# Study of the reactivity of nitrate radical towards substituted phenols in aqueous solution

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## Motivation

Oxygenated aromatic compounds like phenols, cresols and nitrophenols have been detected both in the gaseous and aqueous phase of the atmosphere. Substituted phenols may be emitted directly or formed by the atmospheric oxidation of aromatic hydrocarbons. Due to their toxicity and phytotoxicity, their chemical behaviour in the atmosphere is of note. The predominant sink process for some of these compounds is their reaction with atmospheric radicals, i.e. OH and $NO_3$. Rate constants for the reactions of $NO_3$-radicals with different para-substituted phenols in aqueous solution have been measured. Beside, for the first time the ionic strength dependence of $NO_3$ reactions with several p-substituted phenols have been investigated. The observed rate constants and literature data were used to find correlations between the measured rate constants and properties of the phenols. The kinetic data will be used as input parameters for the multiphase tropospheric chemistry model CAPRAM (Chemical Aqueous Phase Radical Mechanism).
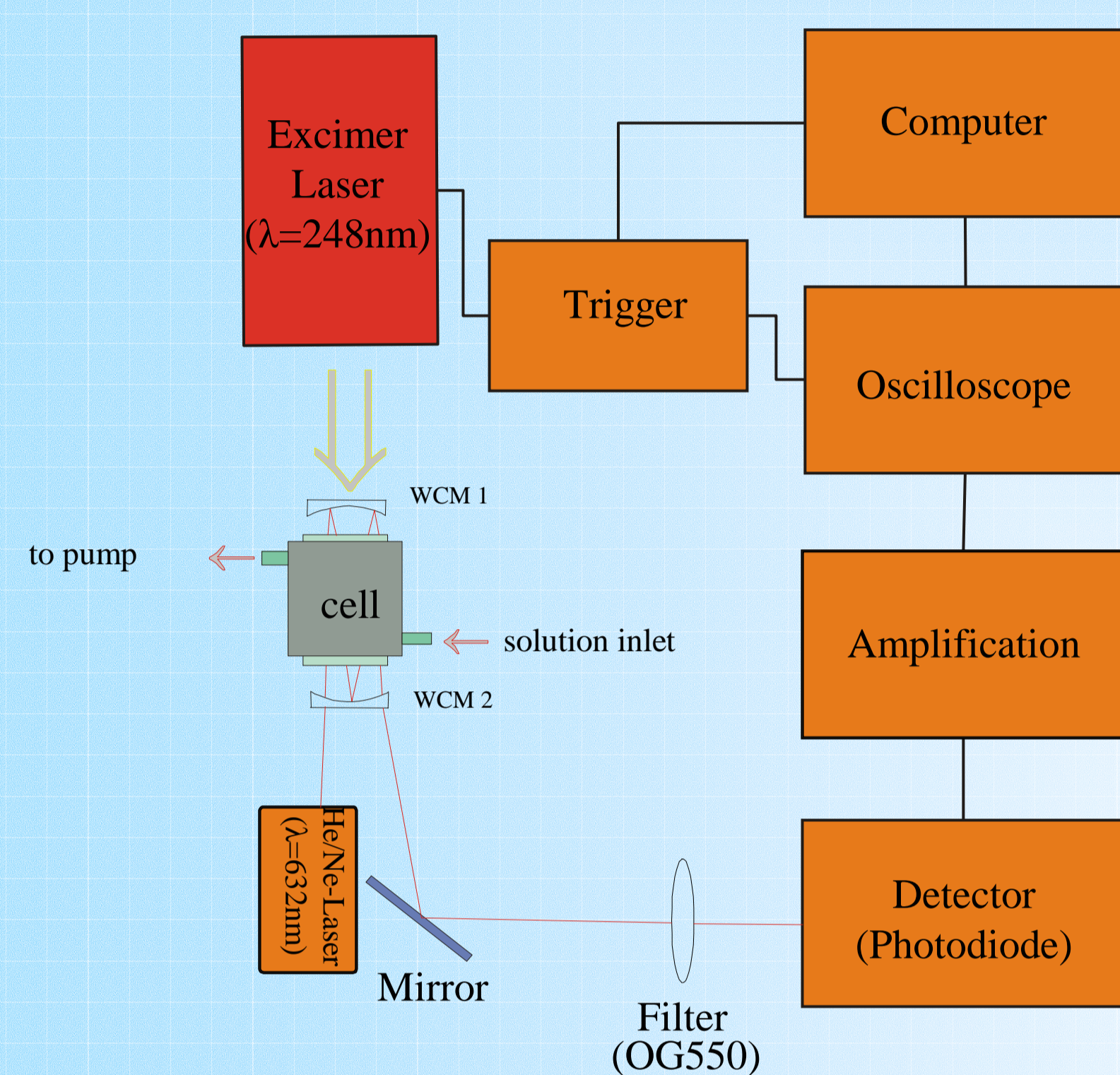
## Experimental



