Kinetic and Mechanistic Investigations of Oxidation Reactions of Selected Phenols in Aqueous Phase by OH /NO$_2$ /NO$_3$ System

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Motivation

Phenols are known to be formed in the atmosphere by the OH-initiated atmospheric oxidation of aromatic hydrocarbons and a number of product studies reported in the literature show that their yields could be relatively high. Emissions of aromatic hydrocarbons (benzene, toluene, and isomers of xylene) from vehicles fuel exhaust result in the formation of phenol or cresols and ring fragmentation products (Berndt et al., 1999). Phenols may be converted by OH/NO$_2$ or NO$_3$ into nitrophenols in both the gas and the aqueous phase. In fact, nitrophenols have been found in rainwater in the µg l^{-1} range in the Rhein-Ruhr area in western Germany and in urban Los Angeles rain. The phytotoxicity of nitro- and dinitrophenols is well documented and strongly depends on the position of the nitro group(s) relative to the phenolic moiety (Gramatica et al.,1999).

In order to better understand the reactivity of the nitrate radical in the trophosperic aqueous phase a study of the reaction that occurs between some selected phenols and nitrate radical was performed by a laser - photolysis longpath laser absorbance (LP-LPA) experiment (Herrmann et al., 1995) combined with a product study performed with a HPLC-DAD technique (Fig.1).
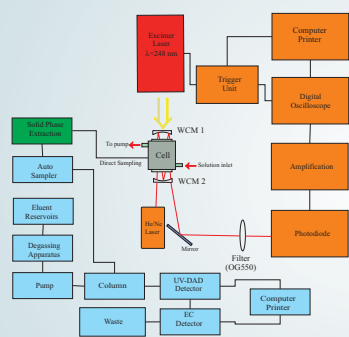
Experimental Set-up

The flash photolysis set-up consists of a multigas excimer laser filled with a Kr/F gas mixture that delivers a 10 - 40 ns pulse at 248 nm. The optical detection system comprises a He/Ne laser operated at 632.8 nm. The laser light is passed into a combination of two dieletrically coated mirrors in White configuration and multiply folded through the thermostated reaction cell (118 ml) obtaining a total optical pathlength of 192 cm. The electrical output from the detector, a photodiode, is amplified and fed to a digital storage oscilloscope connected to a computer (Herrmann et al., 1995). After irradiation a solid phase extraction passage is applied. The separation of product compounds is achieved using a HPLC-DAD-EC apparatus.

Fig. 1: Experimental set-up LP-LPA - product study (HPLC-UV-EC) experiment

Results: Kinetic Investigation

The reactions of nitrate radical with differently ortho-substituted phenols were investigated. In this experiments the influence of the temperature, in the range of 278-318 K, was studied. The obtained rate constants and the activation parameters are summarised in Table 1.

Tab. 1: Summary of the obtained rate constants at 298 K and the activation parameteres derived from the T-dependence studies.

Compound	$k_{(298K)}$ / l mol^{-1} s^{-1}	A / l mol^{-1} s^{-1}	E_A / kJ mol^{-1}	$\Delta G^{\ddagger}$ / kJ mol^{-1}	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}
OH CH$_3$	$(8,5 \pm 0,1) \cdot 10^8$	$(1,0 \pm 0,2) \cdot 10^{13}$	22 ± 7	22 ± 8	19 ± 7	-11 ± 3
OH CH$_2$CH$_3$	$(6,7 \pm 0,4) \cdot 10^8$	$(2,2 \pm 0,3) \cdot 10^{12}$	18 ± 2	23 ± 4	16 ± 3	-24 ± 6
OH OH	$(5,6 \pm 0,8) \cdot 10^8$	$(8,5 \pm 0,8) \cdot 10^{15}$	39 ± 9	23 ± 11	36 ± 7	45 ± 15
OH OCH$_3$	$(1,1 \pm 0,1) \cdot 10^8$	$(5,3 \pm 0,1) \cdot 10^{12}$	25 ± 4	27 ± 8	22 ± 3	-11 ± 2

