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Optimization of the rate rules for the large alkanes

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A consistent set of rate rules for the large alkanes reactions has been optimized and validated using the three pentane isomers, five hexane isomers, nine heptane isomers, and *iso*-octane. The initial mechanism of these fuels were auto-generated by a modified version of MAMOX++ [1], based on the central Arrhenius curve of their prior uncertainty range, which was determined by a comprehensive review of theoretical studies of typical rate conststants in alkanes. To accelerate the optimization process, we employed the Reduction-Assisted Parameter Optimization and Mechanism Development (RAPOD) approach [2], enabling the creation of accurate reduced mechanisms via the DRGEP method [3,4]. The Arrhenius parameters (*A*, *n*, *E*) were optimized within their prior uncertainty bounds using the Optima++ code [5–7]. To address the challenge of finding a global optimum, a two-step optimization strategy was implemented to reduce the parameter space: (1) optimization of rate rules involving only primary and secondary carbon centers, followed by (2) optimization of rate rules involving tertiary carbons. Additionally, the thermodynamic data (heat of formation and entropy) of RH, Ṙ, $R\dot{O}_2$, $\dot{Q}OOH$, and $\dot{O}_2QOOH$ were optimized within a carefully evaluated uncertainty range of each species. The two-step optimization reveals a generally good performance for these target fuels compared to the other mechanisms. The trend of the optimized rate rule constants was analysed and found to generally follow a reasonable trend: $1^o < 2^o < 3^o$, consistent with the BDE trend for C–H ($1^o > 2^o > 3^o$). The rate rules were further extended—with some necessary adjustments—to establish mechanisms for straight-chain alkanes from C_8 to C_{14}. The simulated ignition delay times reveal a clear trend: larger alkanes exhibit faster reactivity, with their reactivities beginning to converge starting from C_{11}.

References

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