

Temperature dependent reactions of the NO₃-radical with *para*-substituted phenols in aqueous solution



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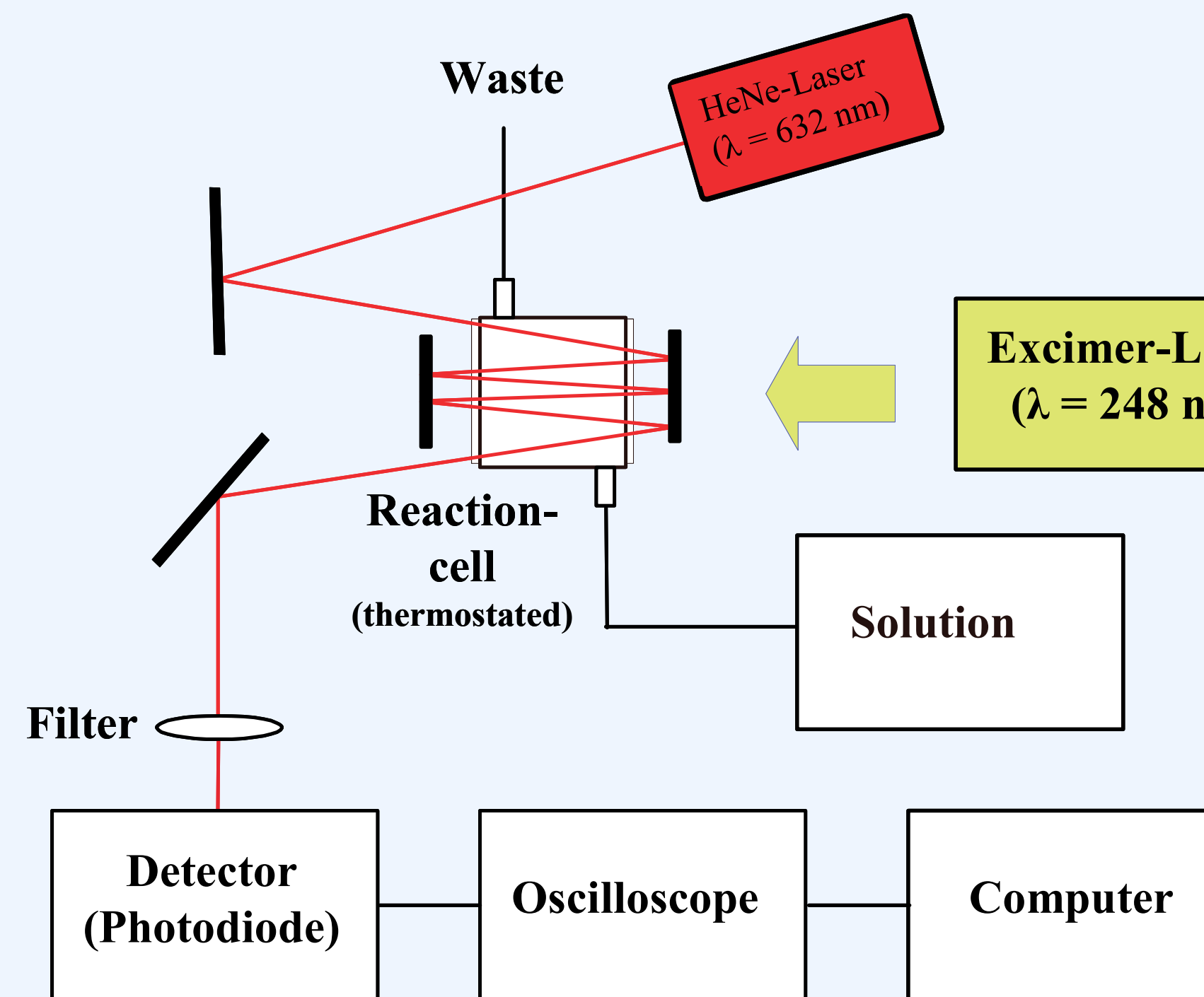
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Motivation and background

