

## Motivation and Background

### Free radical chemistry in the tropospheric aqueous phase

- Nighttime oxidation of organic compounds such as phenols by NO<sub>3</sub>
- Substituted phenols in the troposphere
- Sources: Emissions from combustion and industrial processes or secondary formation from oxidation of benzene derivatives
- Toxic and phytotoxic compounds
- Tracer compounds for biomass burning

### Scope of study

- Multiphase chemistry still poorly understood and characterized
- Kinetic and thermodynamic data for tropospheric chemical modeling
- Investigation of the influence of the different substituents for the NO<sub>3</sub>-radical reaction with phenolic compounds in aqueous solution

## Experimental

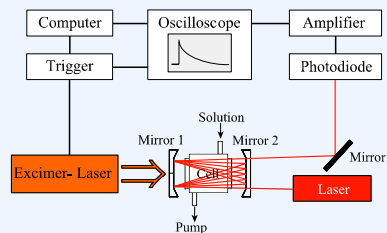


Figure 1: Laser photolysis long path absorption set-up (LP-LPA).

- Laser flash photolysis of nitrate anions at  $\lambda = 248 \text{ nm}$  at  $\text{pH} = 0.5$  (HClO<sub>4</sub>)
- $\text{NO}_3^- + \text{hv} + \text{H}^+ \longrightarrow \text{NO}_2 + \text{OH}$
- $\text{HNO}_3 + \text{OH} \longrightarrow \text{NO}_3 + \text{H}_2\text{O}$
- $[\text{NO}_3]_0 \approx 1.8 \cdot 10^{-7} \text{ M}$ , laser energy = 950 mJ
- $[\text{NaNO}_3] = 5 \cdot 10^{-2} \text{ M}$ ; [reactant] =  $2 - 10 \cdot 10^{-5} \text{ M}$
- Pseudo first order conditions
- Measurements were done as a function of temperature ( $278 \text{ K} \leq T \leq 318 \text{ K}$ )

## H-atom abstraction

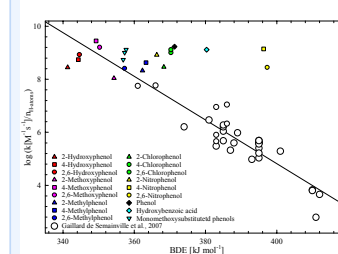


Figure 4: Evans-Polyani type correlation ( $\log k_{\text{H,cal}}$  vs. BDE) for the rate constants in Table 1 as well as literature values [1,2].

- Regression line for H-atom abstraction reactions of aliphatic and cyclic compounds [1,2]:  $\log(k_{\text{H}} / [\text{M}^{-1} \text{s}^{-1}]) = (37.7 \pm 5.8) + (-0.082 \pm 0.015) \cdot \text{BDE} [\text{kJ mol}^{-1}]$
- The values of  $k_{\text{H,cal}}$  for the substituted phenols in Table 2 were calculated using the regression equation
- Ratios of ( $k_{\text{H,cal}}/k_{298\text{K}}$ ) in Table 2 provide the theoretical contribution of H-atom abstraction
- The ratios indicate the subordinate role of the H-atom abstraction mechanism with the exceptions of the hydroxyl substituted phenols

## Results and Discussions

Table 1: Measured rate constants at 298 K, activation parameters,  $E_{\text{HOMO}}$  and bond dissociation energy (BDE) for the investigated NO<sub>3</sub> reactions in aqueous solution.

