

# Free Radicals Oxidation of Phenol in the Aqueous Phase

Contribution to subproject: CMD-APP

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## Summary

Flash photolysis of nitrate anions at  $\lambda = 248$  nm and of peroxydisulphate anions at  $\lambda = 351$  nm was used to study the oxidation process of phenol by OH / NO<sub>2</sub> and NO<sub>3</sub> / NO<sub>2</sub> in aqueous solution under different experimental conditions. Two different mononitrophenols (*ortho* - and *para* -) and a dihydroxy derivative (catechol) were identified as the main reaction products by means of HPLC-DAD-ED technique and their yields of formation were directly compared with the initial radical concentrations of OH, NO<sub>2</sub> and NO<sub>3</sub>, respectively. Product yields were determined for different pH and as a function of the number of laser photolysis pulses down to single pulse experiments, where yields of 70 nM *o*-nitrophenol, 60 nM *p*-nitrophenol and 10 nM catechol have been obtained starting with [OH]<sub>0</sub> = [NO<sub>2</sub>]<sub>0</sub> = 160 nM which lead to the formation of 50 nM of NO<sub>3</sub> radicals at pH = 0.5 and T = 298 K.

From single pulse experiments under varying conditions a mechanism involving (i) initial attack of phenol by OH and (ii) initial attack of phenol by NO<sub>3</sub> followed by the reaction of the intermediate with NO<sub>2</sub> is suggested.

Absolute product yields are determined. For OH / NO<sub>2</sub> the *o*- / *p*-nitrophenol product ratio is  $\rho = 1.5$  whereas for the NO<sub>3</sub> / NO<sub>2</sub> reaction sequence it is  $\rho = 1.0$ . Implications for tropospheric chemistry are discussed.

## Introduction

Emissions produced by combustion processes of fossil fuels by power plants, factories, households, and automobile exhaust contain precursors of phenols (BTX) and phenols as well. These compounds may affect human health (Savicki, 1977; Escher et al., 1996). Furthermore, the phytotoxicity of nitro- and dinitrophenols is well documented and appears to be linked with position of the nitro group(s) relative to the phenolic moiety (Rippen et al., 1987; Natangelo et al., 1999).

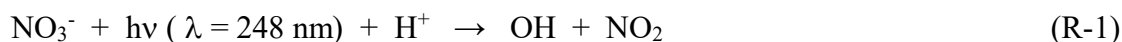
The tropospheric oxidation of aromatic hydrocarbons (benzene, toluene, and isomers of xylene) result in the formation of phenols or cresols as well as ring fragmentation products (Berndt et al., 1999). Phenols are known to be formed directly in the atmosphere by the OH-initiated atmospheric oxidation of aromatic hydrocarbons and product studies (Atkinson et al., 1992) show yields of about 25 %.

Phenols may be converted by OH / NO<sub>2</sub> or NO<sub>3</sub> / NO<sub>2</sub> into nitrophenols in both the gas and the aqueous phase in the troposphere.

In the present study the reactions between phenol and OH / NO<sub>2</sub> and NO<sub>3</sub> / NO<sub>2</sub> were studied by a laser photolysis / longpath laser absorption (LP-LPLA) experiment combined with product studies performed with a HPLC-DAD-ED.

## Objectives

NO<sub>3</sub> radical was produced under only slightly oxidizing conditions by the sequence of reactions (R-1) and (R-2) at pH = 0.5.



Only at low pH, when considerable amounts of  $\text{HNO}_{3(\text{aq})}$  exist, the  $\text{NO}_3$  radical is formed and directly observed by time – resolved laser absorption. Both radical concentration measurement as well as product studies were used to characterise the oxidation reaction. Hence, a direct comparison of concentration of the nitrate radical produced with the amount of products directly sampled from the reaction cell became possible.

## Results

The radicals formed in (R-1) and (R-2) react with phenol ( $1 \cdot 10^{-5}$  M) leading to product yields of nitro derivatives as a function of number of pulses summarised in Table 1.

