

# Oxidation Process of Phenol by Nitrate Radical in Aqueous Phase. A Product Study



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## Introduction

Phenols are known to be formed by the OH-initiated atmospheric oxidation of aromatic hydrocarbons [1,2,3, 4] and a number of product studies are reported in literature [5] show that their yields could be relatively high. Emission of aromatic compounds (benzene, toluene, and isomers of xylene) from vehicles exhaust result in the formation of phenol or cresols and ring fragmentation products. The subsequent fates of these compounds in the atmospheric system are not well understood at present. Phenols may be converted by OH/NO<sub>2</sub> or NO<sub>3</sub> in both gas and aqueous phase.

The nitrate radical in aqueous solution may undergo reactions with aromatic compounds which have been shown to proceed faster than the corresponding gas-phase reactions by orders of magnitude. In order to better understand the reactivity of the nitrate radical in tropospheric aqueous phase we studied the reaction that occurs between phenol and nitrate radical by a laser-photolysis-longpath-laser absorbance (LP-LPA) experiment combined with a product study performed with a HPLC-DAD-EC technique.

## Experimental

In this study the concentration and temporal behaviour of nitrate radical, produced by few pulses into an acidic aqueous solution (pH=0.5 with perchloric acid) of nitrate ion (0.02 M) at 248 nm, is compared with the concentration of the reaction products.

The flash photolysis set-up (Fig. 1) consists of a multigas excimer laser Mod. Compex 201(Lambda-Physik) filled with a Kr/F gas mixture that delivers a 10 - 40 ns pulse with an average energy about 750 mJ at 248 nm. The optical detection system comprises a He/Ne laser (Spindler and Hoyer) operated at 632.8 nm; the laser light was 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 (Ref.[6,7] for details). The electrical output from the detector, a photodiode, was amplified and fed to a digital storage oscilloscope Mod. Delta Classic (Gould) connected to a computer. The timing of the reaction of the experiment was controlled by a delay-pulse generator (ModDg535, SRS).

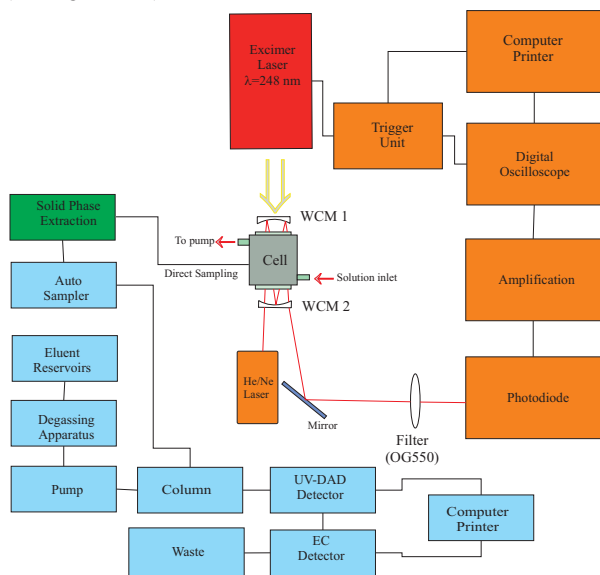


Fig. 1: experimental set-up LP-LPA - product study (HPLC-UV-EC) experiment

After irradiation the samples were extracted with LiChrolut ENV cartridges, a 12-20 ml sample was applied at flow-rate of 1 ml/min Breakthrough volumes for this of cartridges were measured by percolating equivalent volume of standard solutions using the method described above: no breakthrough was observed in our experimental conditions and the recovery rates are quantitative (Tab. 1).

The separations of the compounds was achieved using a HPLC-DAD-EC apparatus configured like showed in Fig. 1. For the stationary phase a stainless steel column was chosen (250 x 4 mm) packed with a regular spherical silica Kromasil (particle size of 5µm derivatized with octadecyl chain). The analysis was performed by an isocratic elution with a mobile phase composed by 80% KH<sub>2</sub>PO<sub>4</sub> 30 mM (pH=4 adjusted with H<sub>3</sub>PO<sub>4</sub>) and 20% CH<sub>3</sub>CN at flow-rate of 0,6 ml/min. The analytes were identified by directly comparison of the retention time and absorption spectrum and the quantification was performed using calibration curve at different wavelength where the compound present a relative absorption maximum. The correlation coefficient and the detection limit are good for all the compounds (Tab. 1).

