

Mechanisms of the Gas-Phase Reactions of PAHs OH and NO₃ Radicals

Roger Atkinson¹, Janet Arey¹, Noriko Nishino¹, Lin Wang¹

¹Air Pollution Research Center, University of California

The dominant gas-phase chemical loss process for aromatic hydrocarbons not containing unsaturated substituent groups, both monocyclic (such as benzene, toluene and xylenes) and PAHs (such as naphthalene and alkylnaphthalenes), is by reaction with the OH radical. These reactions proceed mainly by initial addition to form an OH-aromatic or OH-PAH adduct. For the monocyclic aromatic hydrocarbons, the OH-aromatic adducts react with O₂ and NO₂, with the O₂ reaction dominating under atmospheric conditions, even in heavily polluted urban areas. In contrast, the available product data, including the observation of nitro-PAH isomers in ambient air which are those formed from OH radical- or NO₃ radical-initiated reactions of PAHs, suggest that the OH-PAH adducts react dominantly with NO₂ at NO₂ concentrations much lower than is the case with OH-monocyclic aromatic adducts, and with the NO₂ reaction occurring even under ambient atmospheric conditions. The available product and mechanistic data concerning these reactions will be presented, including recent work carried out in our laboratory on the formation of the ring-cleavage product glyoxal from the OH radical-initiated reaction of naphthalene as a function of the NO_x concentration.