Reactivity of the NO₃-radical towards poly-substituted phenols in aqueous solution

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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
- Sources: Emissions from combustion and industrial processes or secondary formation from oxidation of benzene derivatives
- Toxic and phytotoxic compounds
- Tracer compounds for biomass burning
- Multiphase chemistry still poorly understood and characterized

Scope of study
- Kinetic and thermodynamic data for tropospheric chemical modeling

Experimental
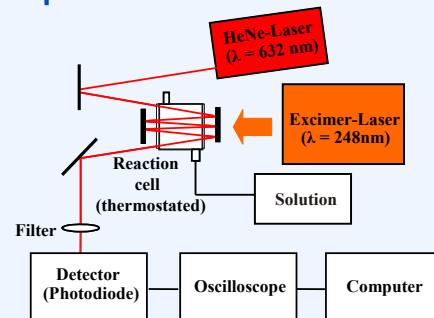
- Laser flash photolysis of nitrate anions at λ = 248 nm at pH = 0.5 (HClO₄)

$$NO_3^- + h\nu + H^+ \longrightarrow NO_2 + OH$$

$$HNO_3 + OH \longrightarrow NO_3 + H_2O$$

- $[NO_3]_0 \approx 1.8 \cdot 10^{-7}$ M, laser energy = 950 mJ
- $[NaNO_3]$ = 5·10⁻² M; [reactant] = 2 – 10 · 10⁻⁵ M
- pseudo first order conditions
- errors given in this work are statistical errors for a confidence interval of 95%

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

Kinetics and Reactivity Results and Discussion

NO₃ radical reactions with different poly-substituted phenols have been investigated as a function of temperature (Table 1). The temperature dependent kinetic measurements were done between 278 K and 318 K. Spectra of the reactants in aqueous solution were recorded (Figure 2) in order to check the possible influence of photolysis processes on the reactant concentration.

Table 1: Measured rate constants at each temperature and activation parameters for the investigated NO₃ reactions in aqueous solution.

	2,6-Dimethylphenol	2,6-Dichlorophenol	2,6-Dihydroxyphenol	2,6-Dimethoxyphenol	4-Hydroxy-3,5-dimethoxybenzaldehyde	4-Hydroxy-3,5-dimethoxybenzoic acid
k_{278K} [M⁻¹s⁻¹]	(0.9 ± 0.3)·10⁹	(0.8 ± 0.1)·10⁹	(1,2 ± 0,5)·10⁹	(0.9 ± 0.4)·10⁹	(1.1 ± 0.4)·10⁹	(1.0 ± 0.2)·10⁹
k_{288K} [M⁻¹s⁻¹]	(1.2 ± 0.4)·10⁹	(1.2 ± 0.2)·10⁹	(1,4 ± 0,5)·10⁹	(1.3 ± 0.5)·10⁹	(1.3 ± 0.2)·10⁹	(1.1 ± 0.4)·10⁹
k_{298K} [M⁻¹s⁻¹]	(1.8 ± 0.3)·10⁹	(1.3 ± 0.2)·10⁹	(1,7 ± 0,2)·10⁹	(1.6 ± 0.4)·10⁹	(1.7 ± 0.3)·10⁹	(1.4 ± 0.6)·10⁹
k_{308K} [M⁻¹s⁻¹]	(2.1 ± 0.6)·10⁹	(1.5 ± 0.3)·10⁹	(1.9 ± 0.4)·10⁹	(2.0 ± 0.4)·10⁹	(2.2 ± 0.4)·10⁹	(1.8 ± 0.4)·10⁹
k_{318K} [M⁻¹s⁻¹]	(2.3 ± 0.6)·10⁹	(1.9 ± 0.2)·10⁹	(1.9 ± 0.4)·10⁹	(2.1 ± 0.3)·10⁹	(2.8 ± 0.5)·10⁹	(2.8 ± 0.4)·10⁹
E_A [kJ mol⁻¹]	17.0 ± 5.6	14.2 ± 4.8	9.3 ± 5.1	16.2 ± 6.9	18.3 ± 4.1	18.6 ± 9.5
A [M⁻¹ s⁻¹]	(1.5 ± 0.1)·10¹²	(3.9 ± 0.3)·10¹²	(6.9 ± 0.6)·10¹⁰	(1.0 ± 0.1)·10¹²	(2.8 ± 0.2)·10¹²	(2.8 ± 0.4)·10¹²
$\Delta H^{\ddagger}$ [kJ mol⁻¹]	14.5 ± 4.8	11.7 ± 3.9	6.8 ± 3.7	13.9 ± 5.8	15.8 ± 3.5	16.1 ± 8.2
$\Delta S^{\ddagger}$ [J mol⁻¹ K⁻¹]	-(20.1 ± 1.6)	-(31.4 ± 2.3)	-(45.8 ± 3.8)	-(23.2 ± 2.3)	-(14.9 ± 0.9)	-(15.1 ± 2.0)
$\Delta G^{\ddagger}$ [kJ mol⁻¹]	20.5 ± 8.5	21.0 ± 8.6	20.5 ± 12.9	20.6 ± 10.9	20.3 ± 5.7	20.6 ± 13.3
BDE [kJ mol⁻¹][1]	357.3	370.3	-	350.3	-	-

Table 2: Rate constants, literature values and rate constant ratios for phenols substituted in 2- and 4-position.

