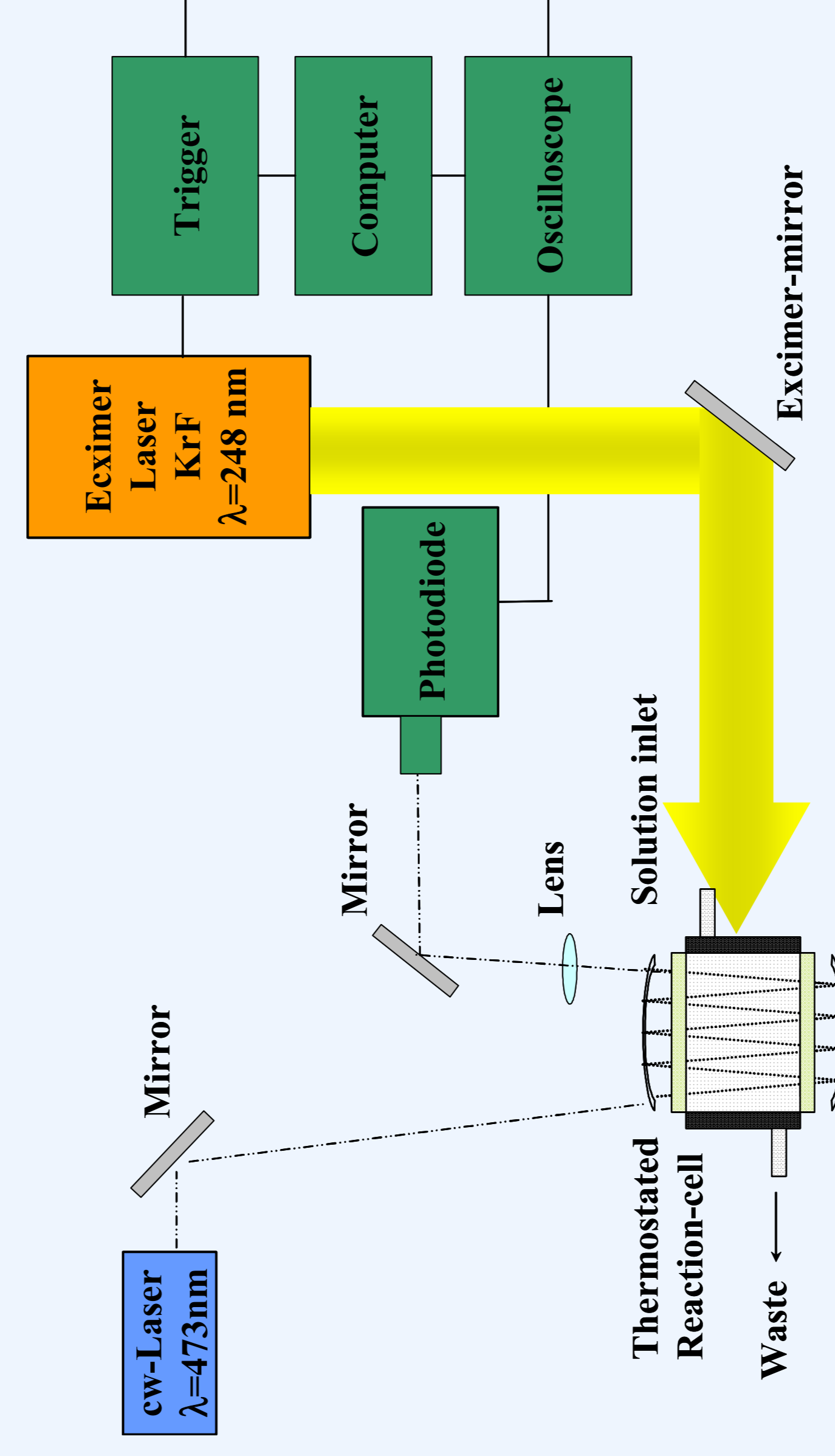


Figure 1: Laser photolysis long path absorption set-up (LP-LPA)