- Free-radical chemistry in the aqueous tropospheric phase**
- Nighttime oxidation of organic compounds such as phenols by NO₃
- Substituted phenols in the troposphere**
- Primary sources: Emissions from combustion and industrial processes
 - Secondary sources: Formation from oxidation of benzene derivatives
 - Toxic and phytotoxic compounds
 - Occurrence in rain, clouds and fog
- Reactions of phenols with NO₃-radicals**
- Competitive reaction mechanisms
- Scope of study**
- Kinetic and thermodynamic data for tropospheric chemical modeling
 - Reactivity correlations → Insight into the different reaction mechanisms involved

Experimental



NO₃-radical generation

- Laser flash photolysis of nitrate anions at wavelength of $\lambda = 248$ nm at pH = 0.5 (HClO₄)
 $\text{NO}_3^- + h\nu + \text{H}^+ \longrightarrow \text{NO}_2 + \text{OH}$
- Reaction of OH with undissociated HNO₃ to form NO₃
 $\text{HNO}_3 + \text{OH} \longrightarrow \text{NO}_3 + \text{H}_2\text{O}$

Kinetic investigations

- Reaction of NO₃ with the organic reactant
- Observation of the temporal decline of the NO₃ concentration with He-Ne laser at NO₃ absorption maximum with wavelength $\lambda = 632$ nm
- Determination of second order rate constants between 278 and 318 K

Figure 2: Laser photolysis long path absorption set-up (LP-LPA)

Kinetic and thermodynamic results and reactivity discussion

Table 1: Activation energy (E_A), activation entropy (ΔS^\ddagger), free energy of activation (ΔG^\ddagger), observed rate constants at 298 K, bond dissociation energy (BDE) of the easiest abstractable H-atoms, calculated theoretical rate constant of a pure H-abstraction ($k_{H \text{ calc}}$), ratio of $k_{H \text{ calc}}$ to the observed rate constant for the investigated phenols

Compound	E_A [kJ mol ⁻¹]	ΔS^\ddagger [J K ⁻¹ mol ⁻¹]	ΔG^\ddagger [kJ mol ⁻¹]	$k_{\text{obs } 298}$ [M ⁻¹ s ⁻¹]	BDE ^a [kJ mol ⁻¹]	Bond	$k_{H \text{ calc}}^b$ [M ⁻¹ s ⁻¹]	$k_{H \text{ calc}} / k_{\text{obs}}$ [%]
4-Nitrophenol	14.0 ± 2.5	-(31.1 ± 1.2)	20.7 ± 4.6	(1.37 ± 0.4) · 10 ⁹	396.3	O-H	1.62 · 10 ⁵	0.01
4-Hydroxybenzoic acid	13.2 ± 2.5	-(32.9 ± 1.2)	20.5 ± 4.6	(1.61 ± 0.5) · 10 ⁹	360 ^[3]	O-H	1.82 · 10 ⁸	11.3
4-Methylphenol	5.8 ± 2.0	-(56.9 ± 1.9)	20.3 ± 7.5	(1.66 ± 0.3) · 10 ⁹	363.3	O-H	9.61 · 10 ⁷	5.8
					357 ^[4]	CH ₂ -H	9.75 · 10 ⁸	58.8
4-Aminophenol	9.8 ± 3.2	-(42.2 ± 2.1)	19.9 ± 7.4	(2.02 ± 0.3) · 10 ⁹	331.3	O-H	4.69 · 10 ¹⁰	> 100
4-Methoxyphenol	14.6 ± 5.0	-(24.3 ± 1.8)	19.4 ± 8.1	(2.81 ± 0.5) · 10 ⁹	349.3	O-H	1.44 · 10 ⁹	51.3

^a phenolic BDE from [2], ^b calculated with regression line $\lg k_H \sim \text{BDE}$ from [1], displayed in Fig. 4

- Substituted phenols have different k_{obs} in the order of 10⁹ M⁻¹s⁻¹

Are the different k_{obs} due to different reaction mechanisms?

