

An Investigation of the Thermochemical Parameter and Rate Coefficient Assignments for the Low-Temperature Oxidation Pathways of Alkanes: A Case Study using the Pentane Isomers

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This study probes our developing understanding of low-temperature oxidation kinetics. We have investigated the ignition of the pentane isomers in a rapid compression machine over a wide range of temperatures and pressures including the negative temperature coefficient behaviour temperature range. The pentane isomers are small alkanes, yet have structures that are complex enough to allow for the application of their kinetic and thermochemical rules to larger molecules. Updates to the thermochemistry of the species important in the low-temperature oxidation of hydrocarbons have been made based on a thorough literature review. An evaluation of recent quantum-chemically derived rate coefficients from the literature pertinent to important low-temperature oxidation reaction classes has been performed, and new rate rules are recommended for these classes. Several reaction classes have also been included to investigate their importance with regard to simulation results, and we find that they should be included when developing future chemical kinetic mechanisms. A comparison of the model simulations with pressure-time histories from experiments in a rapid compression machine shows very good agreement for both ignition delay time and pressure rise for both the first- and second-stage ignition events. We show that revisions to both the thermochemistry and the kinetics are required in order to replicate experiments well. The results of this study enhance our understanding of the combustion of straight- and branched-chained alkanes.