|   | 2,6-Dimethylphenol            | 2,6-Dichlorophenol            | 2,6-Dihydroxyphenol  | 2,6-Dinitrophenol             | 2,6-Dimethoxyphenol           | 4-Hydroxy-3,5-dimethoxybenzaldehyde | 4-Hydroxy-3,5-dimethoxybenzoic acid | 4-Hydroxy-3-methoxybenzaldehyde | 4-Hydroxy-3-methoxybenzoic acid | 3-Hydroxy-4-methoxybenzoic acid |
|---|-------------------------------|-------------------------------|--|-------------------------------|-------------------------------|-------------------------------------|-------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| $k_{298\text{K}} [\text{M}^{-1} \text{s}^{-1}]$       | $(1.8 \pm 0.3) \cdot 10^9$    | $(1.3 \pm 0.2) \cdot 10^9$    | $(1.7 \pm 0.2) \cdot 10^9$                                       | $(2.8 \pm 0.9) \cdot 10^8$    | $(1.6 \pm 0.4) \cdot 10^9$    | $(1.7 \pm 0.3) \cdot 10^9$          | $(1.4 \pm 0.6) \cdot 10^9$          | $(1.1 \pm 0.2) \cdot 10^9$      | $(1.0 \pm 0.3) \cdot 10^9$      | $(1.3 \pm 0.4) \cdot 10^9$      |
| $E_a [\text{kJ mol}^{-1}]$                            | 17 ± 6                        | 14 ± 5                        | 9 ± 5  | 18 ± 9                        | 16 ± 7                        | 18 ± 4                              | 19 ± 10                             | 16 ± 4                          | 15 ± 4                          | 11 ± 4                          |
| $A [\text{M}^{-1} \text{s}^{-1}]$                     | $(1.5 \pm 0.1) \cdot 10^{12}$ | $(3.9 \pm 0.3) \cdot 10^{12}$ | $(6.9 \pm 0.6) \cdot 10^{10}$                                    | $(3.2 \pm 0.4) \cdot 10^{11}$ | $(1.0 \pm 0.1) \cdot 10^{12}$ | $(2.8 \pm 0.2) \cdot 10^{12}$       | $(2.8 \pm 0.4) \cdot 10^{12}$       | $(7.8 \pm 0.4) \cdot 10^{11}$   | $(3.8 \pm 0.4) \cdot 10^{11}$   | $(9.0 \pm 0.6) \cdot 10^{10}$   |
| $\Delta H^\ddagger [\text{kJ mol}^{-1}]$              | 15 ± 5                        | 12 ± 4                        | 7 ± 4  | 15 ± 8                        | 14 ± 6                        | 16 ± 4                              | 16 ± 4                              | 14 ± 3                          | 12 ± 3                          | 8 ± 3                           |
| $\Delta S^\ddagger [\text{J mol}^{-1} \text{K}^{-1}]$ | (-20 ± 2)                     | (-31 ± 2)                     | (-46 ± 4)  | (-33 ± 5)                     | (-23 ± 2)                     | (-15 ± 1)                           | (-15 ± 2)                           | (-26 ± 1)                       | (-32 ± 2)                       | (-44 ± 3)                       |
| $\Delta G^\ddagger [\text{kJ mol}^{-1}]$              | 21 ± 9                        | 21 ± 9                        | 21 ± 13  | 25 ± 16                       | 21 ± 11                       | 20 ± 6                              | 21 ± 13                             | 22 ± 6                          | 22 ± 8                          | 21 ± 9                          |
| $E_{\text{HOMO}} [\text{eV}]^{\text{[8]}}$            | -8.9631                       | -9.1938                       | -8.8097  | -10.6995                      | -8.7809                       | -9.5300                             | -9.4144                             | -8.7809                         | -9.4118                         | -9.2175                         |
| BDE [kJ mol <sup>-1</sup> ]                           | 357.3 <sup>[6]</sup>          | 370.3 <sup>[6]</sup>          | 358.1/ <sup>[6]</sup> 349.3/ <sup>[6]</sup> 344.1 <sup>[8]</sup> | 397.3 <sup>[6]</sup>          | 350.3 <sup>[6]</sup>          | -                                   | -                                   | 356.9 <sup>[9]</sup>            | 357.3 <sup>[9]</sup>            | 357.7 <sup>[9]</sup>            |

Table 2: Rate constants, literature values and rate constant ratios for the substituted phenols.

| Compound                       | Rate constant $k_{298\text{K}} [\text{M}^{-1} \text{s}^{-1}]$ |                                |                                |                                |                                |
|--------------------------------|---|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
|                                | -NO <sub>2</sub>  | -Cl                            | -CH <sub>3</sub>               | -OCH <sub>3</sub>              | -OH                            |
| 2-                             | $(8.3 \pm 1.4) \cdot 10^{8*}$                                 | $(2.9 \pm 0.3) \cdot 10^{8*}$  | $(8.5 \pm 0.2) \cdot 10^{8*}$  | $(1.1 \pm 0.1) \cdot 10^{9*}$  | $(5.6 \pm 0.8) \cdot 10^{8*}$  |
| 4-                             | $(1.4 \pm 0.2) \cdot 10^{9**}$                                | $(1.0 \pm 0.4) \cdot 10^{9**}$ | $(1.8 \pm 0.3) \cdot 10^{9**}$ | $(2.8 \pm 0.5) \cdot 10^{9**}$ | $(1.6 \pm 0.6) \cdot 10^{9**}$ |
| 2,6-                           | $(2.8 \pm 0.9) \cdot 10^8$                                    | $(1.3 \pm 0.2) \cdot 10^9$     | $(1.8 \pm 0.2) \cdot 10^9$     | $(1.6 \pm 0.2) \cdot 10^9$     | $(1.7 \pm 0.2) \cdot 10^9$     |
| Rate constant ratios           |   |                                |                                |                                |                                |
| $k_{\text{H,cal}}/k_2$ [%]     | 6   | 11                             | 12                             | 40                             | >100                           |
| $k_{\text{H,cal}}/k_4$ [%]     | 0   | 2                              | 5                              | 41                             | >100                           |
| $k_{\text{H,cal}}/k_{2,6}$ [%] | 0   | 2                              | 14                             | 59                             | >100/ 88/ 17                   |

