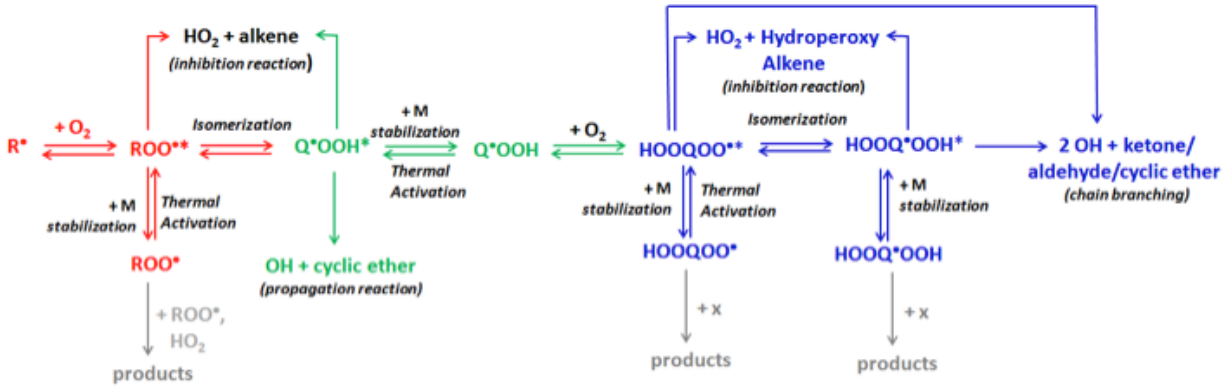
Free Radical Kinetics of Alternative Fuels: From Diesel Ignition to Biocorrosion

Anthony M. Dean

Colorado School of Mines, Golden, CO, USA
amdean@mines.edu

The improved understanding of elementary chemical reactions has markedly improved our ability to describe "real-world" systems. Such approaches require development of accurate, detailed chemical mechanisms, which in turn require careful analysis of different types of elementary reactions. This talk will describe our approach to the characterization of elementary reactions, the construction of detailed mechanisms, and the application to several systems, ranging from hydrocarbon oxidation to biocorrosion. We will focus on the development of rate rules for various types of free radical reactions and discuss how these can then be applied to begin the understand the impact of introducing various types of alternative fuels.

One such system involves the reactions of peroxy and hydroperoxy alkyl radicals[1]. High pressure rate constant estimation rules for the reactions of RO_2 and QOOH are derived from a systematic investigation of sets of reactions within a given reaction class using electronic structure calculations performed at the CBS-QB3 level of theory. Pressure-dependent rate constants can then be calculated and incorporated into mechanisms to predict the impact of various fuel structures on ignition in diesel engines.



Peroxy radical reactions that important for hydrocarbon ignition

[1] Villano, S. M.; Huynh, L. K.; Carstensen, H.-H.; Dean, A. M. J. Phys. Chem. A 2011, **115**, 13425–13442.

THURSDAY