- Intercomparison of E_A and ΔS^\ddagger with k_{obs} cannot explain the differences in k_{obs} or point towards a certain reaction mechanism
- Negative ΔS^\ddagger of all measured phenols indicates an activated complex that is more ordered than the reactants
- Higher rate constants correspond to lower free energy of activation (ΔG^\ddagger)
- Use of reactivity correlations to learn more about contribution from different reaction mechanisms

Are the measured activation energies or rate constants a function of the H-atom bond dissociation energy (BDE)?

→ Indication of H-atom abstraction!

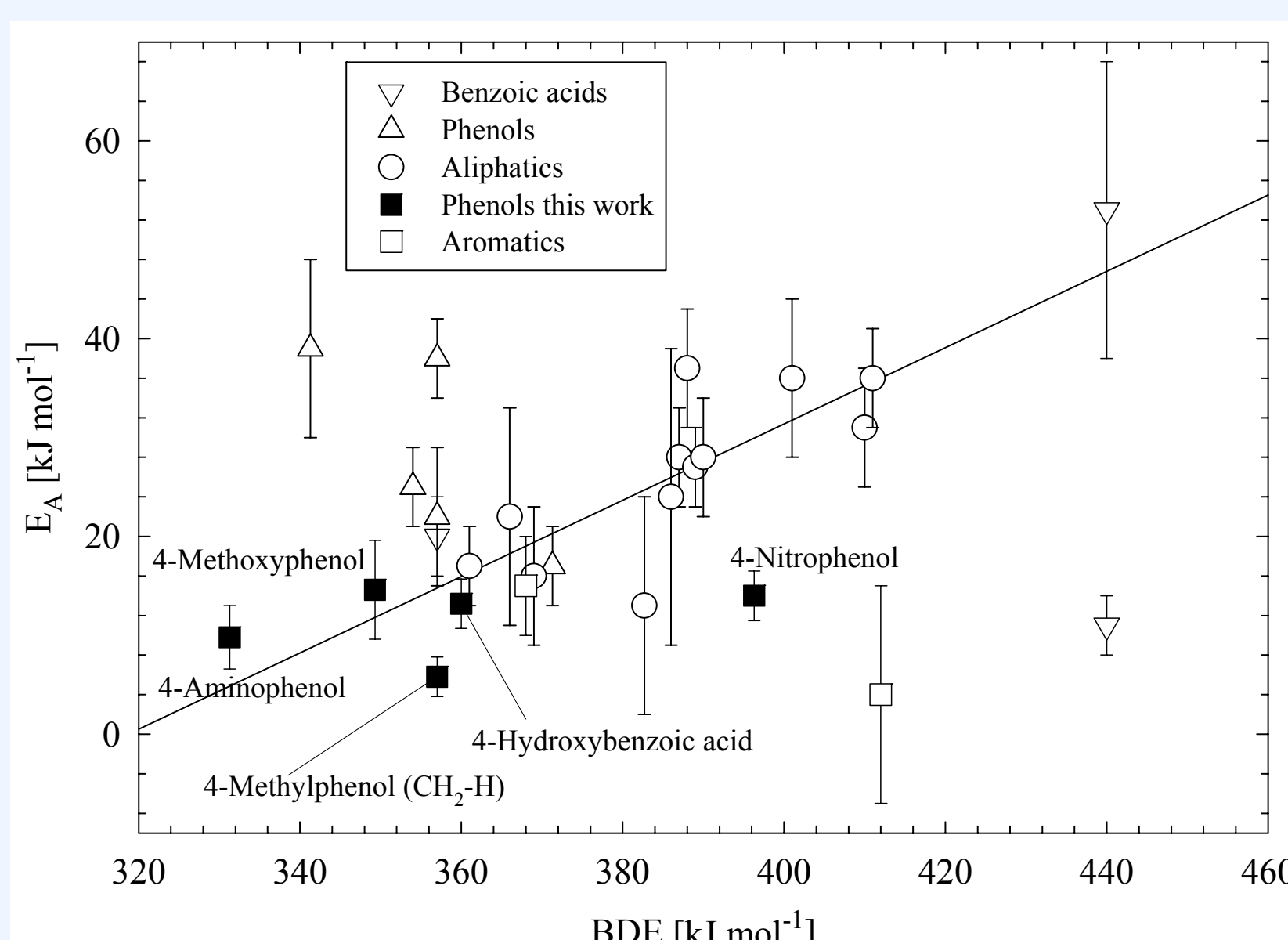


Figure 3: Plot of measurement obtained E_A and literature values [1,3,5, 6,7] versus bond dissociation energy

- Measured phenols have lowest activation energies among other aromatics and aliphatic compounds
- Regression line only for H-abstraction reactions of aliphatics:
 E_A [kJ mol⁻¹] = (0.39 ± 0.2) · BDE [kJ mol⁻¹] - (123 ± 86)
 with n = 12; R² = 0.75

- 4-Methoxy-, 4-Amino-, 4-Methylphenol, 4-Hydroxybenzoic acid are close to the regression lines in both Fig.3 and 4 → likelihood of H-abstraction contribution
- E_A and $\lg k_H$ of 4-Nitrophenol seems independent of the BDE (Fig.3 and 4) → H-abstraction unlikely

