

Shock tube investigations of PAH formation and particle formation

par

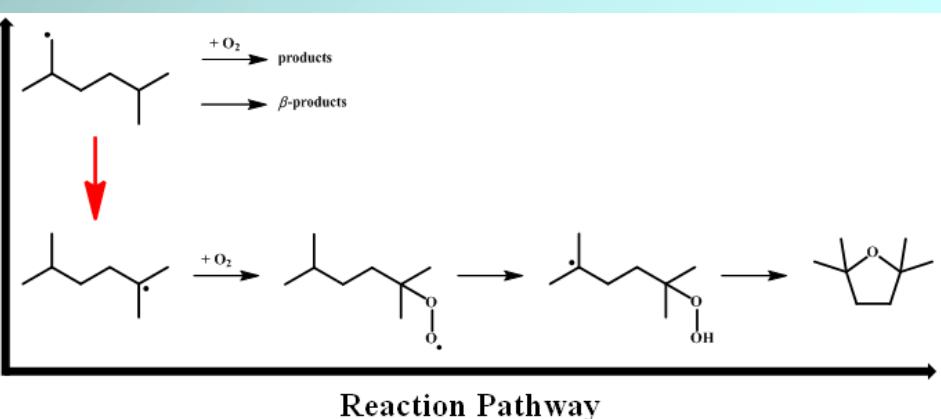
Dr Robert TRANTER

Argonne National Laboratory

**le mercredi 8 octobre 2014 à 11h
salle de réunion ICARE**



Production of particles by combustion is both beneficial and detrimental to society. This duality arises from the fact that a considerable amount of material that is critical to modern life styles e.g. carbon black and fumed silica, is produced by combustion synthesis. However, combustion systems are also responsible for a considerable amount of the pollution that we contend with including soot from power plants and vehicle exhausts. Carbonaceous particulate matter is formed by a complex series of chemical processes starting with reactions between small resonantly stabilized radicals which lead to large polycyclic aromatic hydrocarbons and ultimately what we identify as particulate matter. The formation of particles spans many length and timescales and is extremely challenging to study. The seminar will cover some recent shock tube studies of the early stages of PAH formation. Some upcoming investigations of particle formation with a new, unique shock tube will also be discussed.



**Decomposition pathways and
product formation of alkylperoxy
radicals in low-temperature
oxidation of 2,5-dimethylhexane**

par

Dr Brandon ROTAVERA
Sandia National Laboratories

**le jeudi 9 octobre 2014 à 14h
salle de réunion ICARE**

Alkylperoxy (ROO) decomposition pathways relevant to low-temperature autoignition chemistry were studied for 2,5-dimethylhexane, a symmetrically branched octane isomer, at 550 K and 650 K using Cl-atom initiated oxidation and multiplexed photoionization mass spectrometry (MPIMS), and complementary *ab initio* and Master Equation calculations were conducted on stationary point energies and unimolecular decomposition rates of select radicals. Interpretation of time- and photon-energy-resolved mass spectra led to three specific results important to characterization of the initial steps of 2,5-dimethylhexane oxidation:

- (1) isomer-resolved branching ratios for the stable co-products of HO₂-loss channels indicate an increased yield of 2,5-dimethyl-1-hexene with increasing temperature from 550 K to 650 K, at the expense of 2,5-dimethyl-3-hexene;
- (2) analysis of the cyclic ether species formed as co-products of OH-loss channels from hydroperoxyalkyl radicals (QOOH) indicates substantial formation of 2,2,5,5-tetramethyl-tetrahydrofuran, formed from addition of O₂ to the tertiary alkyl, followed by isomerization of the resulting ROO adduct to tertiary QOOH (tertiary-tertiary ring closure). Quantum-chemical and Master Equation calculations of unimolecular decomposition pathways for the primary alkyl corroborate the experiments by revealing that isomerization to the tertiary alkyl, the precursor to 2,2,5,5-tetramethyl-tetrahydrofuran is the most favorable pathway, and isomerization is favored over O₂-addition at 650 K under the conditions herein. As a result, at higher temperature, primary alkyl radicals also contribute to the formation of 2,2,5,5-tetramethyl-tetrahydrofuran via facile isomerization to tertiary alkyl radicals;
- (3) carbonyl species (acetone, propanal, and methylpropanal) were identified and formed in significant concentration. Formation timescales are consistent from β -scission of QOOH radicals.

The motivation for characterizing the initial steps of low-temperature 2,5-dimethylhexane oxidation is a component-centered approach towards the study of structurally-complex biofuels. In the present work, the influence on chain-propagation trends of close-proximity tertiary alkyl radicals, and the role of primary alkyl radicals were uncovered. The results bring to light the implications of alkyl radical isomerization being favored over R + O₂ reactions, which affects chain-reaction trends and product distribution. More broadly, the results herein extend to similar systems with tertiary carbon-centered radicals, including next-generation biofuels such as bisabolane (1-methyl-4-(6-methylhept-2-yl)cyclohexane) or farnesane (2,6,10-trimethyldodecane).