Exp.	Number of pulse	$[\text{OH}]_{\text{max}}/\text{nM} = [\text{NO}_2]_{\text{max}}/\text{nM}^*$		$[\text{NO}_3]_{\text{max}}/\text{nM}^{**}$		$[\text{NO}_2^-]/\text{nM}$		Prod. Conc./nM <sup>***</sup>
		1 pulse	Total	1 pulse	Total	1 pulse	Total	
A	20	41	820	18	360	14	280	2: $89 (94) \pm 12$ ; 3: $520 \pm 48$ ;
B	15	53	795	19	285	19	285	2: $100 (105) \pm 14$ ; 3: $490 \pm 7$ ;
C	10	59	590	18	180	21	210	2: $110 (114) \pm 22$ ; 3: $500 \pm 37$ ;
D	4	52	208	12	48	18	72	2: $97 (99) \pm 2$ ; 3: $90 \pm 2$ ;
E	1	160	160	47	47	56	56	2: $67 \pm 8$ ; 3: $59 \pm 9$ ; 4: $10 \pm 10$ ;

\*: Calculated after OH yield measurement ;

\*\* : Direct time-resolved  $\text{NO}_3$  absorption measurement ( $\epsilon_{(\text{NO}_3, 635 \text{ nm})} = 1240 \pm 40 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) (Sehested et al., 1994).

\*\*\*: In parenthesis are reported the yield of formation corrected for rate of photolysis.

**Table 1:** Initial maximal radical concentration and the identified reaction products in the flash photolysis experiment.

It is interesting to note that in the reported series of experiments (**A-E**) the *o/p* ratio changes with decreasing number of pulses (Table 2).

This appears to be due to secondary reactions which could include (i) photolysis of primary products as well as (ii) reactions of primary products with the abundant radicals OH,  $\text{NO}_2$  and  $\text{NO}_3$  and (iii) reactions involving nitrate photolysis by- products like nitrite anions and  $\text{N}_2\text{O}_5$ . Furthermore, it was observed that *p*-nitrophenol is decreasing in concentration in the experimental runs **A-C**, whereas the yield of *o*-nitrophenol is nearly constant.

Flashing several times into a non – flowing nitrate anions solution leads to the accumulation of nitrate ion photolysis products. It was experimentally determined by ion chromatography analysis, that nitrite anions were accumulating in the reactions solutions (Table 1). It has been suggested that in acidic aqueous conditions in the presence of nitrous acid nitration of phenol occurs and results in the formation of mono-nitrophenols (*o*- and *p*-nitrophenol). In particular it was observed that the main product of the reaction was the isomer *para*- and it was suggested a nitrosation / oxidation mechanism where the first step a nitrosation in *para*- position occurs, followed by oxygen mediated oxidation leading to the formation of 4-nitrophenol.

For this reason the experiment was also performed using a single laser pulse and the results of these experiments (Table 2) can be used better to describe the OH / NO<sub>2</sub> / NO<sub>3</sub> system.

Exp.	pH	O <sub>2</sub>	[OH] <sub>max</sub> / nM = [NO <sub>2</sub> ] / nM*	[NO <sub>3</sub> ] <sub>max</sub> / nM**	Prod. Conc./nM	Sum. of Prod. /nM	o/p Ratio	Remarks
E	0.5	yes	160	47 ± 6	2: 67 ± 8; 3: 59 ± 8; 4: 10 ± 10;	136 ± 9	1.1 ± 0.1	OH/NO <sub>2</sub> /NO <sub>3</sub>
F	0.5	no	160	66 ± 12	2: 71 ± 13; 3: 57 ± 10; 4: 10 ± 8;	138 ± 11	1.3 ± 0.1	OH/NO <sub>2</sub> /NO <sub>3</sub>
G	3.0	yes	160	Trace	2: 29 ± 13; 3: 20 ± 13; 4: trace;	59 ± 13	1.6 ± 0.3	OH/NO <sub>2</sub>
H	3.2	yes	only NO <sub>2</sub>	-	-	-	-	NO <sub>2</sub>
I	3.8	yes	20	124 ± 15	2: trace; 3: trace; 4: n.d.;	-	-	NO <sub>3</sub>

**Remarks:**

E - G: nitrate anions photolysis at λ = 248 nm;

H: nitrate anions photolysis at λ = 248 nm in presence of radical scavenger;

