

FORMATION MECHANISM OF NITROPHENOLS IN AQUEOUS PHASE IN FLASH PHOTOLYSIS EXPERIMENT

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INTRODUCTION

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).

The reactions that occurs between phenol and OH / NO₂ / NO₃ were studied by a laser - photolysis – longpath – laser – absorbance (LP-LPA) experiment combined with a product study performed with a HPLC-DAD technique

METHODS

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.

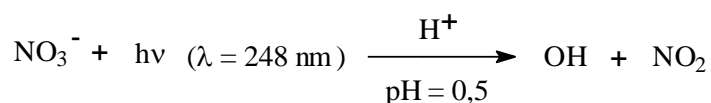
After irradiation a solid phase extraction passage is applied. The separation of product compounds is achieved using a HPLC-DAD-EC apparatus.

CONCLUSIONS

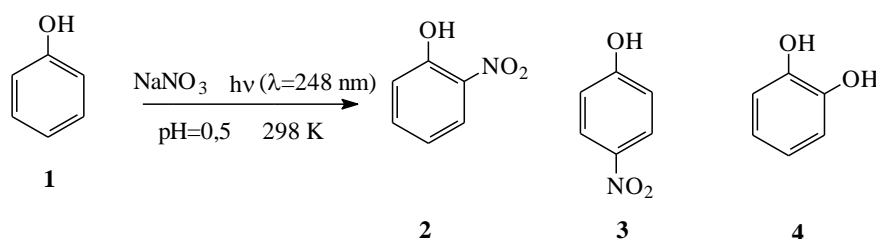
The objective of the work was to clarify the role of nitrate radical as an oxidant in aqueous solution in the presence of the phenol and to identify whether nitration occurs.

From gas-phase studies, it is known that phenol reacts with nitrate radical leading to the formation of 2-nitrophenol (**2**), and in a recent kinetic study it is found that the electron transfer (ET) pathway could contribute close to 40%. Modelling calculations applied to our reaction conditions and first products study experiments at higher pH (pH = 3) where NO₃ is not formed anymore indicate that the formation of nitroproducts by a sequential reaction of OH and NO₂ could account for about 30% of the observed nitrocompounds.

In the flash photolysis of nitrate anions radicals are formed as follows:



The radicals formed react with phenol leading to the formation of nitroderivatives as identified in the product study in the yields summarised in Table 1.



NUMBER OF PULSE	[OH] ₀ /nM = [NO ₂] ₀ /nM (1)		[NO ₃] ₀ /nM (2)		PROD.CONC./nM	o/p RATIO
	1 pulse	Total	1 pulse	Total		
20	41	820	18	360	2: 88,8 ± 12; 3: 520 ± 48;	0.17
15	53	795	19	285	2: 100 ± 14; 3: 490 ± 7;	0.21
10	59	590	18	180	2: 110 ± 22; 3: 500 ± 37;	0.21
4	52	208	12	48	2: 97 ± 1.2; 3: 90 ± 1.7;	1.1
1	160	160	47	47	2: 66.6 ± 8; 3: 59.4 ± 9; 4: 10.2 ± 10;	1.1

(1) Calculated after OH yield measurement.

(2) Direct time-resolved NO₃ absorption measurement ($\epsilon_{(\text{NO}_3, 635 \text{ nm})} = 1240 \pm 40 \text{ l mol}^{-1} \text{ cm}^{-1}$; Sehested *et al.*, 1994).

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

The obtained results show that the agreement between initial radicals yield and product concentrations is generally reasonable. The *o/p* ratio changes with decreasing number of pulses, probably due to the decrease of the influence of secondary reactions.

From the single shot experiments and in view of the first results in similar experiment performed without NO₂ it can clearly be concluded that NO₃ is involved in the initial attack towards phenol. This may occur via addition/elimination, H-abstraction of the phenolic H-atom or electron transfer. In all three cases, intermediates are converted into nitrophenols by NO₂ in a second reaction step. Currently, the single contributions of each pathway are not quantified.

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