

## Detailed Modeling of Low-Temperature Alkane Oxidation: High-Pressure Rate Rules for Alkyl + O<sub>2</sub> Reactions.

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Kinetic models are able to accurately predict the ignition behavior of a wide range of hydrocarbon fuels.<sup>1</sup> Such models when used in computational fluid dynamics codes provide powerful design tools to improve fuel efficiency and emissions in modern internal combustion engines and other applications. However, as engine technologies further advance and new fuels emerge, there continues to be a need for more accurate predictions over a wider range of conditions and for more diverse fuel structures and formulations. These mechanism upgrades consist of, among others, improving the accuracy of existing thermodynamic and kinetic parameters, incorporation of missing reaction pathways, and the inclusion of pressure-dependent rate coefficients to account for the wide range of operating conditions found in combustion devices.

A crucial set of reactions in hydrocarbon low-temperature oxidation is that of alkyl radicals (R) with molecular oxygen, which is responsible for chain-branching and the observed negative-temperature dependence (NTC). In this work<sup>2,3</sup> we employ electronic structure calculations combined with transition state theory to calculate high-pressure rate coefficients for several unimolecular channels of the alkyl peroxy radical (RO<sub>2</sub>) and its hydroperoxy alkyl isomers (QOOH). These rate constants then serve as the basis to develop rate rules for a given reaction class. Since these reactions are pressure dependent, it is important to determine under which conditions (sets of pressures and temperatures) these high pressure rate rules are valid or when falloff effects must be accounted. Using Quantum-Rice-Ramsperger-Kassel/modified strong collision analysis we calculate apparent pressure and temperature dependent rate constants for representative reactions of small, medium, and large alkyl radicals with O<sub>2</sub>. A comparison of concentration-time profiles obtained using either the pressure-dependent rate constants or the corresponding high-pressure values reveals that under most conditions relevant to combustion/ignition problems, the high pressure rate rules can be used directly to describe the reactions of R + O<sub>2</sub>. The modeling results using the high-pressure mechanism are further examined to determine whether the reactants and intermediates equilibrate during the low temperature oxidation reactions.

### References

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