

Oxidation of Phenol by Nitrate Radicals in the Aqueous Phase: A Product Study

A contribution to the sub-project CMD-APP

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Introduction

Phenols are known to be formed in the atmosphere by the OH-initiated atmospheric oxidation of aromatic hydrocarbons (Berndt et al., 1999; Klotz et al., 1997; Lay et al., 1996) and a number of product studies reported in the literature (Carter et al., 1981) 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. The subsequent fates of these compounds in atmospheric systems are not well understood at present. Phenols may be converted by OH/NO₂ or NO₃ 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 (Atkinson, 2000; Herrmann et al., 1995). In order to better understand the reactivity of the nitrate radical (e.g.: formation of phytotoxic compounds like mono-, dinitrophenols) in the tropospheric aqueous phase the reaction that occurs between phenol and nitrate radical was studied by a laser - photolysis – longpath – laser – absorbance (LP-LPA) experiment combined with a product study performed with a HPLC-DAD-EC technique

In this study the concentration and temporal behaviour of nitrate radical, produced by few pulses into an acidic aqueous solution of nitrate ion at 248 nm at room temperature, is compared with the concentration of the reaction products.

Experimental section

The reaction was carried out in triple flashing with different number of pulses (1,4,10,15,20) a solution containing NaNO₃ 1,4x10⁻² M, phenol 1x10⁻⁵ M with the pH adjusted at 0,5 with HClO₄ at 298 °K.

The flash photolysis set-up 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 (Herrmann et al., 1995; Umschlag et al. in press 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 (Mod DG535, SRS).

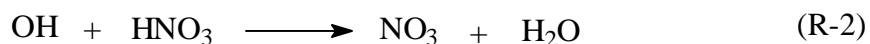
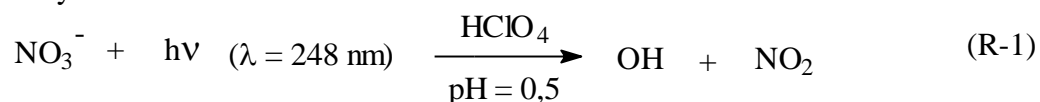
After irradiation the samples were extracted with LiChrolut ENV cartridges (DVB polymer, Merck). No breakthrough was observed in our experimental conditions and the recovery rates are quantitative.

The separations of the compounds was achieved using a HPLC-DAD-EC apparatus. For the stationary phase a RP-C18 stainless steel column (Hyperchrome) was chosen (250 x 4 mm I.D., 5 μ m, 100 Å). The analysis was performed by an isocratic elution with a mobile phase composed by 80% KH₂PO₄ 30 mM (pH = 4 adjusted with H₃PO₄) and 20% CH₃CN at flow-rate of 0,6 ml /min. The analytes were identified by directly comparison of the retention time and absorption spectrum of standard compounds. The correlation coefficient and the detection limit are good for all the compounds.

The electrochemical detector (Coulchem Mod. 5100A, ESA) was operated by applying a fixed dc potential to the working electrode of a flow-trough electrolysis cell (Mod. 5011, ESA) and recording the current resulting from the oxidation of analyte as a function of elution time.

Results

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



In Figure 1 an overview of the possible products formation pathways that may occur under the conditions of this study is given.

From gas-phase studies, it is known that phenol reacts with nitrate radical (R-3) leading to the formation of (2), and in recent kinetic study (Umschlag et al., in preparation) it was found that the H-abstraction pathway (R-4) leading to the formation of (5) 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 nitro-products by a sequential reaction of OH and NO₂ (R-7, R-9a,b) could account for about 30% of the observed nitrocompounds.

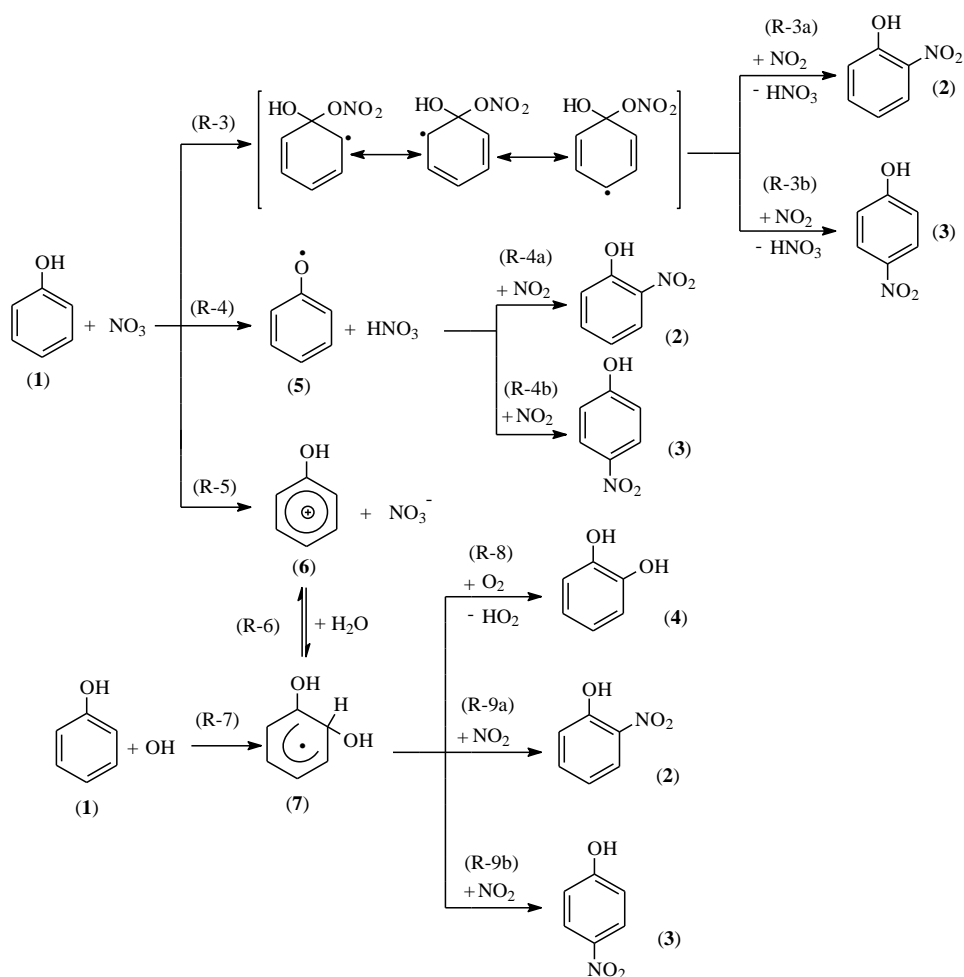


Fig. 1: Reactions involved phenol oxidation and nitration in the flash photolysis experiment.

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

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

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).

Conclusions

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 it can clearly be concluded that NO₃ is involved in the initial attack towards phenol. This may occur via addition/elimination (R-3a,b), H-abstraction of the phenolic H-atom (R-4) or electron transfer (R-5). Currently, the single contributions of each pathway are not quantified. In all three cases, intermediates are converted into nitrophenols by NO₂ in a second reaction step.

In the future, similar experiment without NO₂ will be performed to better identify products formed by only NO₃ interacting with phenols.

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