

## ABSTRACT

**DISSERTATION:** Computational studies of structure-reactivity relationships in the reaction of hydroxyl radical with arenes.

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The primary steps of the decomposition of the aromatic pollutants in the environment involve their reactions with hydroxyl radical (OH•). Structure-reactivity models capable of accurately predicting both the reactivity and selectivity of these reactions in gas and solvent phases, are of interest to the environmental and biochemical communities. High accuracy computational methods (CBS-Q//BH&HLYP/6-31G(d,p)) were employed to explore the possible reaction pathways for reaction of OH• with a range of substituted aromatic compounds with functional groups ranging in activity from strongly electron donating (such as -NH<sub>2</sub>, -OCH<sub>3</sub>) to strongly electron withdrawing (-NO<sub>2</sub>, -CF<sub>3</sub>). It was determined that in the case of addition of hydroxyl radical to arenes, the reactivity was largely controlled by polar effects, demonstrated by linear relationships between the calculated rates of reaction and the ionization potentials and Hammett substituent parameters of the arenes. Addition at

positions *ortho*- and *para*- to the substituent are the dominant modes of addition to arenes in general, but addition at the meta- position becomes more favored, and addition at *ortho*- less favored with rings bearing strongly electron withdrawing groups. Inclusion of solvent effects in the form of a polarizable continuum (SMD) model indicates that these effects become more pronounced in polar solvents. Initial investigations indicate that such effects are less pronounced when considering hydrogen abstraction from side chains. Calculated rate coefficients support solution phase experimental studies that show that addition to the ring is dominant mode of reaction for hydroxyl radicals with alkylated arenes.