

Mechanism development and computational kinetics of PAH growth by propargyl at a chair site

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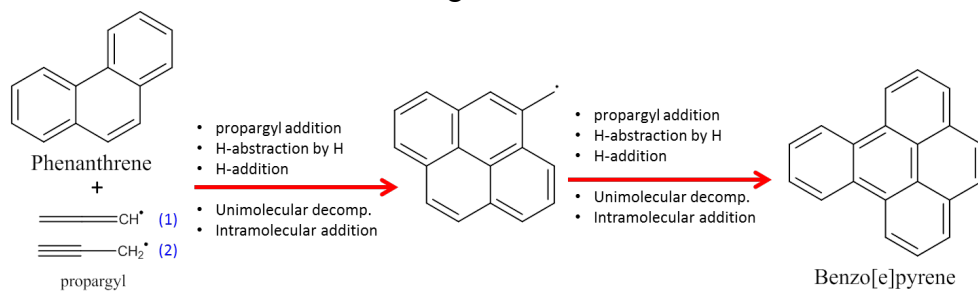
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Soot emission is one of the main concerns of combustion science, which is currently focused on designing new high-efficiency and low-emission fuels. Knowing that soot inception is instigated by PAH growth, a well-developed mechanism of the latter is required to predict soot emissions. Several research studies have shown that the widely used hydrogen abstraction C₂H₂-addition (HACA) mechanism of PAH growth is incapable of predicting some experimental soot concentration profiles(1, 2) and the synergistic effect of fuel mixing (3, 4) on its own. This has prompted the investigation of other mechanisms of PAH growth such as those instigated by resonantly stabilized radicals that attain high concentrations in flames, mainly propargyl and cyclopentadienyl radicals. Previously, we studied the mechanistic pathways and kinetics of propargyl-initiated PAH growth on a zigzag site in naphthalene (A2) (5). In this work, we present the PAH growth mechanism at the chair site in phenanthrene (A3) via propargyl addition and abstraction reactions. The high-pressure temperature-dependent kinetics of all H-abstraction, H-addition, H-migration, β -scission and intra-molecular addition elementary reactions have been calculated at the UB3LYP/6-311++G(d,p)//CBS-QB3 level of theory. Formation enthalpies of all species were calculated using isogyric reactions for better accuracy, and the rotational barriers of non-free rotors were obtained using hindered rotor scan calculations.



References

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