

Kinetic and Mechanistic Investigations of Oxidation Reactions of Selected Phenols in Aqueous Phase by OH /NO₂ /NO₃ System.

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Introduction

Emissions of aromatic hydrocarbons (benzene, toluene, and isomers of xylene) from vehicles fuel exhaust lead to the formation of phenol or cresols and ring fragmentation products (Berndt et al., 1999). 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. In order to better understand the reactivity of the nitrate radical (e.g.: formation of phytotoxic compounds like mono-, or dinitrophenols) in the tropospheric aqueous phase a study of the reaction that occurs between some selected phenols and nitrate radical was performed by a laser photolysis / longpath laser absorption (LP-LPLA) experiment (Herrmann et al., 1995) combined with a product study performed with a HPLC-DAD technique

Methods

The flash photolysis set-up consists of a excimer laser filled with a Kr/F and Xe/F gas mixture that delivers a 10 - 40 ns pulse at $\lambda = 248$ and 351 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.

Results and Conclusions

In the case of phenol a mechanistic study was carried out comparing the concentration of nitrate radical, produced by flashing with a few pulses into an acidic aqueous solution of nitrate ion (pH = 0,5) at 248 nm, with the concentration of the identified reaction products. In the one pulse experiment an *o/p* ratio of 1,1 / 1 and an yield of 79 % (concentration *o*- + *p*-nitrophenol / OH and NO₂ maximal radical concentration) were obtained. In view of the results in similar experiment performed without NO₂ it can clearly be concluded that NO₃ is involved only 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.

The activation parameters of reactions of the NO₃ radical with some selected ortho-substituted phenols (*o*-cresol, catechol, guajacol, 2-ethylphenol) were determined.

References

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- Herrmann, H., H. Exner, W. Jacobi, G. Raabe, A. Reese, and R. Zellner, Laboratory studies of atmospheric aqueous phase free radical chemistry: kinetic and spectroscopic studies of reactions of NO₃ and SO₄⁻ radicals with aromatic compounds, *Faraday Discuss.* 100, (1995) 129-153.