



BTX dealkylation: a novel pathway in the OH initiated oxidation of aromatics

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Aromatic compounds constitute 30-40% of total hydrocarbon mass emitted into the urban atmosphere, contributing degradation of urban air quality via, e.g. formation of ozone and Secondary Organic Aerosols. It is increasingly becoming important to understand the fate of emitted compounds in the atmosphere as population density in urban area increases.

In this work, the OH-radical initiated oxidation of a series of monocyclic compounds (benzene, toluene, o-, m-, and p-xylene) in the presence of oxygen was examined in a flowtube set-up coupled to a Chemical Ionization Mass Spectrometer (CIMS). Previous studies found systematic differences in phenol type product yields in simulation chamber and flowtube setups (i.e. for benzene). Yields in flowtube systems were systematically lower than in simulation chamber experiments, posing questions as to the time scale of phenol formation. Furthermore, it has recently become evident that there is a gap in our understanding of the first stages in aromatic oxidation; the sum of molar branching ratios of these pathways is significantly below unity (Volkamer et al. 2005), indicating that further - currently unidentified - oxidation pathways must be operative.

Our flowtube allows to study the time scale of phenol type product formation from a direct measurement at rather short time scale (35 to 75 ms). The phenol yield from benzene, and cresol yield from toluene are found higher than in previous flowtube studies, i.e. $48.7 \pm 5.6\%$ and $18.8 \pm 2.1\%$ respectively. They are in close agreement with previous chamber studies, and broadly consistent also with HO₂ re-cycling experiments (i.e. benzene; Bohn and Zetzsch, 1999). No time dependence is observed in the yields, which allows us to reduce the upper limit timescale of phenol formation by three orders of magnitude. Surprisingly, among the products from the toluene system,

phenol was unambiguously identified. The formation of phenol from toluene oxidation is proposed to proceed from addition of OH-radicals in the ipso-position, followed by dealkylation and rearrangement to yield phenol. Similar dealkylation reactions were observed also for different alkylbenzenes, suggesting that dealkylation reactions form a small, but currently unrecognized, and more general pathway in aromatic oxidation.

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