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 (CH_3), acetylene (C_2H_2), vinyl radical (C_2H_3), ethyl radical (C_2H_5), ethylene (C_2H_4), allyl radical (C_3H_5), 1,3-butadiene (C_4H_6), cyclopentadienyl radical (C_5H_5), cyclopentadiene (C_5H_6), cyclopentenyl radical (C_5H_7), cyclopentene (C_5H_8), fulvene (C_6H_6), benzene (C_6H_6), toluene (C_7H_8), and 5-methylene-1,3-cyclohexadiene (C_7H_8). 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.