Correlation were published in literature which allow to derive the expected rate constant for H-atom abstraction for a given bond strenght (Herrmann et al., 1998):

$$\lg k_{H\text{-abs}} \ /M^{-1} \ s^{-1} = (42,9 \pm 7,9) - (0,094 \pm 0,020) \cdot BDE \ /kJ \ mol^{-1}$$

Table 2 summarises the weakest X-H bond dissociation energies and the calculated rate constants applying the reported equation. Comparing the expected rates with the experimental ones, it can see that the H-atom abstraction mechanism could play an important role in the nitrate radical reactions with the compounds studied in the present work.

Tab. 2: Comparison of predicted rate constants for H-abstraction reactions with experiemtal data for the reaction of nitrate radical with ortho-substituted phenols .

Compound	BDE / kJ mol^{-1}		$k_{H\text{-abs., calc.}}$ / l mol^{-1} s^{-1}	$k_{exp.}$ / l mol^{-1} s^{-1}
2-methylphenol	$360,8^b$	[O-H]	$3,0 \cdot 10^8$	$(8,5 \pm 0,1) \cdot 10^8$
	357^a	[C-H]	$7,0 \cdot 10^8$	
2-ethylphenol	352^a	[O-H]	$2,0 \cdot 10^9$	$(6,7 \pm 0,4) \cdot 10^8$
2-hydroxyphenol	336^a	[O-H]	$8,5 \cdot 10^{10}$	$(5,6 \pm 0,8) \cdot 10^8$
2-methoxyphenol	$348,1^b$	[O-H]	$4,7 \cdot 10^9$	$(1,1 \pm 0,1) \cdot 10^8$

^{a} Calculated using Benson´s increment method (Benson, 1976); ^{b} Lucarini et al., 1996.

Results: Mechanistic Investigation

The objective of this work is to clarify the role of nitrate radical in the aqueous solution in the presence of phenol and if the nitration reaction occurs whether mechanism is involved. Two different approaches (radical concentration measurement, product study) were used to study the oxidation reaction: a direct comparison of concentration of the nitrate radical produced during the photolysis with the amount of products (direct sampling from the reaction cell) was done.

The reactions were carried out in triple under different experimental conditions (pH, low concentration of nitrogen dioxide, without oxygen, in presence of a radical trap and with different number of pulses) in order to discriminate the different possible pathways (Fig. 2).

The formation of nitrate radical in the flash photolysis experiment of nitrate anions (0,01 M) at 248 nm, is described according to the reaction mechanism as follow:

$$NO_3^- + h\nu \ (\lambda = 248 \ nm) \xrightarrow[pH = 0,5]{HClO_4} OH + NO_2 \quad (R\text{-}1) \qquad OH + HNO_3 \longrightarrow NO_3 + H_2O \quad (R\text{-}2)$$

The radicals formed in (R-1) and (R-2) react with phenol (1 x10^{-5} M) leading to the formation of nitro derivatives as identified in the product yields summarised in Table 3.

Tab.3: Initial maximal radical concentration and the identified reaction products in the single flash photolysis experiment .

Photolysis Wavelength /nm	System	pH	O$_2$	[OH]$_{max}$/nM = [NO$_2$]$_{max}$/nM ^{a}	[NO$_3$]$_{max}$/nM ^{b}	Prod.Conc./nM	Sum of Products /nM	o/p Ratio
248	NaNO$_3$	0,5	yes	160	47 ± 6	**2**: 67 ± 8; **3**: 59 ± 8; **4**: 10 ± 10;	136 ± 9	$1,1 \pm 0,1$
248	NaNO$_3$	0,5	no	160	66 ± 12	**2**: 71 ± 13; **3**: 57 ± 10; **4**: 10 ± 8;	138 ± 11	$1,3 \pm 0,1$
248	NaNO$_3$	3,0	yes	160	trace	**2**: 29 ± 13; **3**: 20 ± 13; **4**: trace;	59 ± 13	$1,6 \pm 0,3$
248	Radical trap S$_2$O$_3^{2-}$ /	3,2	yes	only NO$_2$	-	-	-	-
351	NaNO$_3$	3,8	yes	20	124 ± 15	**2**: trace; **3**: trace; **4**: N.D.;	-	-