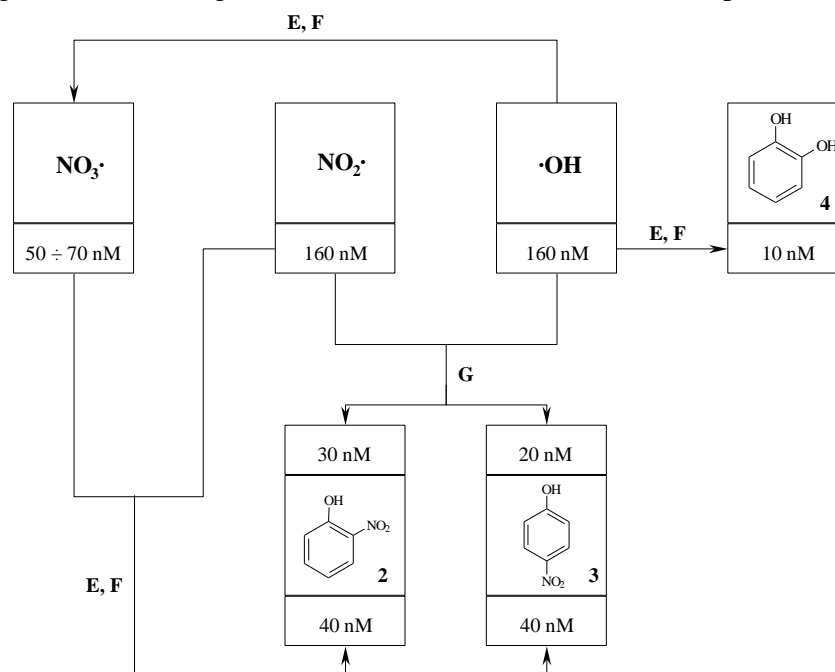
I: peroxodisulphate anions photolysis at λ = 351 nm;

\*: Calculated after OH yield measurement;

\*\* : Direct time-resolved NO<sub>3</sub> absorption measurement ( $\epsilon_{(\text{NO}_3, 635 \text{ nm})} = 1240 \pm 40 \text{ M}^{-1} \text{ cm}^{-1}$ ) (Schested et al., 1994).

**Table 2:** Initial maximal radical concentration and the identified reaction products in the single flash photolysis experiment.

A scheme (Fig. 1) summarising the data from Table 3 could be developed:



**Figure 1:** Summarising scheme where are compared the radical yields and the product yield with the possible reaction pathways.

The obtained results show that the agreement between initial radicals yield and product concentrations is generally reasonable.

In the present experimental conditions the two radical species involved in the first step of the oxidation process are OH (**E-G**) and NO<sub>3</sub> (**E, F**). When the oxidation processes (**E-G**) occurs the nitration derivatives (**2, 3**) are the main products of the overall reaction.

## Conclusions

In this work a laser photolysis / long – path laser absorption apparatus (LP-LPLA) was coupled to a analytic HPLC-DAD-ED - based technique to study the phenol oxidation products in the presence of (i) OH / NO<sub>2</sub> and (ii) NO<sub>3</sub> / NO<sub>2</sub>.

It was shown that in acidic conditions phenol undergoes nitration and the main products of the reaction are the two expected mono-nitrophenol (*o*- and *p*-nitrophenol). It appears that the more important intermediate is the phenoxyl radical which further reacts with a molecule of nitrogen dioxide forming the nitrophenolic compounds. It is shown that NO<sub>3</sub> is only involved in the first step of the reaction.

The present study together with kinetic (Umschlag et al., submitted) and modelling studies on tropospheric multiphase systems (Herrmann et al., 2000) indicates that nitration of phenolic compounds is effectively performed in a two – step mechanism in tropospheric aqueous systems. When initiated by radicals such as OH at daytime and NO<sub>3</sub> during the night intermediates (substituted hydroxy – cyclohexadienyl and / or phenoxyl radicals) are formed which could stabilize by the reaction with aqueous NO<sub>2</sub> to yield nitrophenols.

Tropospheric nitrophenol formation therefore is a good example of possible effects of sequential multiphase processes involving not only gas phase processes but phase transfer and solution phase conversions as well.

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