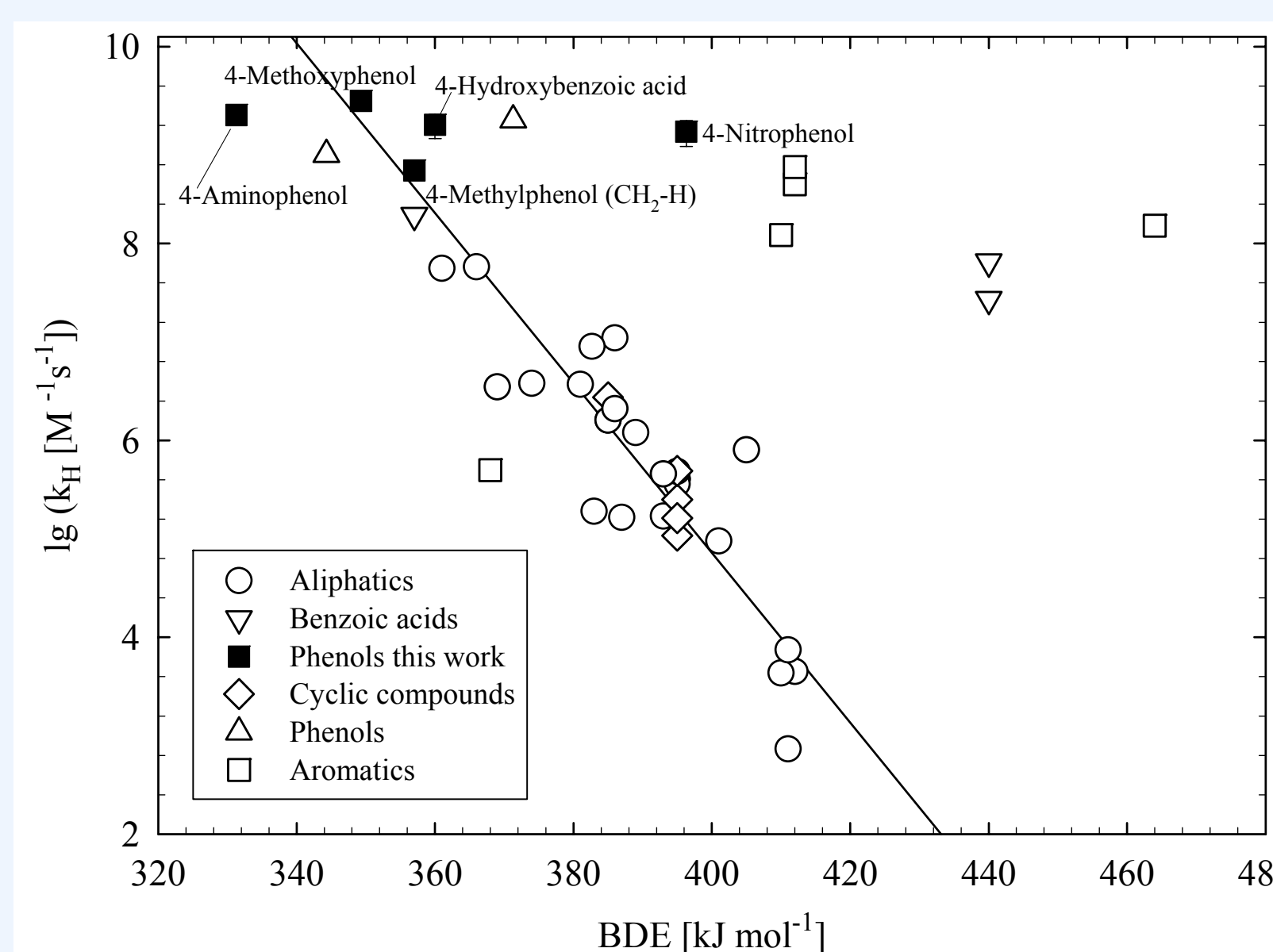


Figure 4: Plot of logarithm of the measured and literature rate constants [1,7] at 298 K divided by the number of easiest abstractable H-atoms $\lg(k_H)$ against the BDE

- Highest measured rate constants of phenols in comparison with other classes of compounds
- Regression line only for H-abstraction reactions of aliphatic and cyclic compounds [1]:
 $\lg(k_H) = (38.5 \pm 5.6) - (0.084 \pm 0.014) \cdot \text{BDE}$ [kJ mol⁻¹]
 with n = 37; R² = 0.89