^{a} Calculated after OH yield measurement ; ^{b} Direct time-resolved NO$_3$ absorption measurement ($\epsilon_{NO3, 635 nm}$ = 1240 ± 40 l mol^{-1} cm^{-1}) (Sehested et al. 1994).

The interaction of nitrate radical with phenol in the presence of low concentrations of aqueous nitrogen dioxide was also studied in order to evaluate the possible contribution to the formation of nitro compounds by the nitrate radical itself.

In there experiments no formation of nitro derivatives was observed and it can clearly concluded that nitrate radicals are involved only in the initial attack towards phenol. This may occur via addition/elimination (R-8a, b), H-abstraction of the phenolic H-atom (R-4) or electron transfer (R-5).

In all three cases, intermediates are converted into nitrophenols by an addition of one molecule of nitrogen dioxide in a second reaction step.

Modelling calculations applied to the reaction conditions and products study experiments at higher pH (pH = 3) where NO$_3$ is not formed anymore, because of the lower concentration of the undissociated nitric acid, indicate that the formation of nitro products by a sequential reaction of OH and NO$_2$ (R-6, R-8a, b) could account for about 30% of the observed nitro compounds.
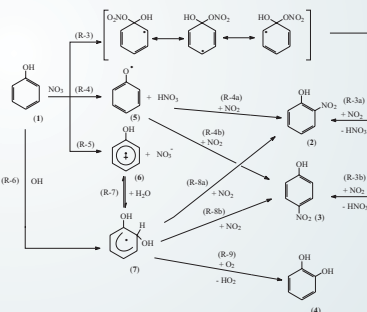
Fig. 2: Reactions involved phenol oxidation and nitration in the flash photolysis experiment

The present product study and a former work on radiolysis of aqueous phenol (Land et al., 1967) suggest that the oxidation process is strongly pH-dependent. In very acidic conditions (pH = 0,5), independent of which mechanism is involved in the first reaction step, the key intermediate is the phenoxyl radical (Fig. 3). The formed phenoxyl radical could undergo nitration by an addition of one molecule of nitrogen dioxide forming a keto-intermediate (**8** a, b) that by rapid proton transfers with water gives (**2**) and (**3**).
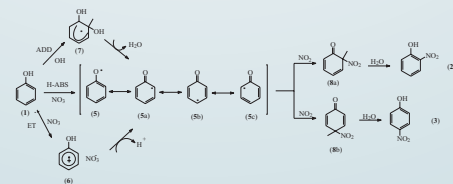
Fig. 3: Proposed oxidation mechanism of phenol by OH/ NO$_2$ or NO$_3$ in strongly acidic conditions.

Summary and Conclusions

It was shown that in acidic conditions phenol undergoes nitration and the main products of the reaction are the two expected mono-nitrophenol in different ratios related to the different possible pathways. It appears that the more important intermediate is the phenoxyl radical that reacts further with nitrogen dioxide forming the nitrophenolic compounds.

The present study together with kinetic and modelling studies on tropospheric multiphase systems indicates that nitration of phenolic compounds is effectively performed in a two step mechanism in tropospheric aqueous system. When initiated by radicals such as OH at daytime and NO$_3$ during the night intermediates (substituted hydroxy cyclohexadienyl and / or phenoxyl radicals) are formed which then stabilise by the reaction with aqueous nitrogen dioxide to yield nitrophenols.
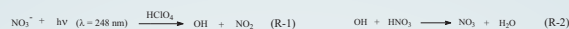
These processes might be competitive to gas phase production of nitrophenolic compounds and possibly even to their direct emission.

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