

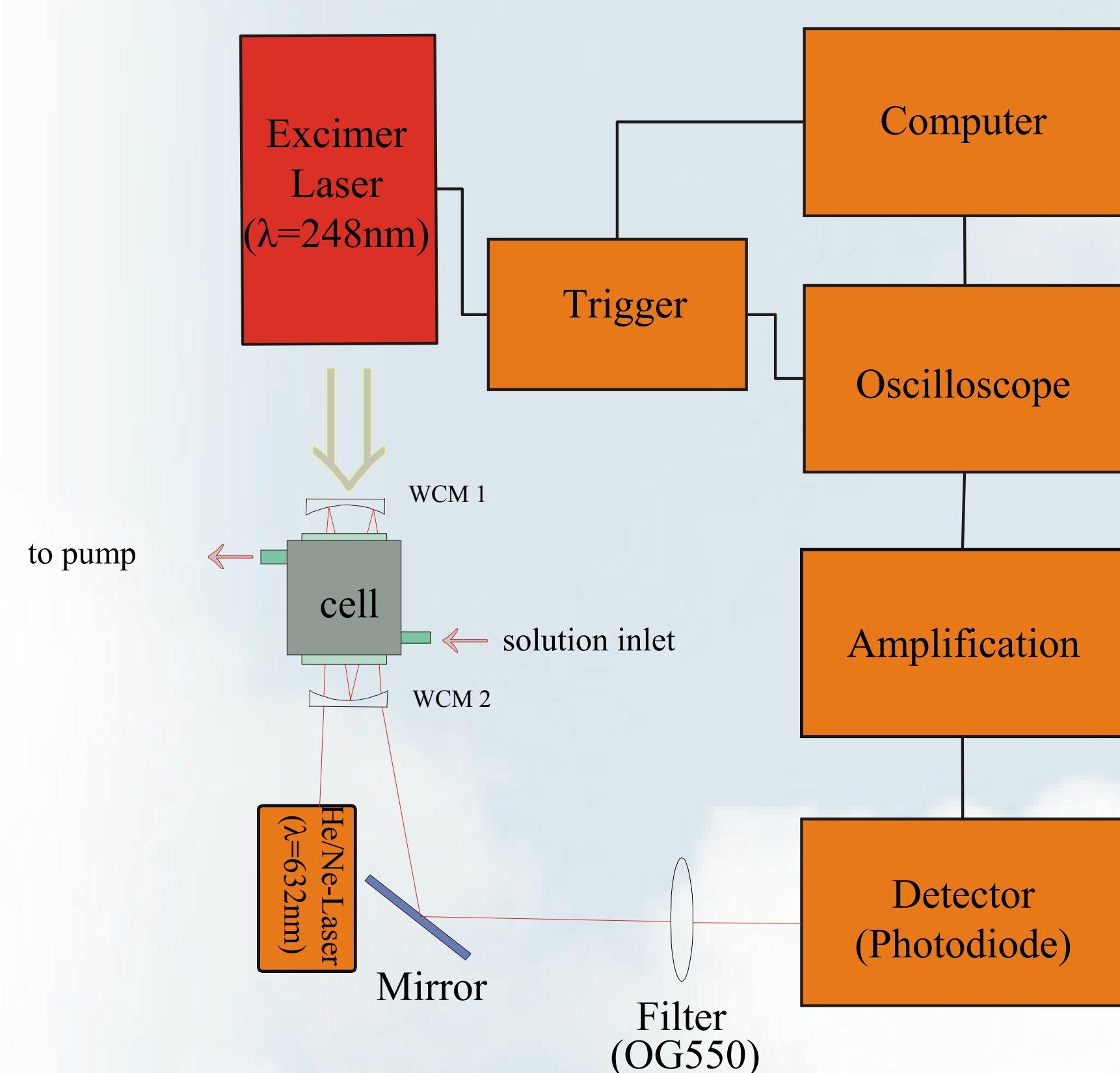
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1. Motivation