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

The nitrate radicals are produced by laser flash photolysis of nitrate anions. Nitrate anions were photolysed at a wavelength of λ = 248 nm in nitric acid solution. The generated OH radicals react further with undissociated nitric acid by an H-abstraction mechanism to the $NO_3$-radicals.

$$NO_3^- + h\upsilon + H^+ \longrightarrow NO_2 + OH$$
$$HNO_3 + OH \longrightarrow NO_3 + H_2O$$

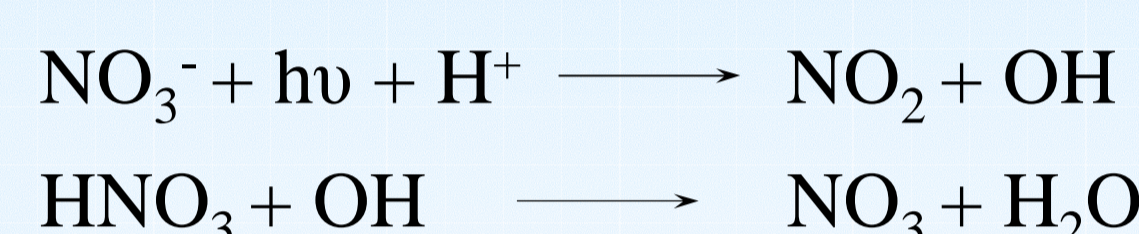Figure 1 shows the laser flash photolysis long path absorption set-up, which was used for the kinetic investigations. The temporal change of the $NO_3$-radical concentration was observed by a He-Ne laser, which operates at 632.8 nm.

## Results and Discussions

Reactions of the $NO_3$-radicals with different p-substituted phenols in aqueous solution were investigated, the observed rate constants ($k_{2nd, 298K}$) are summarized in the following table. The $NO_3$-radical might react with phenols through different mechanisms: (a) H-Abstraction (b) Electron transfer reaction (c) Addition/Elimination. The values for $k_H$(calc) represent calculated rate constants of an H-abstraction reaction. A correlation provided by Herrmann and Zellner [1] was applied.

**Table 1:** Observed rate constants at room temperature

| | Compound | $k_{2nd, 298K}$ $[M^{-1}s^{-1}]$ | $\sigma_p^+$ (i) | BDE [O-H] (ii) kJ mol$^{-1}$ | $k_{H(calc)}$ (iii) $M^{-1}s^{-1}$ | $k_H/k_{2nd}$ [%] | assumed mechanism |
|---|---|---|---|---|---|---|---|
| 1 | p-hydroxyphenol | $(1.1 \pm 0.5) \cdot 10^9$ | -0.92 | 344.3 | $3.8 \cdot 10^9$ | >100 | H-ABS |
| 2 | p-aminophenol | $(1.9 \pm 0.2) \cdot 10^9$ | -1.30 | 331.3 | $4.7 \cdot 10^{10}$ | >100 | H-ABS |
| 3 | p-nitrophenol | $(7.7 \pm 2.1) \cdot 10^8$ | 0.79 | 396.3 | $1.6 \cdot 10^5$ | 0.02 | ETR |
| 4 | p-hydroxybenzoic acid | $(1.3 \pm 0.3) \cdot 10^9$ | 0.42 | 360.0 | $1.8 \cdot 10^8$ | 13.8 | ETR |
| 5 | p-iodophenol | $(3.5 \pm 0.4) \cdot 10^8$ | 0.14 | 370.3 | $2.5 \cdot 10^7$ | 7.1 | ETR |
| 6 | p-cresol | $(1.8 \pm 0.1) \cdot 10^9$ | -0.31 | 357.0 [CH$_2$-H] 363.3 | $3.2 \cdot 10^8$ | 17.8 | H-ABS / ETR |
| 7 | p-methoxyphenol | $(2.6 \pm 0.2) \cdot 10^9$ | -0.80 | 349.3 412.0 [OCH$_2$-H] | $1.4 \cdot 10^9$ | 53.8 | H-ABS / ETR |