Competitive reaction mechanisms

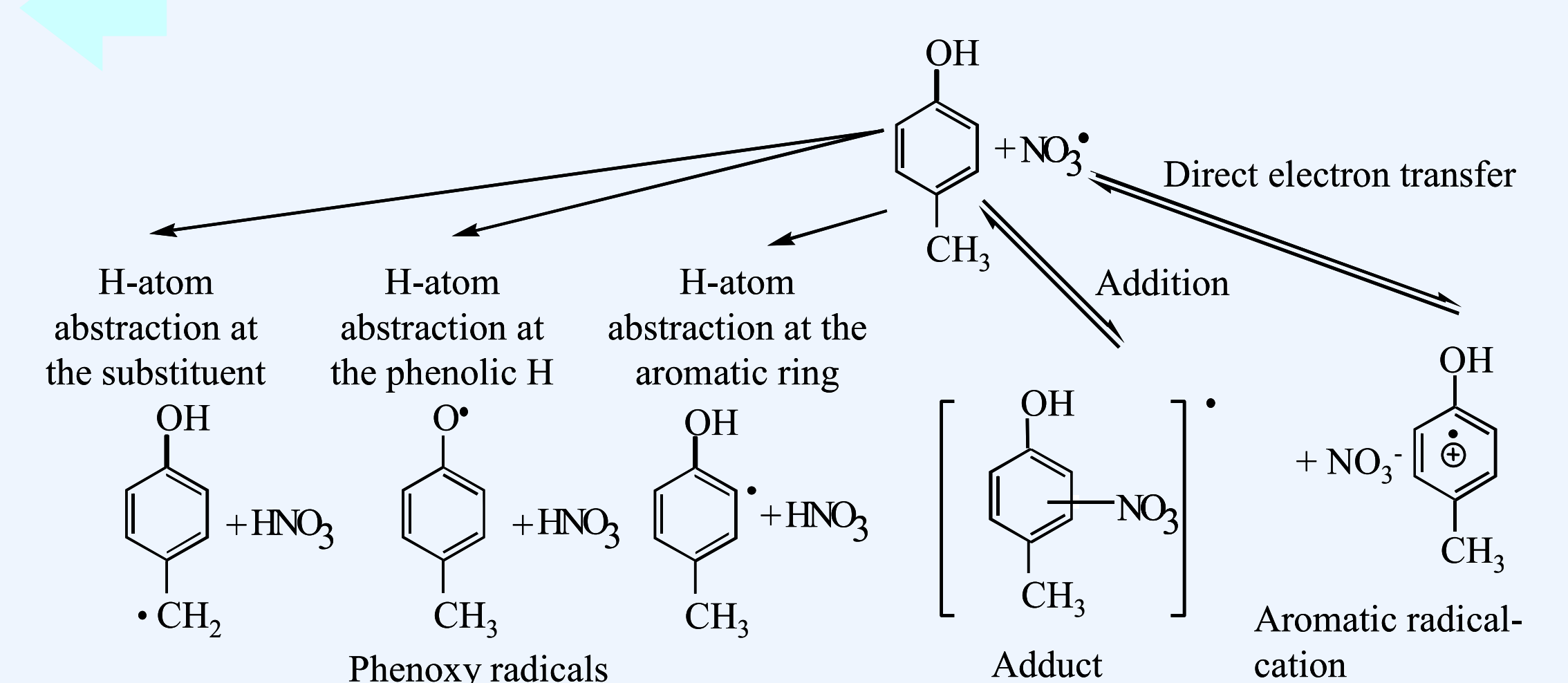


Figure 1: Possible reaction mechanisms for substituted phenols with NO₃ in aqueous solution which may occur at the same time at different speeds → different contribution to overall measured rate constant, after [1]

Are the measured rate constants a function of the Gibbs free energy of reaction (Marcus-Theory)?

→ Indication of direct electron transfer!