OH-radical generation

- Laser flash photolysis of H_2O_2 ($c=1 \cdot 10^{-4} \text{ M}^{-1}$) at wavelength of $\lambda = 248 \text{ nm}$



Kinetic investigations with Competition Kinetics Method using SCN⁻

- Competition-reaction of OH with the organic reactant and SCN⁻

$$\text{OH} + \text{SCN}^- \longrightarrow (\text{SCN})_2 + \text{OH}^-$$

$$\text{OH} + \text{reactant} \longrightarrow \text{products}$$
- Formation of strongly absorbing (SCN)₂ radical anion (peak absorbance 475 nm, $\epsilon = 7650 \text{ M}^{-1}\text{cm}^{-1}$) → analytical light of cw-laser at $\lambda = 473 \text{ nm}$
- Temperature dependent rate constant as reference data set by Chin and Wine (1992) $k_{\text{ref}}(T) = 7.3 \cdot 10^{12} \cdot \exp(-15.8 \text{ kJ mol}^{-1}/RT) \text{ M}^{-1}\text{s}^{-1}$ [1]
- Determination of five second order rate constants between 278 and 318 K

Kinetic and thermodynamic results and reactivity discussion

Table 1: The investigated acids have been measured at pH = 1 fully protonated and at pH = 9 in the fully dissociated form in this work. Listed are activation energy (E_A), activation entropy (ΔS^\ddagger), observed rate constants at 298 K (k_{2nd}), compared with available literature values for the investigated carboxylic acids for comparison

Compound	$k_{2nd} [\text{M}^{-1} \text{s}^{-1}]$ 298K	Ref. k_{2nd}	E_A [kJ mol ⁻¹]	A [kJ mol ⁻¹]	ΔS^\ddagger [J mol ⁻¹ K ⁻¹]
<i>Acid (pH=1)</i>					
Tarttronic acid	$(2.7 \pm 0.5) \cdot 10^8$ $1.7 \cdot 10^8$	this work. 2			
Oxalacetic acid	$(2.5 \pm 0.3) \cdot 10^9$	this work	(17.8 ± 5.3)	$(3.5 \pm 0.3) \cdot 10^{12}$	$-(13.2 \pm 1.0)$
Glutaric acid	$(5.0 \pm 0.5) \cdot 10^8$ $(6.0 \pm 2.0) \cdot 10^8$	this work 3	(13.0 ± 6.4)	$(1.0 \pm 0.1) \cdot 10^{11}$	$-(42.4 \pm 4.3)$
(pH=2)					
(pH=2)	$8.3 \cdot 10^8$	4			
Adipic acid	$(2.0 \pm 0.4) \cdot 10^9$ $(1.7 \pm 0.3) \cdot 10^9$	this work 3	(12.2 ± 6.3)	$(3.1 \pm 0.3) \cdot 10^{11}$	$-(33.2 \pm 3.2)$
(pH=2)					
(pH=2)	$2.0 \cdot 10^9$	4			
Pimelic acid	$(4.4 \pm 2.6) \cdot 10^9$ $(2.4 \pm 0.7) \cdot 10^9$ $2.0 \cdot 10^9$	this work 3 4			
(pH=2)					
(pH=2)					
<i>Anion (pH=9)</i>					
Tarttronic acid	$(5.0 \pm 0.6) \cdot 10^8$ $1.5 \cdot 10^9$ $4.4 \cdot 10^8$	this work 5 2	(9.5 ± 3.9)	$(2.1 \pm 0.1) \cdot 10^{10}$	$-(55.6 \pm 3.7)$
(pH 6-10)					
Glutaric acid	$(8.2 \pm 0.9) \cdot 10^8$ $(1.0 \pm 0.2) \cdot 10^9$	this work 3	(19.6 ± 8.5)	$(2.5 \pm 0.3) \cdot 10^{12}$	$-(16.0 \pm 2.2)$
Adipic acid	$(1.8 \pm 0.5) \cdot 10^9$ $(2.4 \pm 0.2) \cdot 10^9$	this work 3	(16.7 ± 5.4)	$(1.6 \pm 0.1) \cdot 10^{12}$	$-(19.8 \pm 1.5)$
Pimelic acid	$(2.7 \pm 0.6) \cdot 10^9$ $(2.9 \pm 0.8) \cdot 10^9$	this work 3			