The degradation of organic compounds in the atmosphere can be initiated by oxidation reactions with atmospheric radicals such as NO₃. Beside the H-abstraction, also the electron transfer reaction can be of importance as reaction pathway in aqueous solution. In particular, for some phenolic compounds electron transfer is the dominating reaction pathway. Substituted phenols may be emitted directly into the atmosphere or they are formed by the atmospheric oxidation of aromatic precursors (benzene, toluene and xylene)^[1]. Sources of phenols are above all anthropogenic sources, for example car exhaust, industry and agriculture (pesticides). However, phenols (e.g. methoxyphenols), can be emitted to larger extent also during natural biomass burning^[2]. Phenol and its derivatives may affect human health, and the toxicity and phytotoxicity of many of these compounds are well-known. But the knowledge about their chemical behavior in the atmosphere is still limited. Therefore the reactivity of NO₃-radicals towards phenolic compounds in aqueous solution was investigated. Beside the temperature also salt effects can influence the rate constants of reactions. Using a laser-photolysis-long-path-laser-absorption set-up, rate constants for the reactions of nitrate radicals with different substituted phenols in aqueous solution have been measured as a function of the ionic strength.

2. Experimental



NO₃-radicals were generated by laser flash photolysis of nitrate anions^[1]. Nitrate anions were photolysed at a wavelength of $\lambda = 248$ nm in nitric acid solution (pH = 0.5).

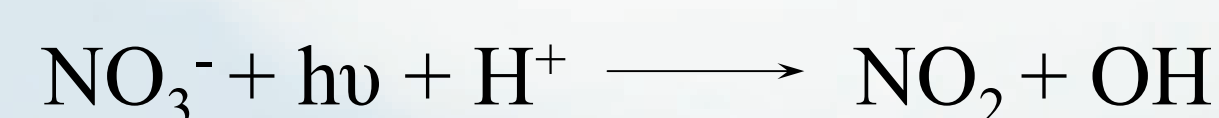


Figure 1 shows the LP-LPA set-up, which was used for the kinetic investigations. The temporal change of the NO₃ concentration was followed using a He-Ne laser operated at $\lambda = 632.8$ nm.

Figure 1: Experimental set-up of laser photolysis long path absorption (LP-LPA) experiment

3. Results and Discussions

Ionic strength dependencies of reactions of the NO₃-radical with several substituted phenols in aqueous solution were investigated. Different ionic strengths were adjusted by adding NaClO₄. The observed ionic strength parameters are summarized in the following table.

Table 1: Observed rate constants and ionic strength parameters

compound	$k_{(I \rightarrow 0)}$ [M ⁻¹ s ⁻¹]	$k_{(I \rightarrow \infty)}$ [M ⁻¹ s ⁻¹]	$k_{(I \rightarrow \infty)} / k_{(I \rightarrow 0)}$ [%]	β [M ⁻¹]	μ [Debye]	reference
1 p-cresol	$5.7 \cdot 10^8$	$2.3 \cdot 10^9$	4.035	0.285	1.227	This work
2 p-hydroxybenzoic acid	$1.2 \cdot 10^9$	$1.5 \cdot 10^9$	1.250	0.131	3.037	This work
3 p-methoxyphenol	$4.3 \cdot 10^8$	$2.6 \cdot 10^9$	6.047	0.456	0.403	This work
4 toluene	$9.5 \cdot 10^8$	$1.8 \cdot 10^9$	1.895	0.384	0.263	[3]
5 benzoic acid	$1.2 \cdot 10^7$	$1.2 \cdot 10^8$	10.000	0.247	2.251	[4]
6 phenol	$2.2 \cdot 10^8$	$2.6 \cdot 10^9$	11.818	0.317	1.142	[4]
7 acetaldehyd	$1.0 \cdot 10^6$	$8.4 \cdot 10^6$	8.400	0.218	2.537	[3]
8 benzene	$8.3 \cdot 10^8$	$1.4 \cdot 10^9$	1.687	0.107	0.000	[3]
9 p-nitrophenol	$8.7 \cdot 10^8$	$8.7 \cdot 10^8$	1.000	0.000	5.561	This work
10 o-nitrophenol	$8.9 \cdot 10^8$	$8.9 \cdot 10^8$	1.000	0.000	4.183	This work
11 2,3-dinitrophenol	$6.2 \cdot 10^8$	$6.2 \cdot 10^8$	1.000	0.000	6.593	This work