(i) Brown Parameter [2]; (ii) Bond dissociation energies [3]; (iii) $k_H$ = rate constant for an H-abstraction reaction

As can be seen from Table 1, the observed rate constants for the reaction of $NO_3$ with p-hydroxyphenol and p-aminophenol can be fully explained with an H-abstraction mechanism. Whereas, p-nitrophenol, p-hydroxybenzoic acid and p-iodophenol show to react with $NO_3$ preferentially through an electron transfer reaction. In the case of p-cresol and p-methoxyphenol a mixed reaction regime is expected.

Figure 2 shows a good correlation for the ETR reactions between the Brown parameter ($\sigma_p^+$) [4] and the measured rate constants of different aromatic compounds. There are similar correlations also for the H-abstraction reaction.



**Figure 2:** Plot of the logarithm of the $k_{2nd}$ versus the $\sigma_p^+$ for the reaction of $NO_3$ with: (a) p-nitrophenol; (b) ethyl-4-hydroxy-benzoat; (c) p-hydroxybenzoic acid; (d) p-iodophenol; (e) p-bromophenol; (f) p-chlorophenol; (g) phenol; (h) p-cresol; (i) p-methoxyphenol

**Ionic strength dependencies:** The ionic strength (I) of a solution can accelerate, slow down or not affect a chemical reaction. In the present work, the effective ionic strength ($I_{eff}$) is considered taking in account the equilibrium constant (K) of the added salt. The $I_{eff}$ of 1:1 electrolyte solution was calculated applying the following equation.

$$I_{eff} = -\frac{1}{2K} + \sqrt{\frac{0.25}{K^2} + \frac{[salt]_0}{K}}$$

→ K = equilibrium constant [M$^{-1}$]     (Equation 1)

These measurements are important because the ionic strength in the aqueous phase of the atmosphere varies strongly [5]. The ionic strength is adjusted with sodium perchlorate, because it shows no disturbing absorptions and chemical reactions. Figure 3 shows a typical I-dependence by the example of p-Cresol. The results of different measurements as well as the dipole moments (μ) of the compounds are summarized in the following table 2.

**Table 2:** Parameter of different ionic strength dependencies; ß = kinetic salting coefficient; μ = dipole moment

| compound | $k_{(I \to 0)}$ $(M^{-1} s^{-1})$ | $k_{(I \to \infty)}$ $(M^{-1} s^{-1})$ | ß $(M^{-1})$ | μ (Debye) | reference |
|---|---|---|---|---|---|
| p-cresol | $5.7 \cdot 10^8$ | $2.3 \cdot 10^9$ | 0.2851 | 1.34 | this work |
| p-hydroxybenzoic acid | $1.2 \cdot 10^9$ | $1.5 \cdot 10^8$ | 0.1310 | 3.00 | this work |
| p-methoxyphenol | $4.3 \cdot 10^8$ | $2.6 \cdot 10^9$ | 0.4558 | 0.55 | this work |
| toluene | $9.7 \cdot 10^8$ | $1.8 \cdot 10^9$ | 0.4162 | 0.26 | [6] |
| benzoic acid | $1.2 \cdot 10^8$ | $1.1 \cdot 10^8$ | 0.2465 | 2.42 | [7] |
| phenol | $2.1 \cdot 10^8$ | $2.5 \cdot 10^9$ | 0.3173 | 1.40 | [7] |
| acetaldehyd | $1.3 \cdot 10^6$ | $7.5 \cdot 10^6$ | 0.1900 | 2.69 | [6] |
| benzene | $8.8 \cdot 10^8$ | $1.3 \cdot 10^9$ | 0.0890 | 0.00 | [6] |

