

DEPARTMENT OF CHEMISTRY, IIT MADRAS

Ph. D. Colloquium

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Kinetic investigations on the low temperature autoignition chemistry of modern oxygenated biofuel compounds

Biofuels are considered as an integral part of a sustainable energy portfolio, where they promise to contribute to energy security and greenhouse gas mitigation.¹ The addition of biofuels to conventional fossil fuels may reduce the emissions of some regulated pollutants originating from transportation,² especially of particulate matter from the combustion of diesel.³ A number of studies have identified promising characteristics of biofuels such as the high research octane number (RON) blending aspect of ethanol for spark ignition engines⁴ or the soot reduction potential of tripropylene-glycol monomethyl ether in compression ignition (CI) engines.⁵ In both cases, oxygen functional groups are responsible for critical fuel properties. Autoignition is driven primarily by gas phase chemical kinetics. Due to its autocatalytic nature of the corresponding chain reactions, the fine details of the chain branching chemistry play a central role. Therefore, it is necessary to study the kinetics for these chain reactions involved in the low temperature regime of the fuel combustion.

The low temperature autoignition chemistry of oxygenated biofuels such as 2-butanone⁶, 2-pentanone and 2-Methyltetrahydrofuran have been studied using computational methods. This study mainly focus on the unimolecular reactions of alkylperoxy (ROO[•]), hydroperoxyalkyl ([•]QOOH) and hydroperoxyalkylperoxy ([•]OOQOOH) radicals. The various reactions include intramolecular H-migration, HO[•]₂-elimination and [•]OH elimination. These chain branching reactions play a significant role in modelling the autoignition of any fuel. The thermochemical properties were calculated using the composite CBS-QB3 method. The kinetic parameters were calculated by Canonical Variational Transition state theory (CVT) and Rice-Ramsperger-Kassel-Marcus (RRKM) methods. The H-migration reactions are favorable energetically whereas the HO[•]₂-elimination reactions dominate the kinetics in some cases owing to their high entropy change when compared to other reactions. The thermochemical and kinetic parameters for the bimolecular reactions of ethylperoxy radicals with ethanol and methylperoxy radicals with dimethoxymethane have been studied using G4 composite method coupled with CVT calculations.

References:

1. Chu, S.; Majumdar, A. *Nature* **2012**, *488*, 294-303.
2. Rakopoulos, D C.; Rakopoulos, C D.; Giakoumis, E G.; Dimaratos, A M.; Kyritsis, D C. *Energy Convers. Manage.* **2010**, *51*, 1989-1997.
3. Kim, H.; Choi, B. *Renewable Energy* **2010**, *35*, 157-163.
4. Leone, T G.; Anderson, J E.; Davies, R S.; Iqbal, A.; Reese, R A.; Shelby, M H.; Studzinski, W M. *Environ. Sci. Technol.* **2015**, *49*, 10778-10789.
5. Dumitrescu, C E.; Mueller, C J.; Kurtz, E. *Appl. Therm. Eng* **2016**, *101*, 639-646.
6. Kuzhanthaivelan, S.; Rajakumar, B. *J. Phys. Chem. A* **2018**, *122*, 6134-6146.

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