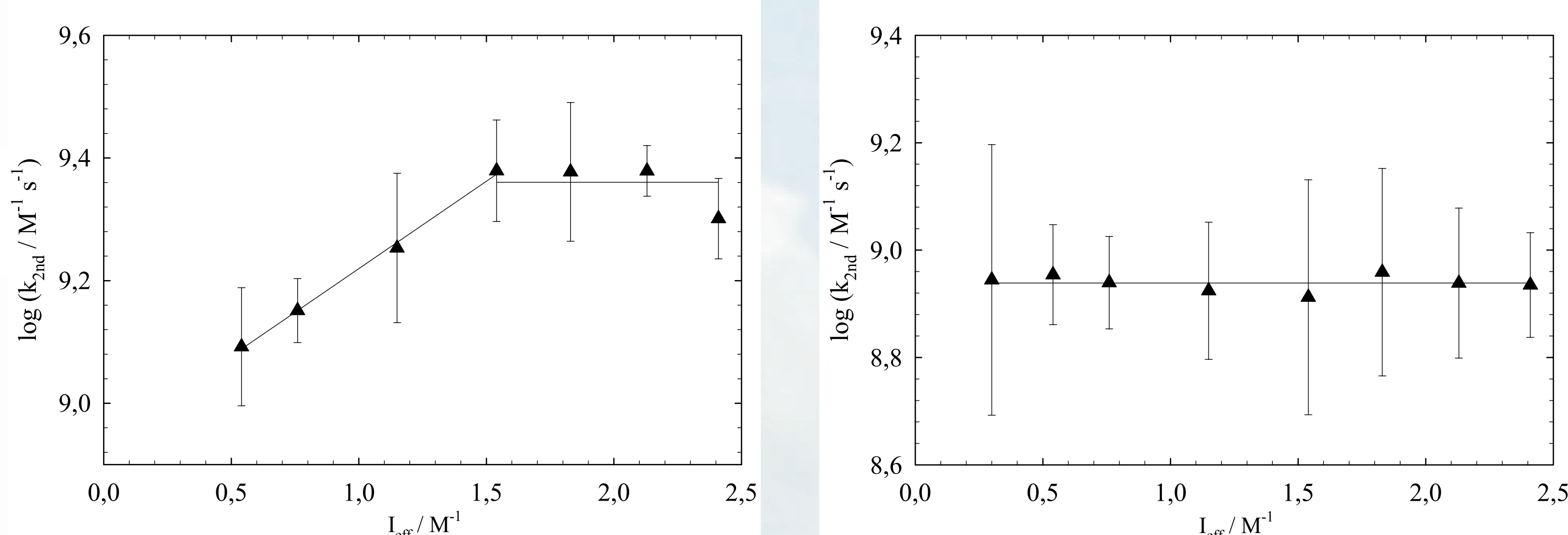


Figure 2: Ionic strength dependencies of p-cresol (left) and p-nitrophenol (right)

The kinetic salting coefficient β (see Table 1) is defined as the slope of the regression line in Figure 2. In addition to the salting coefficient, the plots in Figure 2 can be described by $k_{(I=0)}$ and $k_{(I \rightarrow \infty)}$. While $k_{(I=0)}$ is the intercept of the regression line, $k_{(I \rightarrow \infty)}$ represents an average value from the rate constants on the plateau in Figure 2. Since these are purely empirical parameter, the influence of the ionic strength can't be evaluated for reactions between two neutral compounds.