Since the measurements must be accomplished at a pH value of 0.5, a measurement of the rate constants is not possible with an ionic strength of 0 ($k_{I \to 0}$). Therefore this value is determined theoretically from the intercept of the regression lines (see figure 3). The value for $k_{I \to \infty}$ is against it an average value from the measured rate constants on the plateau in Figure 3.
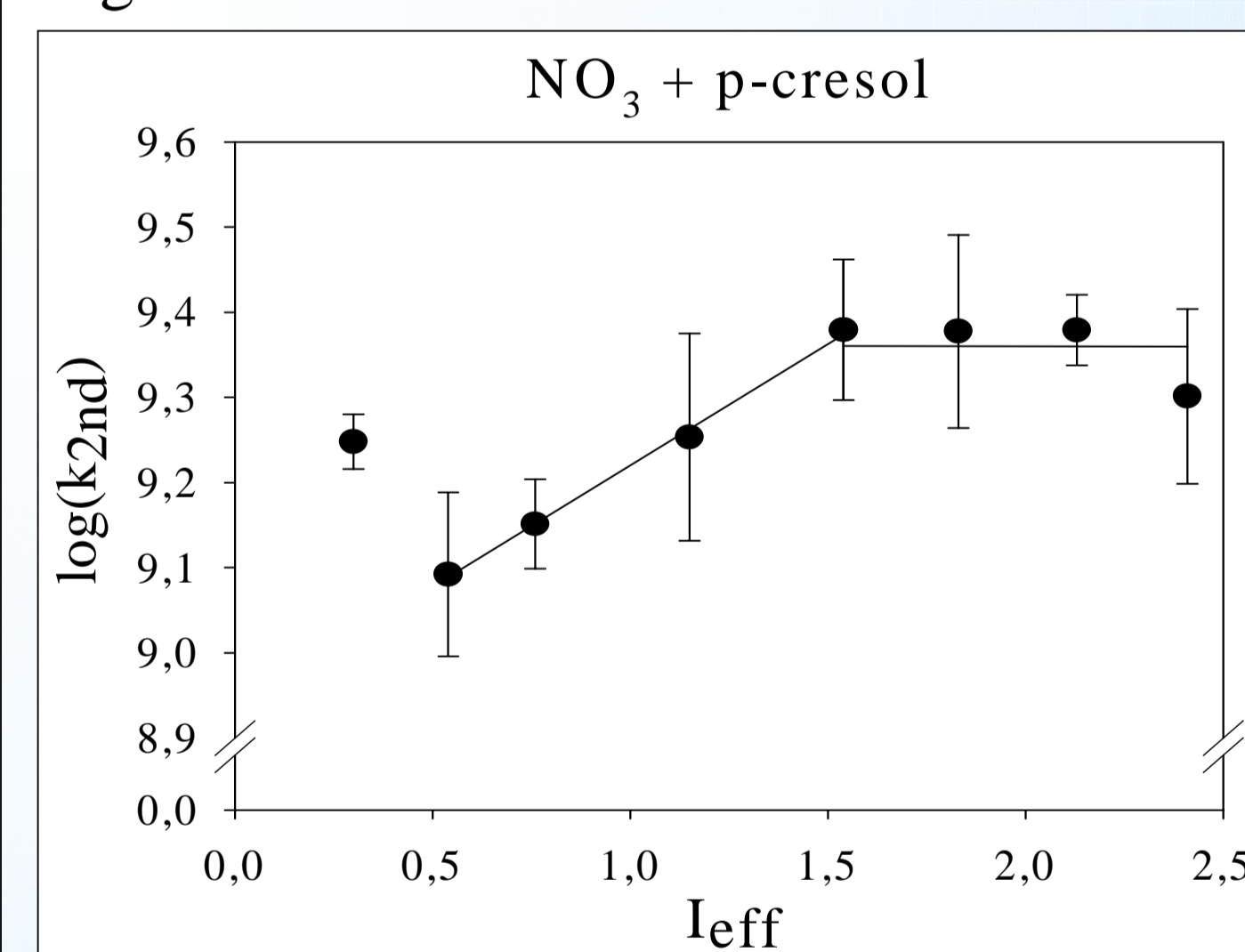

