

A Theoretical Study of Pyrolysis of JP-10 (*exo*-Tetrahydrodicyclopentadiene) and its Primary and Secondary Unimolecular Decomposition Products

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Abstract. Theoretical calculations of the rate constants and product branching ratios in the pyrolysis of *exo*-tetrahydrodicyclopentadiene (JP-10) and its initial decomposition products at combustion-relevant pressures and temperatures have been performed and compared to experimental results from recently reported molecular beam photoionization mass spectrometry study of the pyrolysis of JP-10 (Zhao, L. et al. *Phys. Chem. Chem. Phys.* **2017**, *19*, 15780). The results allow us to quantitatively assess the decomposition mechanisms of JP-10 by a direct comparison with the nascent product distribution - including radicals and thermally labile closed-shell species - detected in the short-residence-time molecular beam photoionization mass spectrometry experiment. In accord with the experimental data, the major products predicted by the theoretical modeling include methyl radical (CH₃), acetylene (C₂H₂), vinyl radical (C₂H₃), ethyl radical (C₂H₅), ethylene (C₂H₄), allyl radical (C₃H₅), 1,3-butadiene (C₄H₆), cyclopentadienyl radical (C₅H₅), cyclopentadiene (C₅H₆), cyclopentenyl radical (C₅H₇), cyclopentene (C₅H₈), fulvene (C₆H₆), benzene (C₆H₆), toluene (C₇H₈), and 5-methylene-1,3-cyclohexadiene (C₇H₈). We found that ethylene, allyl radical, cyclopentadiene, and cyclopentenyl radical are significant products at all combustion-relevant conditions, whereas the relative yields of the other products depend on temperature. The most significant temperature trends predicted are increasing yields of the C₂ and C₄ species and decreasing yields of the C₁, C₆, and C₇ groups with increasing temperature. The calculated pressure effect on the rate constant for the decomposition of JP-10 via initial C-H bond cleavages becomes significant at temperatures above 1,500 K. The initially produced radicals will react away to form closed-shell molecules, such as ethylene, propene, cyclopentadiene, cyclopentene, fulvene, and benzene, which were observed as the predominant fragments in the long-residence-time experiment. The calculated rate constants and product branching ratios should prove useful to improve the existing kinetic models for the JP-10 pyrolysis.