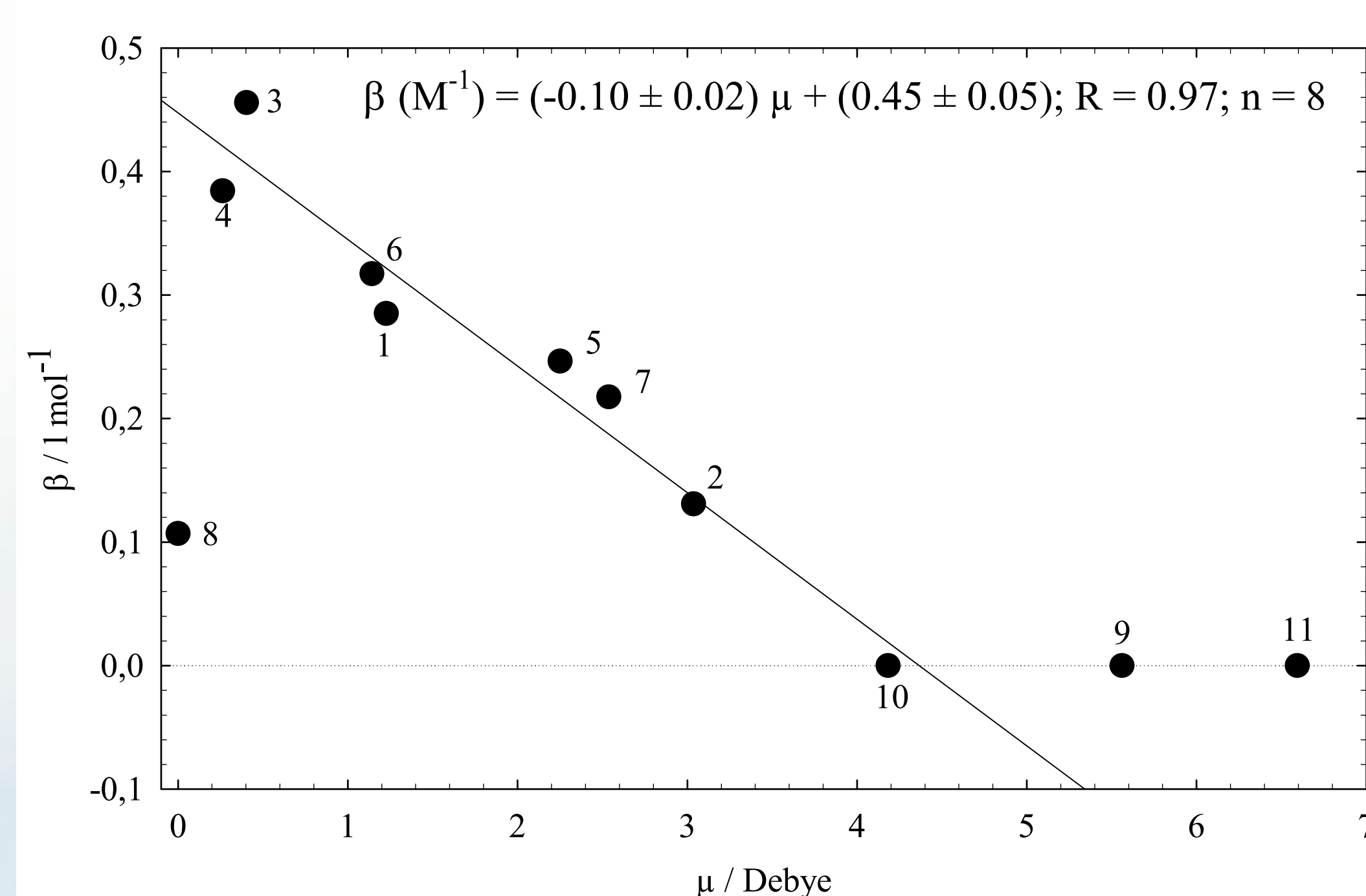


Figure 3: Plot of the dipole moment (μ) versus the kinetic salting coefficient (β)

This plot clarifies that reactants with a high or no dipole moment are not or just weakly affected by the ionic strength of the solution. Since appropriate data are missing, the question remains if there are similar correlations for other neutral radicals. With the exception of acetaldehyde all compounds in Figure 3 belong to the electron transfer reactions. Figure 4 shows that all the measured rate constants for the phenols (\blacktriangle) are fitting with the expectations of the Marcus theory^[5-7] well.

However, the aromatics toluene (4), benzene (8) and benzoic acid (5) reacting faster than expected. It's likely, that the reaction mechanism is changing from an direct electron transfer (SET) to an so called addition-elimination mechanism (A/D) for these three compounds. Beside the dipole moments also the reaction enthalpies were plotted against β (see Fig. 5).