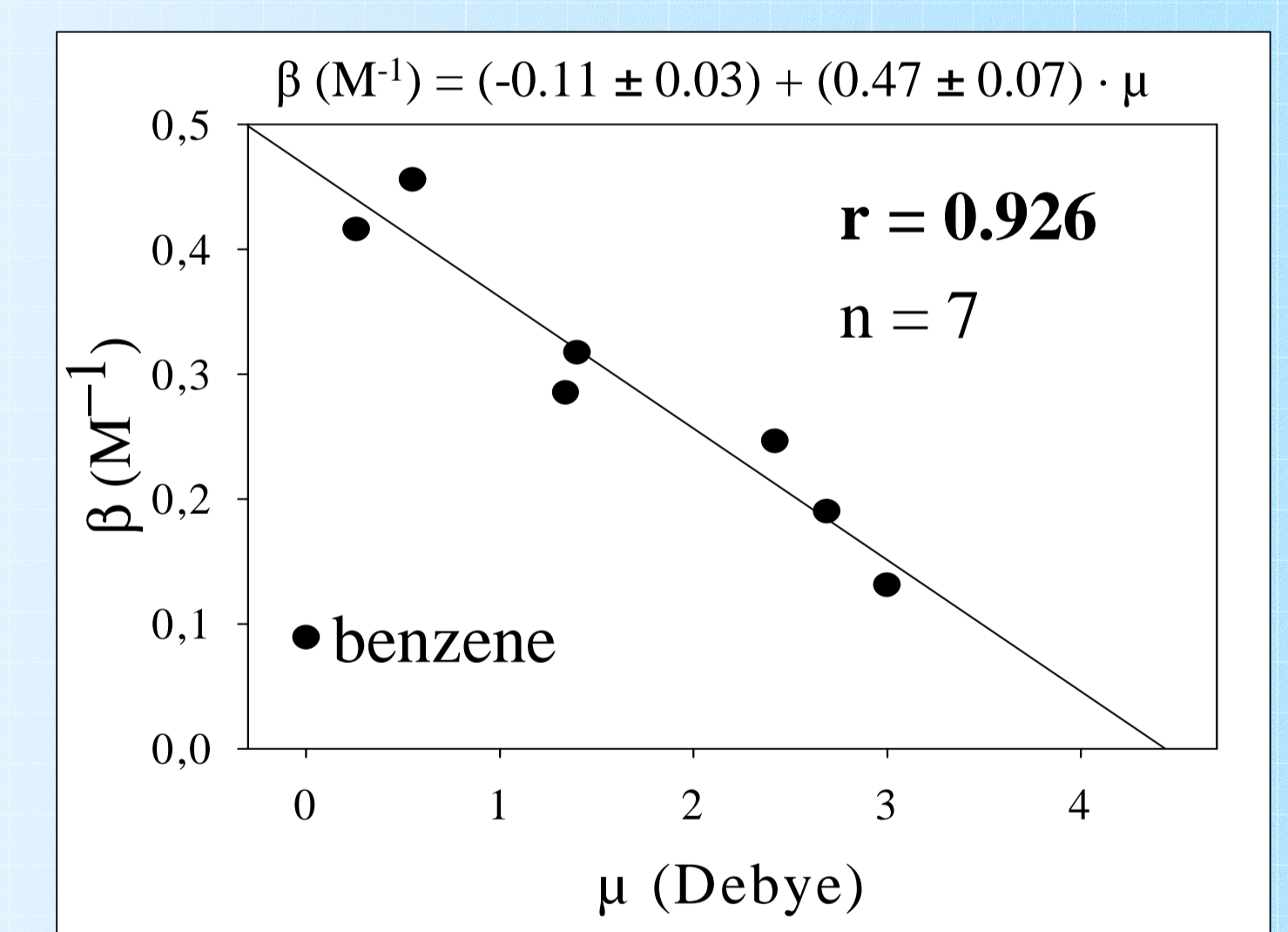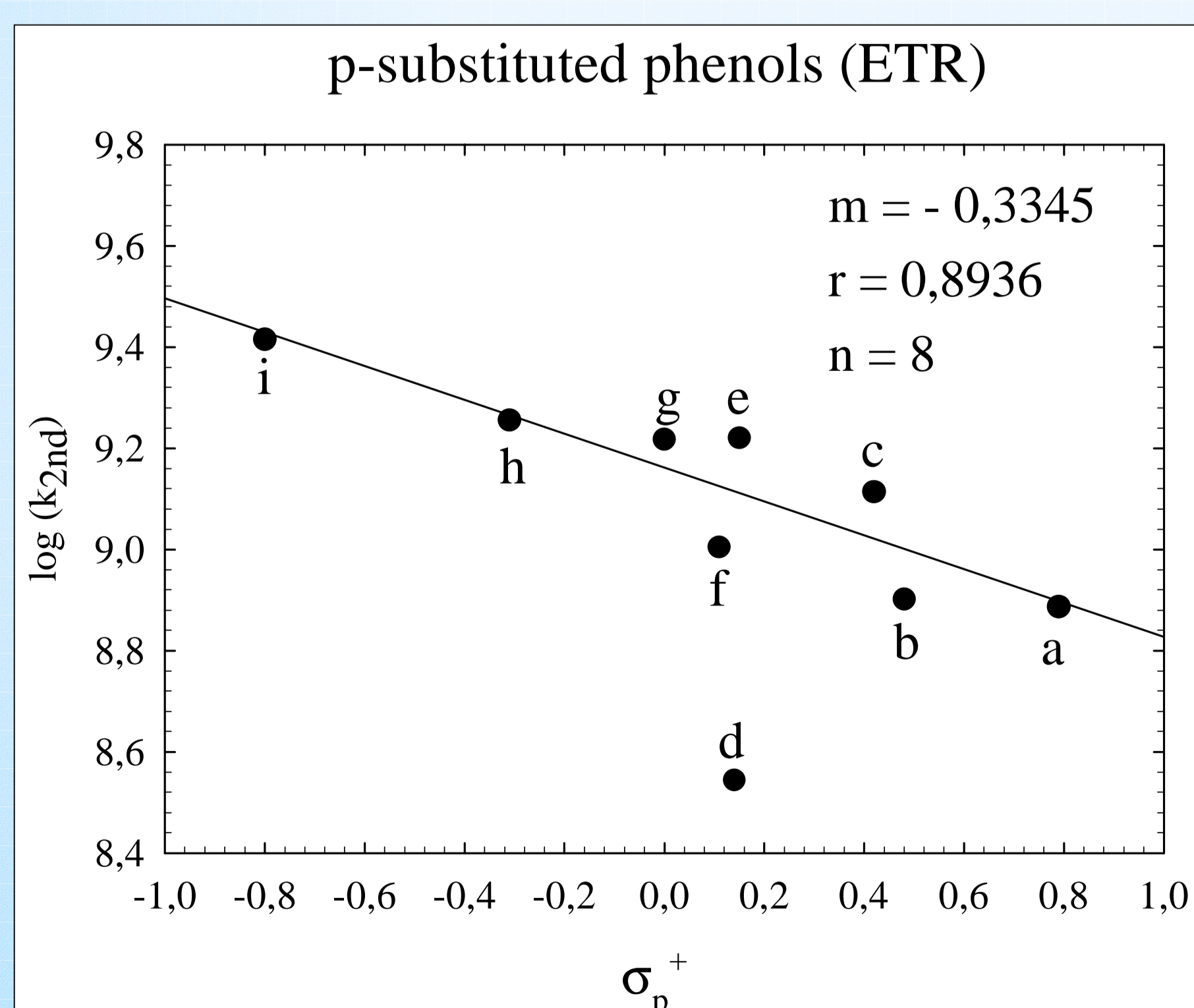
**Figure 3:** Ionic strength dependence of p-cresol



**Figure 4:** Plot of the dipole moment (μ) versus the kinetic salting coefficient (ß)

So far a prediction of the influence of the ionic strength for the reactions of the $NO_3$-radical with neutral compounds is not possible [8]. Figure 4 shows, however, a very good correlation between the dipole moment (μ) and the kinetic salting coefficient (ß). Further it seems, by the example of the benzene, that compounds with μ = 0 are not affected by the ionic strength of the solution.

## Outlook

• Measurement of further rate constants and ionic strength dependencies
• Product studies for some compounds
• Development of an analytical method (LC-MS) for the analysis of substituted phenols in aqueous solutions

## References

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