

# Chemistry of Alkylaromatics in Crude Oil Upgrading

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Due to the rise in demand of crude oil over the long term, technologies to upgrade crude oil need to be developed to ensure maximum use efficiency of future oil sources. In typical carbon rejection processes, coke formation is a common phenomenon that would lead to decreased yield of upgraded oil. As a result, the chemical behavior of coke formation is a potent area of research. Due to the high complexity of the composition of crude oil and coke, this work simplifies the study of supercritical water upgrading of crude oil to a hexylbenzene pyrolysis system. The pyrolysis of hexylbenzene at process conditions of 450°C and 75 creates several hundred products resolved by GCxGC, and the analysis is intractable if one considers only the experimental data, which does not reveal reactive intermediates or reaction paths. However, introducing theoretical considerations using the Reaction Mechanism Generator (RMG) allows analysis of a vast number of species while retaining information of elementary reaction steps and reactive intermediates. Information on these steps and intermediates can be obtained from Quantum Chemistry

Hexylbenzene pyrolysis was characterized using RMG with key steps computed using Quantum Chemistry. The results indicate that the retro-ene reaction, previously thought to carry an important role in hexylbenzene pyrolysis, is much slower than reported in literature. Furthermore, alkylaromatic chemistry at 450°C is extremely sensitive to species thermochemistry. Further investigation was done on the formation of 2-ring aromatic species in hexylbenzene pyrolysis, likely precursors of coke. Thermochemistry and rate calculations were made for 2-ring species as a result of the intramolecular and intermolecular addition pathways, resulting in 27 thermochemistry group additivity values to allow for extrapolation of this work's calculations to analogous species. In addition, 25 training reactions were added to allow rate rules calculated in this work to be extrapolated to similar reactions.

Finally, all this new chemical knowledge was incorporated into RMG, and a detailed kinetic model for hexylbenzene pyrolysis was constructed. The generated model was able to predict the total molar yield of bridged 2-ring aromatics, and fused 2-ring aromatics. However, many individual species had inaccurate molar yield predictions, and some key pathways to form 2-ring species were found to be missing. Additional quantum calculations were performed after the construction of this kinetic model to attempt to resolve these mispredictions.

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