



Secondary HO₂ formation from the OH-initiated photo-oxidation of aromatic hydrocarbons under atmospheric conditions in the absence of NO

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Benzene, toluene and the xylenes are among the most abundant aromatic trace constituents of the atmosphere originating mainly from anthropogenic sources including evaporative emissions of chemical plants and storage tanks as well as incomplete combustion processes.^[1] In the troposphere, the photo-oxidation of aromatic hydrocarbons results in the formation of ozone and secondary organic aerosol. Therefore, aromatics are important trace constituents regarding air pollution levels.^[2]

The reaction of OH radicals with aromatics proceeds mainly via addition to form the OH-aromatic-adduct. Under ambient conditions, the dominant fate of the OH-aromatic-adduct is the reaction with O₂. These subsequent O₂ reactions are yielding ring-retaining and ring-cleavage oxidation products, partly after reaction with NO. However, the reaction mechanisms and the product yields of these subsequent reactions are still not well known. The currently recommended main products of the ring-retaining degradation pathways are phenolic compounds + HO₂, whereas unsaturated epoxy-dicarbonyl-compounds + HO₂ or intermediate peroxy radicals are the proposed products of the ring-cleavage pathways. It has been shown, that the ring-cleavage pathways are more efficient at generating ozone.^[3] Thus, the product yields of the OH-aromatic-adduct + O₂ reaction are important for the impact of aromatic compounds on atmospheric chemistry.

We performed pulsed kinetic experiments in different N₂/O₂ mixtures at atmospheric pressure and room temperature in the absence of NO in order to investigate the secondary HO₂ formation from the OH-initiated degradation of several aromatic hydrocarbons. OH was formed in a reaction cell under laminar flow conditions by laser flash photolysis of O₃ at 266 nm followed by reaction of O(¹D) with water vapour. OH and HO_x (=OH+HO₂) decay curves were detected by means of laser-induced fluorescence technique (LIF). We observed HO_x decay curves for the first time and extracted total HO₂ yields as well as reaction rate constants by employing analytical solutions and curve-fitting procedures. Experiments with deuterated aromatics were performed to further elucidate the degradation mechanisms and to differentiate between HO₂ formation resulting from ring-retaining and ring-cleavage reaction channels.

References:

- [1] T.J. Fortin, B.J. Howard, D.D. Parrish, P.D. Goldan, W.C. Kuster, E.L. Atlas, R.A. Harley, *Environmental Science and Technology*, 2005, 39, 1403-1408
- [2] J. G. Calvert, R. Atkinson, K.H. Becker, R.M. Kamens, J.H. Seinfeld, T.J. Wallington, G. Yarwood: *The mechanisms of atmospheric oxidation of aromatic hydrocarbons*, Oxford University Press, 2002
- [3] C. Bloss, V. Wagner, A. Bonzanini, M.E. Jenkin, K. Wirtz, M. Martin-Reviejo, M.J. Pilling, *Atmospheric Chemistry and Physics*, 2005, 5, 623-639