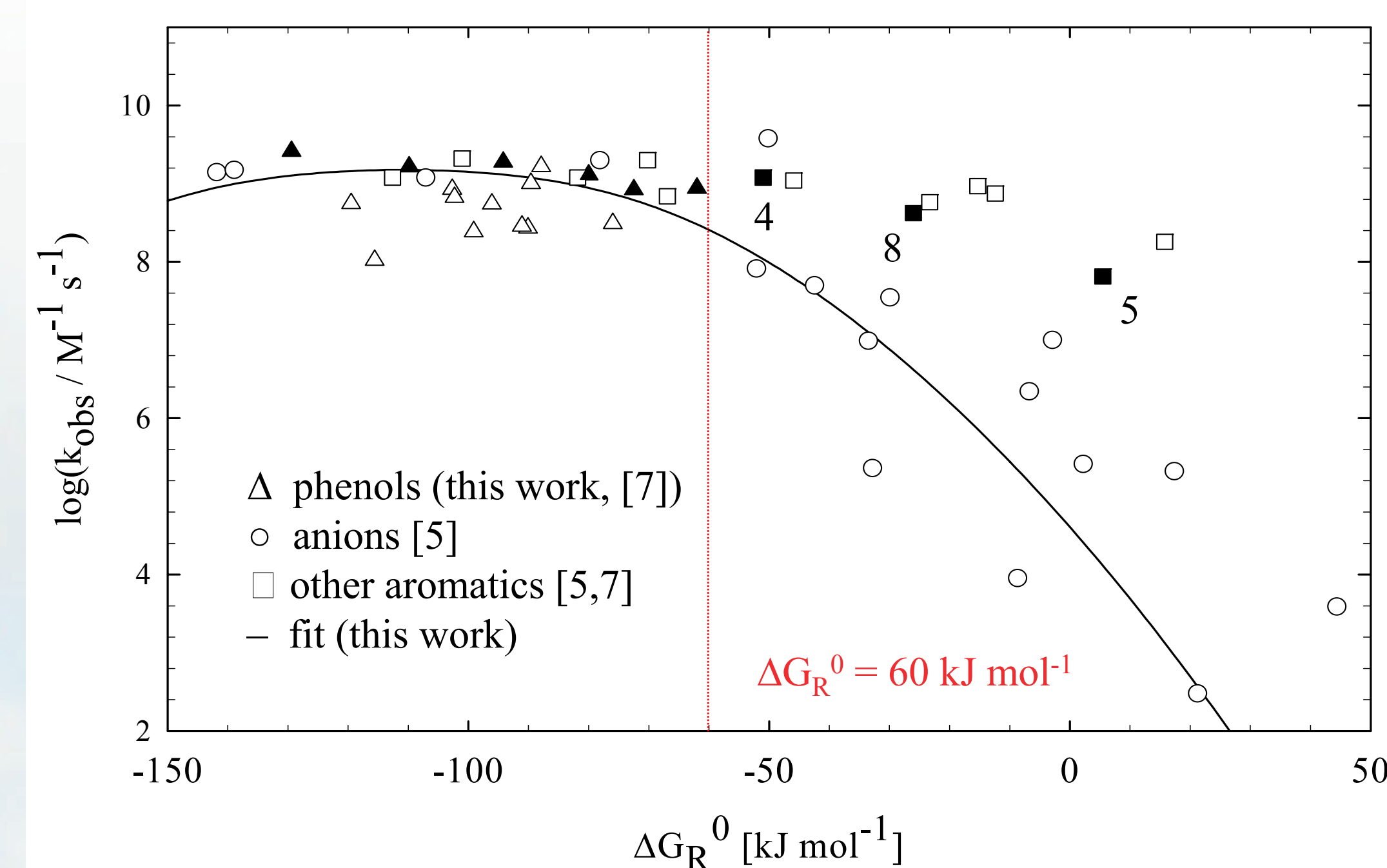


Figure 4: Plot of the Gibbs free reaction enthalpy (ΔG_R^0) versus the observed rate constant for electron transfer reactions