- The activation parameters for the compounds investigated in this work have been measured for the first time
- Measured k_{2nd} at room temperature (298K) show a good agreement with literature values
- Previous studies [2, 6] have shown the reaction mechanism H-atom abstraction as the main reaction pathway for OH with carboxylic acids for both the undissociated and dissociated form
- k_{2nd} for the acids and their respective anionic form show not very large differences, but generally the anions react slightly faster, caused by different inductive effects of the carboxyl groups on the C-H bond strengths in the molecule

→ Evans-Polanyi reactivity correlation to learn more about contribution from H-atom abstraction mechanism

- From the Arrhenius equation can be seen that $\ln k$ is proportional to the energy of activation E_A

$$\ln k = \ln A - E_A/R \cdot 1/T \quad \text{Arrhenius-equation}$$

$$\ln k \sim E_A$$

- It was shown empirically that E_A is proportional to the bond energy (BDE) of the most weakly bonded H-atoms in a molecule, consequently also $\ln k$ should be proportional to the BDE [7]

$$E_A \sim \text{BDE}_{\text{R-H}}$$

$$\Rightarrow \ln k \sim \text{BDE}_{\text{R-H}}$$

- Requirement for this correlation is a similarity of the preexponential factor A for the considered group of compounds (see Fig. 2)
- Fig. 2 shows that preexponential factors of aldehydes and alcohols are quite similar whereas those of carboxylic acids are more scattered

