

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/NO₂ or NO₃ 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 tropospheric aqueous phase it was studied the reaction that occurs between phenol and OH/NO₂ or NO₃ system by a laser photolysis / longpath laser absorption (LP-LPLA) experiment combined with a product study performed with a HPLC-DAD-EC technique (Fig.1).

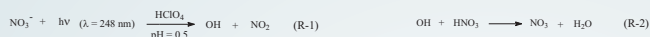
Results and Discussion

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 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 dielectrically 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.

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.

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:



The radicals formed in (R-1) and (R-2) react with phenol (1 x 10⁻⁵ M) leading to the formation of nitro derivatives as identified in the product yields summarised in Table 1

Tab. 1: 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 ^a [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 ± 0,1
248	NaNO ₃	0,5	no	160	66 ± 12	2: 71 ± 13; 3: 57 ± 10; 4: 10 ± 8;	138 ± 11	1,3 ± 0,1
248	NaNO ₃	3,0	yes	160	trace	2: 29 ± 13; 3: 20 ± 13; 4: trace;	59 ± 13	1,6 ± 0,3
248	Radical trap	3,2	yes	only NO ₂	-	-	-	-
351	S ₂ O ₈ ²⁻ / 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 NO₂ absorption measurement ($\epsilon_{\text{NO}_2, 635 \text{ nm}} = 1240 \pm 40 \text{ l mol}^{-1} \text{ cm}^{-1}$) (Sehested *et al.*, 1994).

It was noted in the experiment with different number of pulses that the o/p ratio changes with decreasing number of pulses (Table 2). Flashing several times into a non flowing solution leads to the accumulation of the nitrate ion photolysis by-products and this implies increasing yields of nitro derivatives probably due to a major contribution of secondary reaction pathways. For this reason the experiment was also performed using a single laser pulse and the results coming out (Table 1) can be used to better describe the OH/NO₂/NO₃ system. In Figure 2 an overview of the possible products formation pathways that may occur under the conditions of this study is given.

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

Number of pulse	[OH] _{max} /nM = [NO ₂] _{max} /nM ^a		[NO ₃] _{max} /nM ^b		Prod. Conc./nM	Sum of Products/nM	o/p Ratio
	1 pulse	Total	1 pulse	Total			
20	41	820	18	360	2: 89 ± 12; 3: 520 ± 48;	608 ± 25	0,17
15	53	795	19	285	2:100 ± 14; 3: 490 ± 7;	590 ± 10	0,21
10	59	590	18	180	2: 110 ± 22; 3: 500 ± 37;	610 ± 27	0,21
4	52	208	12	48	2: 97 ± 2; 3: 90 ± 2;	187 ± 2	1,1
1	160	160	47	47	2: 67 ± 8; 3: 59 ± 9; 4: 10 ± 10;	136 ± 9	1,1

^a Calculated after OH yield measurement; ^b Direct time-resolved NO₂ absorption measurement ($\epsilon_{\text{NO}_2, 635 \text{ nm}} = 1240 \pm 40 \text{ l mol}^{-1} \text{ cm}^{-1}$) (Sehested *et al.*, 1994).

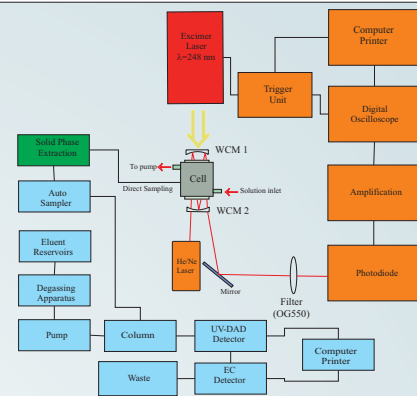


Fig. 1: Experimental set-up LP-LPLA - product study (HPLC-UV-EC) experiment

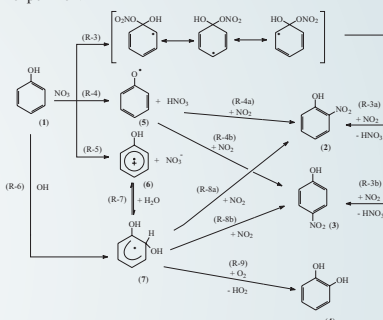


Fig. 2: Reactions involved phenol oxidation and nitration in the flash photolysis experiment

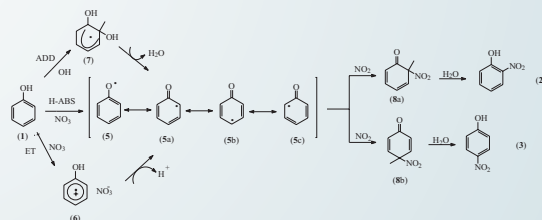


Fig. 3: Proposed oxidation mechanism of phenol by OH/NO₂ or NO₃ in strongly acidic conditions.

Tab. 3: Product study results in phenol oxidation experiments by means of nitrate anion photolysis with lamp and laser technique. The values are expressed like percentage of reacted phenol.

Irradiation Time	pH	Identified Products / Phenol Reacted									
		OH	OH	OH	OH	OH	OH	OH	OH	OH	OH
Niessen <i>et al.</i> 1988 ^a	1 h	5,2	31	4	2	13	7	-	12	3	72
Niessen <i>et al.</i> 1988 ^a	1 h	5,2	32	4,6	2,8	9,8	3,4	-	6,4	4,8	64
Niessen <i>et al.</i> 1988 ^a	1 h	3,6	14,1	3,4	3,4	-	< 0,3	-	4,8	11,3	44
Machado <i>et al.</i> 1995 ^b	1 h	5,5	51,6	9,6	14,7	-	-	2,2	3,3	1,8	83
This work	20 ns	0,5	3,7	-	-	-	-	-	21,6	24,5	49,8 (86,4) ^c
This work	20 ns	3,0	trace	-	-	-	-	-	14,7	10,1	24,9 (80,7) ^c

^a ^b Sets of results for other experimental conditions are available in the referenced paper; ^c Considering the contribution of direct photolysis of phenol ($\epsilon = 200 \text{ M}^{-1} \text{ cm}^{-1}$ at 248 nm) assuming $\Phi = 1$.

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 NO₃ 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.

References

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