Compound	Rate constant k_{298K} [M⁻¹s⁻¹]			
	-Cl	-CH₃	-OCH₃	-OH
2-	(2.9 ± 0.3)·10⁸*	(8.5 ± 0.2)·10⁸*	(1.1 ± 0.1)·10⁹*	(5.6 ± 0.8)·10⁸*
4-	(1.0 ± 0.4)·10⁹*	(1.7 ± 0.3)·10⁹**	(2.8 ± 0.5)·10⁹**	(8.8 ± 0.5)·10⁸*
2,6-	(1.3 ± 0.2)·10⁹	(1.8 ± 0.2)·10⁹	(1.6 ± 0.2)·10⁹	(1.7 ± 0.2)·10⁹
	Rate constant ratios			
$k_{2,6-}/k_{2-}$	4.5	2.1	1.5	3.0
$k_{H,calc}/k_{2,6-}$ [%]	1.7	14.8	59.6	-

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

The differences between the rate constants of the 2- and 2,6-substituted reactants strongly depend on the nature of the substituent. This difference decreases with increasing theoretically calculated contribution of an H-Abstraction reaction channel ($k_{H,calc}/k_{2,6-}$ [%]). The values of $k_{H,calc}$ for the 2,6-substituted phenols where calculate using the following equation.

$$\log\left(k_{H,calc} / M^{-1}s^{-1}\right) = (37.7 \pm 5.8) - (0.082 \pm 0.015) \cdot BDE\left[kJ\, mol^{-1}\right]^{[4]}$$

In order to check the underlying reaction mechanism the logarithm of the rate constants in Table 2 are plotted versus the bond dissociation energies (BDE). While the methyl- and methoxy-substituted phenols follow the correlation in Figure 5 quite well, the rate constants for the chloro-substituted compounds are more scattered.

The structures of the investigated phenols are shown on the top. For all investigated reactions the obtained rate constants and activation parameters are quite similar. Even additional substituents in the case of 4-Hydroxy-3,5-dimethoxybenzaldehyde and 4-Hydroxy-3,5-dimethoxybenzoic acid do not change the results significantly. Only the activation entropy and the Arrhenius preexponential factor of 2,6-Dihydroxyphenol are significantly different from the other values. Figure 3 and 4 show the corresponding Arrhenius plots (log k_{2nd} vs. 1/T) for the investigated NO₃ reactions with phenolic compounds. Table 2 compares the measured rate constants of this work with corresponding rate constants of 2- and 4-substituted phenols. As can be seen the 2-substituted compounds show always the lowest reactivity towards NO₃. The much higher reactivity of 4-Methoxyphenol compared to the other methoxy-substituted phenols in Table 2 is remarkable. The rate constant of methoxyphenols seems to be strongly affected by H-Abstraction mechanism as can be seen in Table 2 ($k_{H,calc}/k_{2,6-}$ [%]) and Figure 5. Therefore the higher reactivity of 4-methoxyphenol might be due to steric effects of the methoxy-group in ortho position.
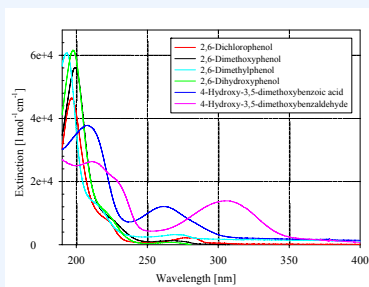

Figure 2: Measured UV spectra of the investigated phenols (c = 3 · 10⁻⁶ M) in aqueous solution.
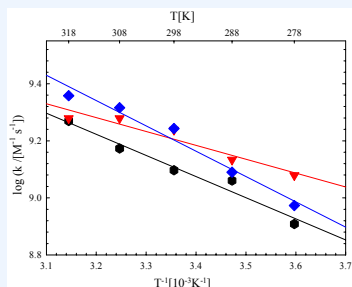

Figure 3: Arrhenius plot for 2,6-Dichlorophenol (●), 2,6-Dimethylphenol (●) and 2,6-Dihydroxyphenol (●).
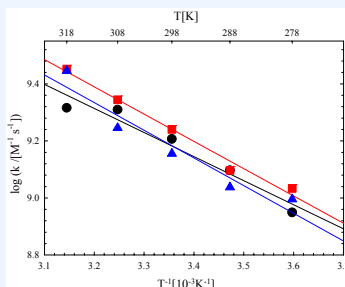

Figure 4: Arrhenius plot for 2,6-Dimethoxyphenol (●), 4-Hydroxy-3,5-dimethoxybenzaldehyde (●) and 4-Hydroxy-3,5-dimethoxybenzoic acid (●).
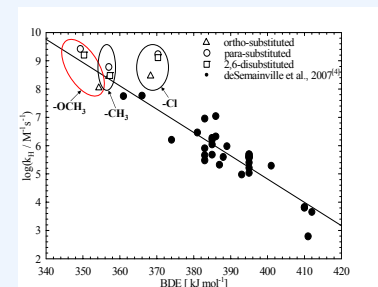

Figure 5: Evans-Polyani type correlation (log k_H vs. BDE) for the rate constants in Table 2 as well as literature values.

Conclusions
- Investigated phenols show high reactivity towards NO₃ in the aqueous phase (tropospheric lifetimes between 55 min and 75 min; [NO₃] = 1.7·10⁻¹³ M[5])
- Higher reactivity of 2,6-substituted reactants compared to the corresponding 2-substituted phenols
- Evidence that these differences strongly depend on the underlying reaction mechanism

Outlook
- Further measurements of other 2,6- and 2,4-substituted reactants towards NO₃ as well as OH in the aqueous phase
- Product studies in order to identify and quantify the oxidation products formed in the presence of NO₃ and/or OH

References
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