The electrochemical detector was operated by applying a fixed dc potential to the working electrode of a flow-trough electrolysis cell and recording the current resulting from the oxidation of analyte as a function of elution time. It was used in screen-out mode setting the voltage of the first electrode and the second electrode, respectively, at 0,80 v and 1,15 v.

## References

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Tab. 1: Summary of the values obtained with the analytical set-up for all the possible interested compounds.

COMPOUND	SPE RECOVERY (%)	UV/DAD CALIBRATION CURVE CORR. COEFF.	UV/DAD DETECTION LIMIT [ng/ml]	EC DETECTION LIMIT [ng/ml]
Phenol	99 ± 4	0.993	40	1.89
2-nitrophenol	89.9 ± 7	0.998	52	2.28
3-nitrophenol	91 ± 6	0.989	59	3.15
4-nitrophenol	98.2 ± 6	0.999	59	1.35
2,4-dinitrophenol	99.1 ± 4	0.997	47	N.D.
2,6-dinitrophenol	89.3 ± 5	0.997	48	N.D.
1,2-dihydroxybenzene	96.1 ± 7	0.995	45	2.56
1,3-dihydroxybenzene	99.2 ± 4	0.991	56	N.D.
1,4-dihydroxybenzene	97.5 ± 5	0.997	50	2.02
1,2,3-trihydroxybenzene	91.1 ± 3	0.988	62	N.D.
1,3,5-trihydroxybenzene	93 ± 6	0.988	57	N.D.
4-nitrocathecol	92.2 ± 8	0.997	68	N.D.

## Results

The objective of the work was to clarify the role of nitrate radical as an oxidant in aqueous solution in the presence of the phenol and to identify whether nitration occurs.

The formation of the nitrate radical and the subsequent reactions are described in Figure 2.

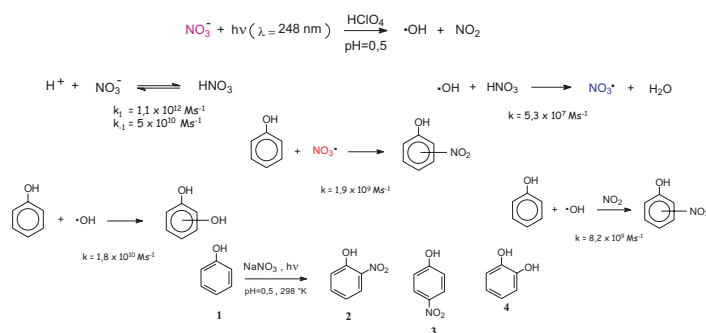


Fig. 2: Reactions involved phenol oxidation and nitration in the flash photolysis experiment

The reaction was carried out in triple flashing with different number of pulse (1,4,10,15,20) a solution containing NaNO<sub>3</sub> 1,4x10<sup>-2</sup> M, phenol 1x10<sup>-5</sup> M with the pH adjusted at 0,5 with HClO<sub>4</sub> at 298 °K. The nitrate radical formed reacts with the phenol leading to the formation of nitroderivatives as we found in the products study represented in the following table.

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

NUMBER OF PULSE	COMPOUND	[OH]₀/nM = [NO₂]₀/nM		[NO₃]₀/nM		PROD.CONC./nM	o/p RATIO
		1 pulse	Total	1 pulse	Total		
20	Phenol	41	820	18	360	2: 88,8 ± 12; 3: 520 ± 48;	0.17
15	Phenol	53	795	19	285	2: 100 ± 14; 3: 490 ± 7;	0.21
10	Phenol	59	590	18	180	2: 110 ± 22; 3: 500 ± 37;	0.21
4	Phenol	52	208	12	48	2: 97 ± 1.2; 3: 90 ± 1.7;	1.1
1	Phenol	160	160	47	47	2: 66.6 ± 8; 3: 59.4 ± 9; 4: 10.2 ± 10;	1.1

## Discussion and Outlook

- ✓ Agreement between initial radicals yield and product concentrations is generally reasonable.
- ✓ The o/p ratio changes with decreasing number of pulses. This is probably due to the decrease of the influence of secondary reactions.
- ✓ Modelling calculations show that the formation of nitroproducts by a sequential reaction of OH and NO<sub>2</sub> could only account for about 10% of the observed nitrocompounds.
- ✓ Therefore, and in view of recently available kinetic data, it is concluded that also direct reaction of NO<sub>2</sub> with phenols occurs and may contribute to the observed product concentrations.

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