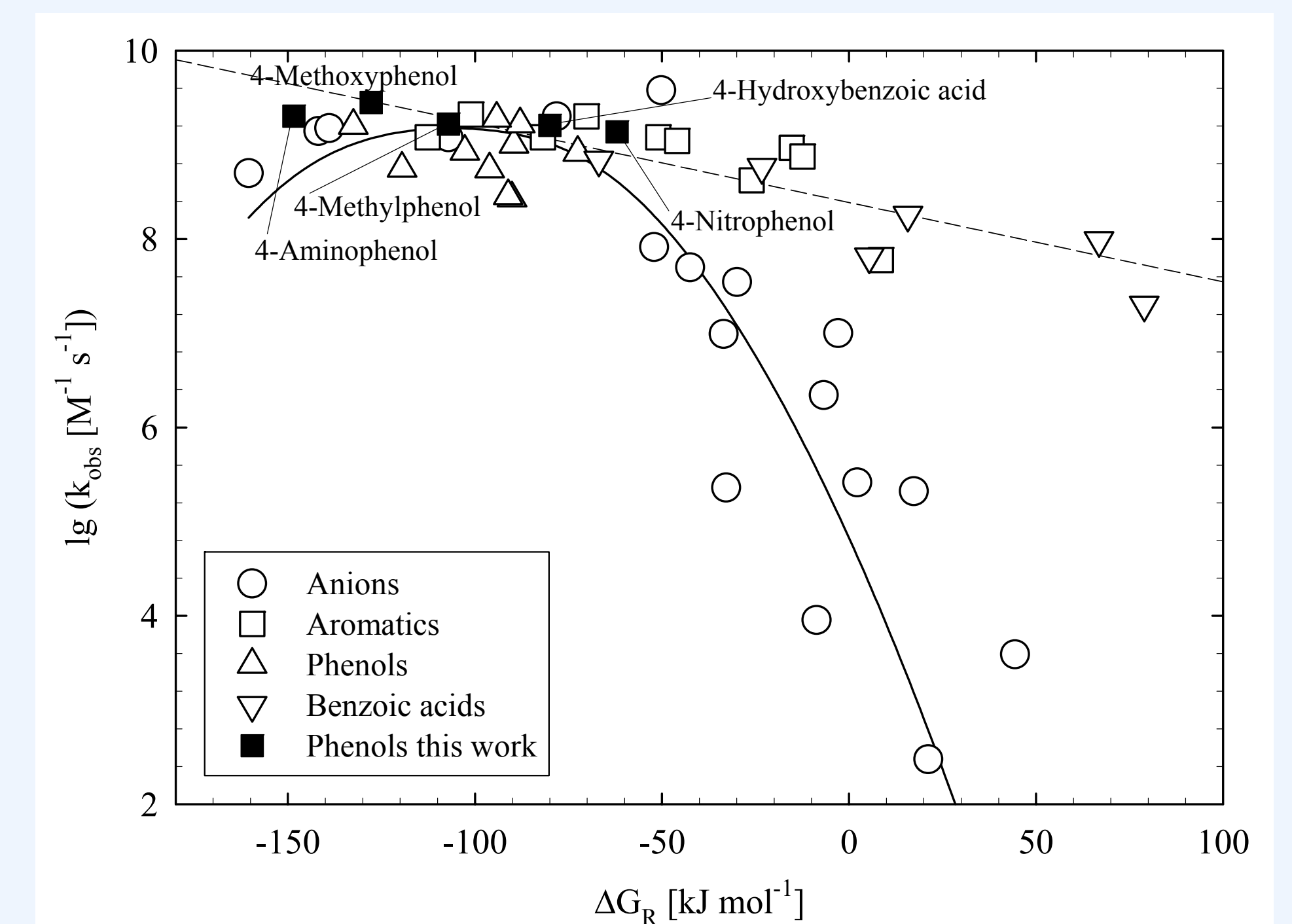


Figure 5: Plot of logarithm of the measured and literature rate constants [1,3,5,6] at 298 K as a function of the Gibbs free energy of reaction (ΔG_R), solid line: Marcus-curve fit to the Anions [1], dashed line: empirical correlation for para- and mono-substituted aromatics [this work]

- All rate constants of the investigated phenols are a function of ΔG_R according to the Marcus-theory → contribution to the reactivity from direct electron transfer is also likely
- Rate constants of aromatics and benzoic acids with ΔG_R greater than -40 kJ mol⁻¹ cannot be described by the Marcus-Theory → maybe indication for an addition mechanism [1]
- Empirical correlation for para- and mono-substituted aromatics $\lg k_{\text{obs}} \sim \Delta G_R$ was found:

$$\lg(k_{\text{obs}} [\text{M}^{-1} \text{s}^{-1}]) = (8.4 \pm 0.2) - (8.4 \pm 2) \cdot 10^{-3} \cdot \Delta G_R [\text{kJ mol}^{-1}]$$

with n = 24; R² = 0.88

Conclusions

- Investigated Phenols react via mixed mechanisms with NO₃
- Possible contributions of different reaction mechanisms in Tab. 2
- Fast spectroscopic measurements that are able to identify first reaction intermediates and ab-initio calculations could determine exact mechanism

Table 2: Likelihood of the contributions from the discussed mechanisms

Compound	H-Atom abstraction at		Direct electron transfer	Addition/ Elimination
	Substituent	O-H		
4-Nitrophenol	NO ₂	0	XX	X
4-Hydroxybenzoic acid	COO-H	0	X	X
4-Methylphenol	CH ₂ -H	X	X	X
4-Aminophenol	NH ₂ -H ⁺	XX	X	X
4-Methoxyphenol	OCH ₂ -H	0	X	X

0 = unlikely, X = possible, XX = likely

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