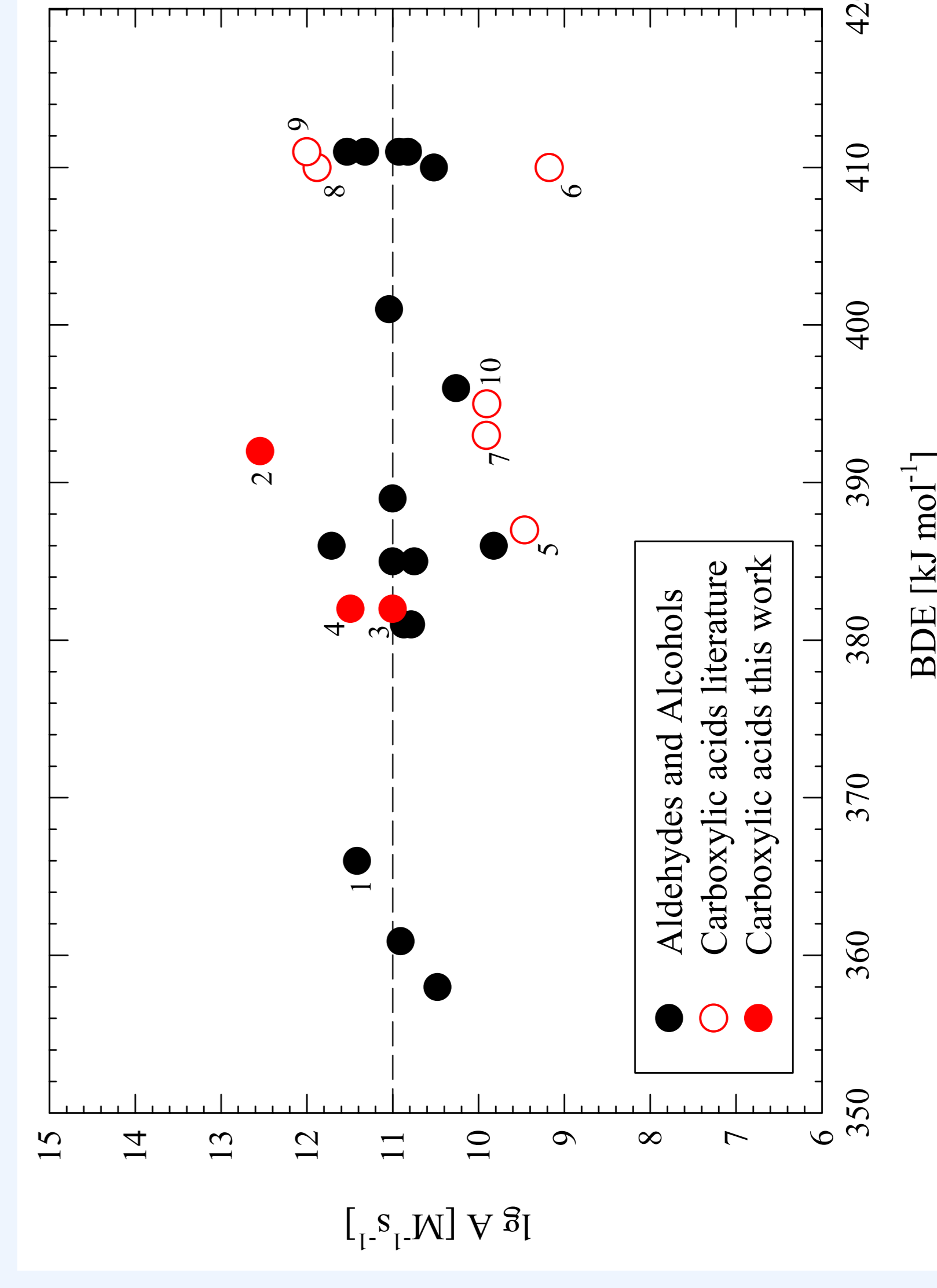


Figure 2: Plot of obtained preexponential factors and literature values [8, 9] versus bond dissociation energy, for numbering see Tab. 2

Table 2: Legend for Fig. 2 and 3

No	Compound
1	Tarttronic acid
2	Oxalacetic acid
3	Glutaric acid
4	Adipic acid
5	Formic acid
6	Acetic acid
7	Glyoxylic acid
8	Propionic acid
9	Pyruvic acid
10	Succinic acid