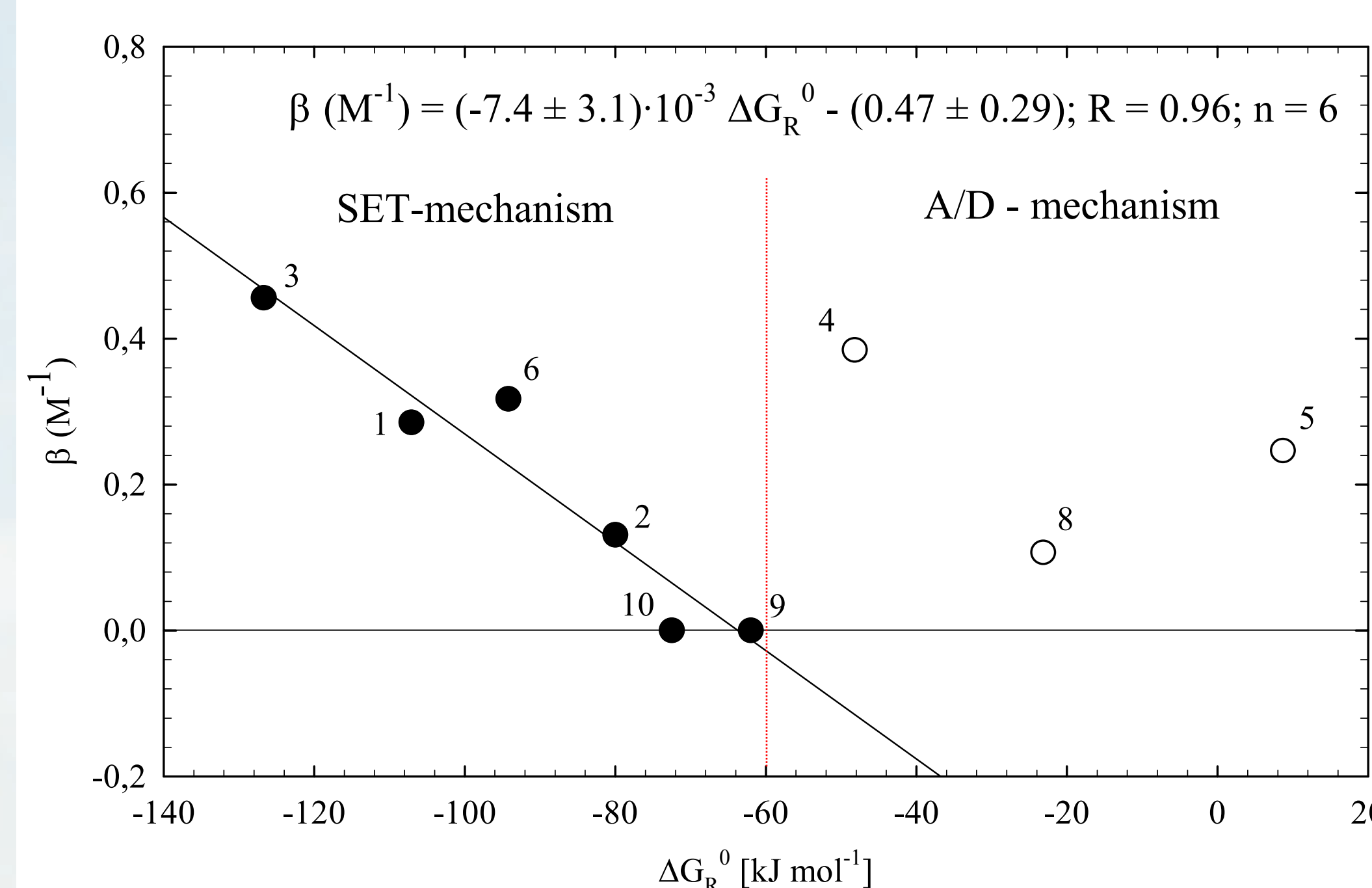


Figure 5: Plot of the Gibbs free reaction enthalpy (ΔG_R^0) versus the kinetic salting coefficient (β)

Fig. 5 indicates that the more exergonic a reactions is the higher is the influence of the ionic strength. The reason for this behavior is maybe a different charge, stability or structure of the transition state. Toluene (4), benzene (8) and benzoic acid (5) are not included in the regression line (Fig. 5), because of the different reaction mechanism.

4. References

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