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Consecutive reactions of aromatic-OH adducts with NO, NO₂ and O₂: benzene, naphthalene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline

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Abstract. Consecutive reactions of adducts, resulting from OH radicals and aromatics, with the tropospheric scavenger molecules O₂, NO and NO₂ have been studied for benzene, naphthalene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline by observing decays of OH at temperatures where the thermal back-decomposition to OH is faster than 3 s⁻¹, typically between 300 and 340 K. The experimental technique was resonance fluorescence with flash photolysis of water as source of OH. Biexponential decays were observed in the presence of either O₂ or NO, and triexponential decays were obtained in the presence of NO₂. The kinetic analysis was performed by fitting the relevant rate constants of the reaction mechanism to whole sets of decays obtained at various concentrations of aromatic and scavenger. In the case of hexamethylbenzene, the biexponential decays suggest the existence of the ipso-adduct, and the slightly higher necessary temperatures show that it is even more stable.

In addition, smog chamber experiments at O₂ concentrations from atmospheric composition down to well below 100 ppm have been carried out for benzene, toluene and p-xylene. The drop of the effective rate constant of removal by OH occurs at reasonable O₂ levels, given the FP/RF results. Comparison of the adduct reactivities shows for all aromatics of this study that the reaction with O₂ predominates over that with NO₂ under all tropospheric conditions, and that a reaction with NO may only occur after the reaction with O₂.

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