

Quantum Chemical and Kinetic Study of the Oxidation Mechanisms of Naphthalene Initiated by Hydroxyl Radicals: The H Abstraction Pathway

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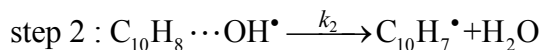
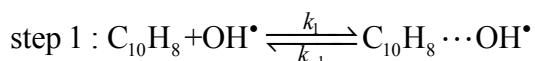
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Abstract

Reaction mechanisms for the initial stages of naphthalene oxidation at high temperatures ($T \geq 600$ K) have been studied theoretically using density functional theory along with various exchange-correlation functionals, as well as the benchmark CBS-QB3 quantum chemical approach. These stages correspond to the removal of hydrogen atoms by hydroxyl radical and the formation thereby of 1- and 2-naphthyl radicals.

The oxidation mechanisms of naphthalene by OH radicals under inert (He) conditions and at temperatures larger than 600 K have been studied [1] using Density Functional Theory (DFT) along with various exchange-correlation functionals. Comparison is made with benchmark CBS-QB3 theoretical results. Kinetic rate constants were estimated by means of Transition State Theory (TST). Effective rate constants have been calculated according to a steady state analysis using a two-step model:



The excellent agreement obtained with experimental kinetic rate constants demonstrates the validity of this model. Comparison with results obtained using density functional theory in conjunction with various exchange-correlation functionals also shows that DFT remains unsuited for quantitative enough insights into kinetic rate constants. Analysis of the computed structures, bond orders and free energy profiles demonstrates that the reaction steps involved in the removal of hydrogen atoms by OH radicals satisfy Leffler-Hammond's principle. Computations of branching ratios also show that this reaction does not exhibit a particularly pronounced site-selectivity.

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References:

[1] A. Shiroudi, M. S. Deleuze, J. Phys. Chem. A, **118** (2014) 3625.