\* Barzaghi 2004 [2], \*\* Weller 2006 [3]

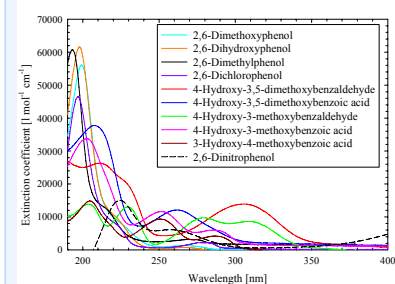


Figure 2: Measured UV spectra of the investigated phenols ( $c = 3 \cdot 10^{-6} \text{ M}$ ) in aqueous solution.

## Conclusions

- Correlations indicate that direct electron transfer in aqueous solution is the main reaction mechanism
- Differences in the rate constants are attributed to different contributions of the proposed reaction mechanisms and to the substituent effects
- Atmospheric lifetimes of the investigated biomass burning tracers [7] should be carefully evaluated in modelling studies applying the fast NO<sub>3</sub> rate constants in aqueous solution obtained as well as a proper phase transfer description
- The obtained equations may be applied for the prediction of rate constants for reaction of nitrate radical with substituted phenols in aqueous solution

## Competitive reaction mechanisms

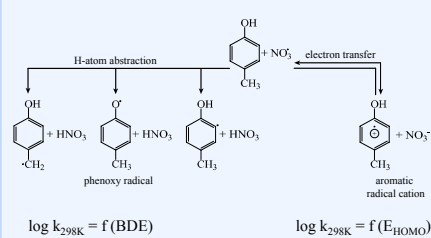


Figure 3: Possible reaction mechanism of the nitrate radical with substituted phenols in aqueous solution [1].

## Electron transfer

- $E_{\text{HOMO}}$  is the energy of the highest occupied molecule orbital and a measure for the the electron donor capacity
- For pure electron transfer reactions (red regression line) compounds, such as Phenol [3], 4-Nitrophenol [4], 4-Fluorophenol [3], 4-Bromophenol [3], 4-Chlorophenol [3], 4-Hydroxybenzoic acid [4], 2,6-Dinitrophenol and 2,6-Dichlorophenol with a ratios of ( $k_{\text{H,cal}}/k_{298\text{K}}$ ) smaller 5% were selected
- Comparison of the rate constants in Table 2 shows that the rate constants are dominated by electronic and steric effects
- Compounds with electron withdrawing substituents react slower because of the destabilization of the formed intermediate see Figure 3
- The exclusion of H-atom abstraction as an possible reaction pathway indicate that the investigated phenols react mainly with the electron transfer mechanism

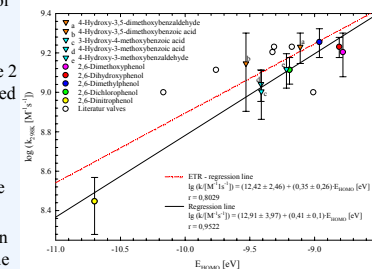


Figure 5: Correlation ( $\log k_{298\text{K}}$  vs.  $E_{\text{HOMO}}$ ) of investigated phenolic compounds in Table 1.

## References

- [1] H. Herrmann, R. Zellner, *Reactions of NO<sub>3</sub>-Radicals in Aqueous Solution in N-Centered Radicals*; Z.B. Alfassi (Ed.) Wiley: New York, 1998, 291. [2] Ph. G. deSemainville, D. Hoffmann, C. George and H. Herrmann, *Phys. Chem. Chem. Phys.*, 2007, 9, 958. [3] P. Barzaghi and H. Herrmann, *Phys. Chem. Chem. Phys.*, 2004, 4, 3669. [4] C. Weller, Diploma Thesis, University Freiburg, 2006. [5] calculated with Hyper Chem Released 7.5 Inc. Hypercube. [6] M.M. Bizarro, B.J. Costa Cabral, R.M. Borges de Santos and J.A.M. Simoes, *Pure Appl. Chem.*, 1999, 71, 1249. [7] B. R. T. Simoneit, *Appl. Geochem.*, 2002, 17, 129. [8] H.F. Ji, and H.Y. Zhang, *New J. Chem.*, 2005, 29(4), 535. [9] J.S. Wright, E.R. Johnson, and G.A. DiLabio, *J. Am. Chem. Soc.*, 2001, 123(6), 1173.

## Outlook

- Further measurements of other 2,6- and 2,4-substituted phenolic reactants towards NO<sub>3</sub> as well as OH in the aqueous phase
- Spectroscopic investigations to study the formation of transient reaction products (e.g. organic peroxy radicals)
- Product studies in order to identify and quantify the oxidation products formed in the presence of NO<sub>3</sub> and/or OH