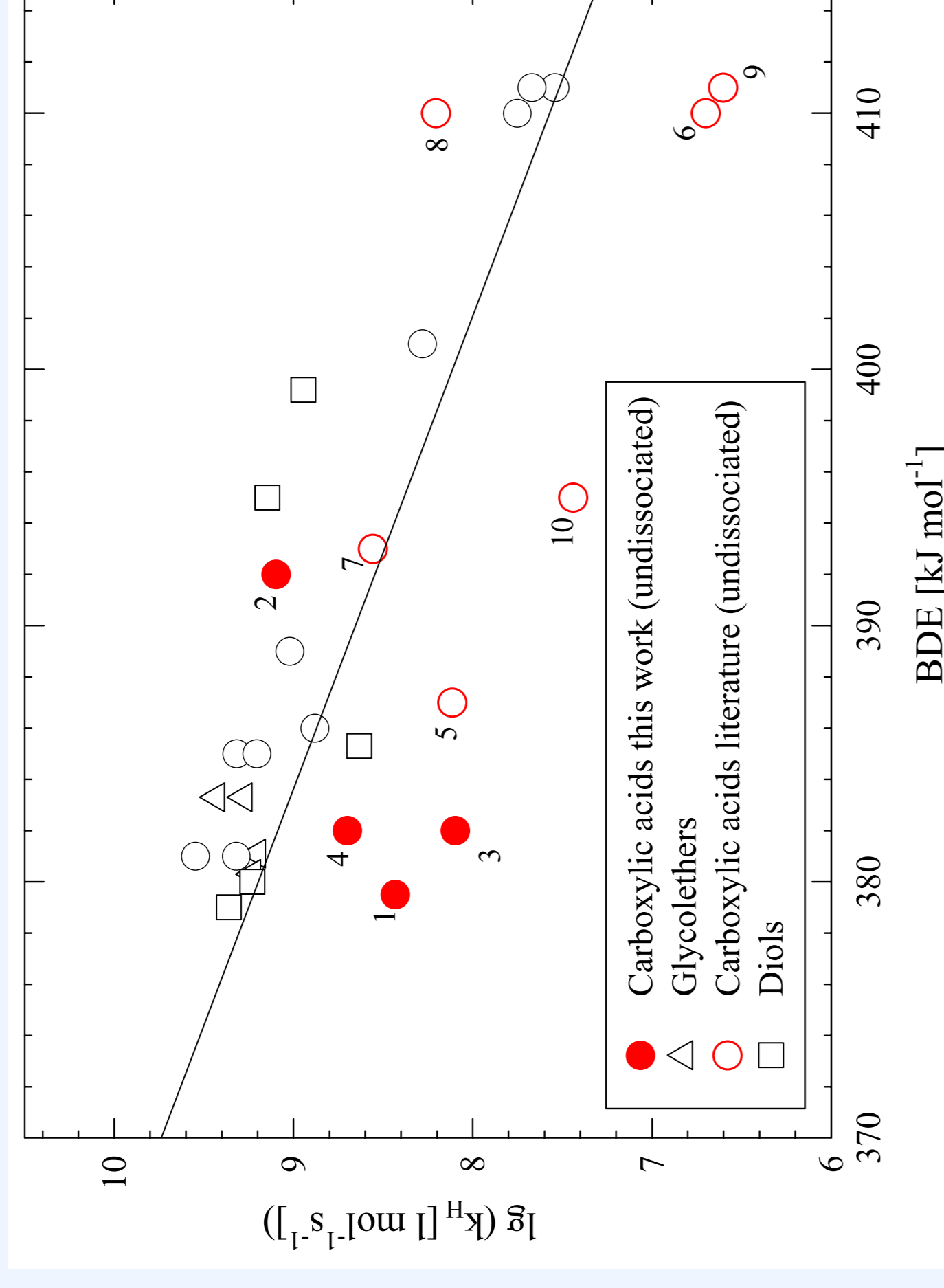
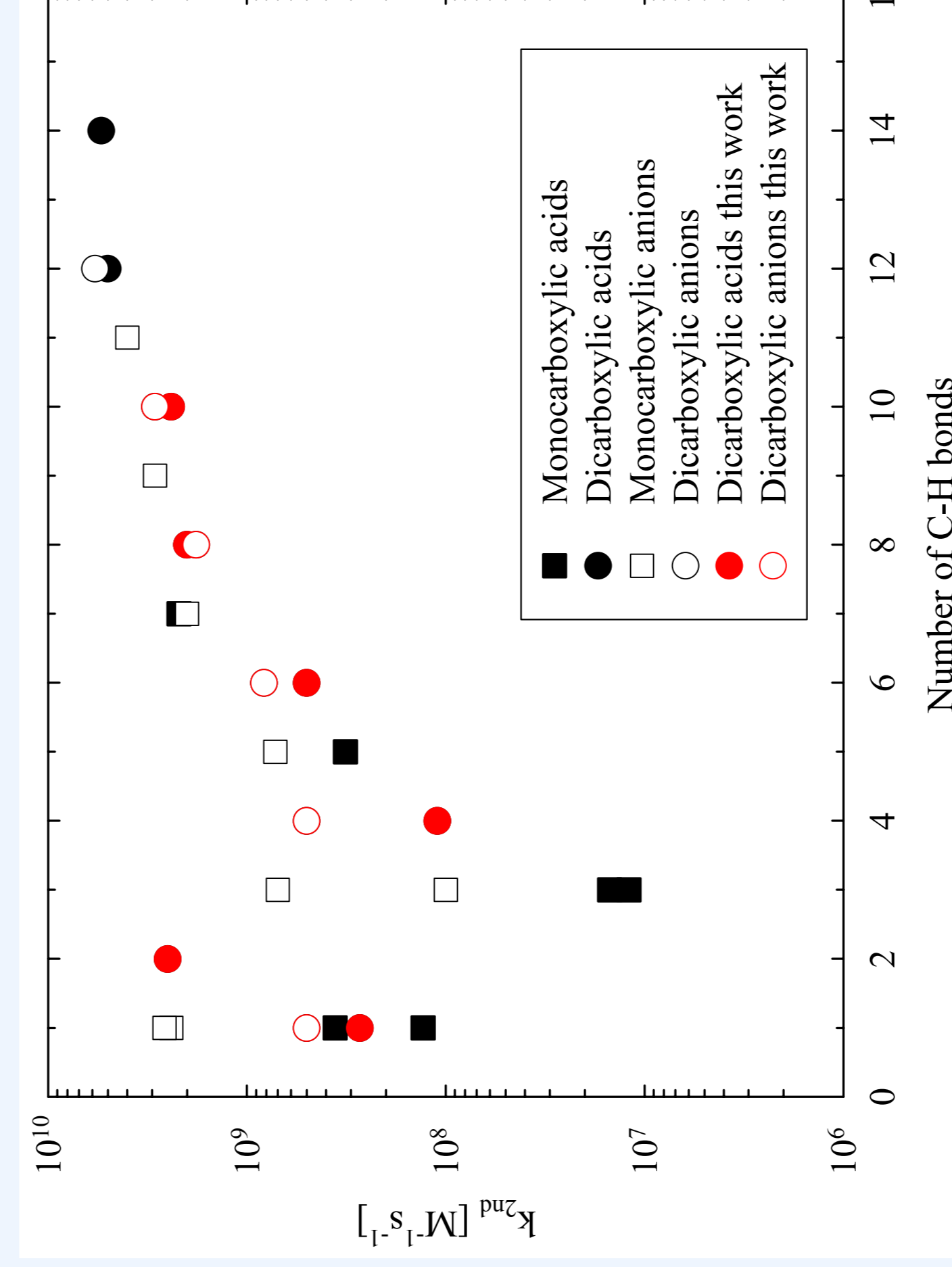


