

NO₃-Radical Reactions of poly-substituted Phenols in aqueous Solution



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Motivation and Background

Free radical chemistry in the tropospheric aqueous phase

Reactions of atmospheric radicals (OH or NO₃) can initiate the degradation and conversion of organic compounds such as phenols in the atmosphere.

Substituted phenols in the troposphere

Sources of phenolic compounds are the direct emissions from combustion processes or the atmospheric oxidation of benzene derivatives. Due to their properties, the chemistry of the phenols can take place in all atmospheric phases as for example in the liquid phase (cloud droplet, fog, rain or hygroscopic particle).

Scope of study

Investigation of the influence of the different substituents on NO₃-radical reaction rate constants with phenolic compounds in aqueous solution.

Experimental

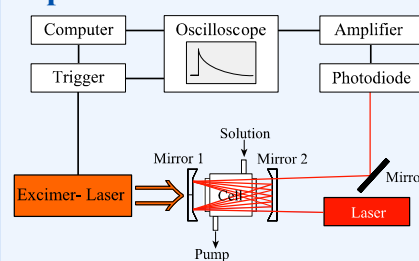


Figure 1: Laser photolysis long path absorption set-up (LP-LPA).

- Laser flash photolysis of nitrate anions at $\lambda = 248$ nm at pH = 0.5 (HClO₄)
- $\text{NO}_3^- + hv + \text{H}^+ \longrightarrow \text{NO}_2 + \text{OH}$
- $\text{HNO}_3 + \text{OH} \longrightarrow \text{NO}_3 + \text{H}_2\text{O}$
- $[\text{NO}_3]_0 \approx 1.8 \cdot 10^{-7}$ M, laser energy = 950 mJ
- $[\text{NaNO}_3] = 5 \cdot 10^{-2}$ M; $[\text{reactant}] = 2 - 10 \cdot 10^{-5}$ M
- Pseudo first order conditions
- Measurements were done as a function of temperature ($278\text{K} \leq T \leq 318\text{K}$)

Results and Discussions

Table 1: Measured rate constants at 298 K, activation parameters, E_{HOMO} and bond dissociation energy (BDE) for the investigated NO₃ 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	16.1 ± 8.2	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
$E_{\text{HOMO}} [\text{eV}]^{\text{SI}}$	-8.9631	-9.1938	-8.8097	-10.6995	-8.7809	-9.1109	-9.5300	-9.4144	-9.4118	-9.2175
$\text{BDE} [\text{kJ mol}^{-1}]$	357.316 ⁶	370.316 ⁶	358.1/349.3/344.1 ⁸	397.316 ⁶	350.316 ⁶	-	-	356.9 ⁹	357.3 ⁹	357.7 ⁹

H-atom abstraction

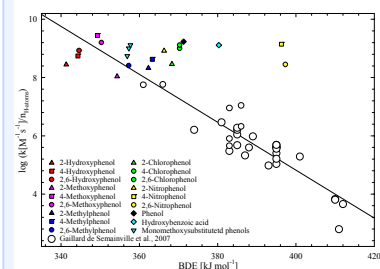


Figure 4: Evans-Polyani type correlation ($\log k_{\text{H-abstr}} / k_{\text{H-abstr}}^{\text{H}}$ vs. BDE) for the rate constants in Table 1 as well as literature values [1,2].

- Regression line for H-atom abstraction reactions of aliphatic and cyclic compounds [1,2]:

$$\lg(k_{\text{H-abstr}} / [\text{M}^{-1} \text{s}^{-1}]) = (37.7 \pm 5.8) + (-0.082 \pm 0.015) \cdot \text{BDE} [\text{kJ mol}^{-1}]$$

- The values of $k_{\text{H-cal}}$ for the substituted phenols in Table 2 where calculated using the regression equation

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 ₂	-Cl	-CH ₃	-OCH ₃	-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]

- 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

Competitive reaction mechanisms

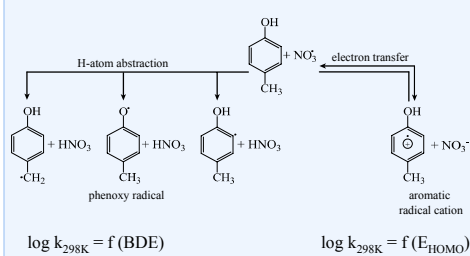


Figure 3: Possible reaction mechanism of the nitrate radical with substituted phenols in aqueous solution [1].

- E_{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-Nitro-phenol^[4], 4-Fluorophenol^[3], 4-Bromophenol^[3], 4-Chloro-phenol^[3], 4-Hydroxybenzoic acid^[4], 2,6-Dinitrophenol and 2,6-Dichloro-phenol 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

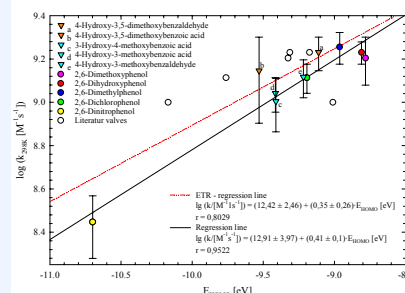


Figure 5: Correlation ($\log k_{298\text{K}}$ vs. E_{HOMO}) of investigated phenolic compounds in Table 1.

- 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 indicates that the investigated phenols react mainly with the electron transfer mechanism

Conclusions

- Correlations indicate that direct electron transfer is the main reaction mechanism in aqueous solution
- Differences in the rate constants are attributed to changing contributions of the different reaction pathways and to the substituent effects
- Atmospheric lifetimes of the investigated biomass burning tracers^[7] should be carefully evaluated in modelling studies applying the fast NO₃ 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

References

- H. Herrmann, R. Zellner, *Reactions of NO₃-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 Freiberg, 2006. [5] calculated with Hyper Chem Release 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 NO₃ 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 NO₃ and/or OH