

Reactions of the CH Radical with Hydrocarbons Involved in Biofuel Combustion

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Combustion involves many short-lived, excited state species and highly reactive radicals; one such species is the methylidyne radical (CH). The CH radical is extremely reactive due to the presence of one singly occupied and one vacant non-bonding orbital on the carbon. This radical has been detected in combustion environments in myriad studies^{1,2} and plays a critical role in kinetics of NO_x formation and destruction.¹ The primary formation mechanism for CH in non-premixed fuel flames is the reaction between CH₂ and OH yielding CH and H₂O.¹ With regards to reactivity, the CH radical is known to undergo very rapid insertion-elimination reactions with unsaturated hydrocarbons, often close to the diffusion-limited rate.³ Insertion of the CH radical into either π or σ molecular sites followed by H- or H₂-elimination contributes to molecular growth. Alternatively, CH₃-elimination proffers a route to functional group change.

There is currently a growing shift away from petroleum-based fuels towards biofuels derived from biomass and micro-algal oils.⁴ World biodiesel production for transport fuel expanded eleven-fold between 2000 and 2007 from 1 billion to almost 11 billion litres.⁵ Biodiesel comprises highly oxygenated unsaturated species, predominantly esters. It is the presence of these oxygenated functional groups that dramatically reduces particulate and soot emissions.⁶ Currently, our understanding of how functional groups are interchanged by reaction with CH is almost non-existent. Studies of several reactions of this type have been carried out employing the synchrotron radiation from the Advanced Light Source in conjunction with a multiplexed photoionization mass spectrometer. Specifically, CH + acrolein, CH + oxirane and CH + dimethylether have been investigated. Where unsaturated bonds are present the chemistry is very complex and in the case of acrolein, the CH readily inserts into either the C=O or C=C bonds, resulting in a wide variety of reaction products. The mechanisms of such reactions have been elucidated *via* selective deuteration of the reactants, thus a deep understanding of the dynamics has been achieved. These insights may help to predict the chemistry that will occur during combustion between molecules that cannot be experimentally investigated. Moreover, employing the tunable synchrotron radiation has yielded quantitative branching ratios, obtained for the first time for these reactions and which are invaluable for combustion modeling.

References

- (1) Naik, S.V. and Laurendeau, N.M. *Appl. Phys. B-Lasers Opt.* **2004**, 79, 891-905.
- (2) Kohler, M.; Brockhinke, A.; Braun-Unkhoff, M. and Kohse-Hoinghaus, K. *J. Phys. Chem. A* **2010**, 114, 4719-4734.
- (3) Goulay, F.; Trevitt, A.J.; Meloni, G.; Selby, T.M.; Osborn, D.L.; Taatjes, C.A.; Vereecken, L. and Leone, S.R. *J. Am. Chem. Soc.* **2009**, 131, 993-1005.
- (4) Zador, J.; Taatjes, C.A. and Fernandes, R.X. *Prog. Energy Combust. Sci.* **2011**, 37, 371-421.
- (5) Towards sustainable production and use of resources: Assessing Biofuels, Bringezu, S.; Shutz, H.; O'Brien, M.; Kauppi, L.; Howarth, R. and McNeely, J., *United Nations Environment Programme*, 978-92-807-3052-4.
- (6) Graboski, M.S. and McCormick, R.L. *Prog. Energy Combust. Sci.* **1998**, 24, 125-164.