Figure 3: Plot of logarithm of the measured and literature rate constants [8, 9] at 298 K divided by the number of easiest abstractable H-atoms $\lg(k_H)$ versus BDE

- Fig. 3 shows that the correlation is better for aldehydes, alcohols and glycol ethers whereas the carboxylic acids introduce more scatter
- Nevertheless, a clear trend of increasing rate constants with decreasing BDE can be seen with following regression equation:

$$\lg(k_H [\text{M}^{-1} \text{s}^{-1}]) = (29.8 \pm 6.8) - (5.4 \pm 1.7) \cdot 10^{-2} \cdot \text{BDE} [\text{kJ mol}^{-1}]$$

$$\text{with } n = 29; R^2 = 0.77$$



- Fig. 4 shows, that for carboxylic acids with more than one H-atom not only the most weakly bonded determines the rate constant
- A clear trend of higher rate constants with increasing number of C-H bonds is visible in general because of increase in possible reaction sites for H-abstraction

Figure 4: Plot of measured and literature rate constants [10] at 298 K versus the number of C-H bonds

Conclusions

- Measured k_{2nd} agree well with available literature values
- Preexponential factors of carboxylic acids are more scattered than other aliphatic compounds
- A trend of faster reaction with decreasing BDE is visible
- Rate constants depend on the overall number of C-H bonds in the molecule
- Main reaction mechanism is H-atom abstraction

References

- M. Chin and P.H. Wine, J. Photochem. Photobiol., **1992**, A 69, 17
- M.N. Schuchmann, H.-P. Schuchmann and C. von Sonntag, J. Phys. Chem., **1995**, 99, 9122
- J. Hesper, **2003**, Dissertation, University of Leipzig
- G. Scholes and R.L. Willson, Trans. Faraday Soc., **1967**, 63, 2983
- S.R. Logan, J. Chem. Soc., **1989**, 751
- M. Simić, P. Neča and E. Hayon, J. Phys. Chem., **1969**
- M.G. Evans and M. Polanyi, Trans. Faraday. Soc., **1938**, 34, 11
- B. Ervens, **2001**, Dissertation, University of Leipzig
- S. Gligorovski and H. Herrmann, Phys. Chem. Chem. Phys., **2004**
- H. Herrmann, Chem. Rev., **2003**, 103, 4691