Synchrotron Studies of Combustion Radical Reactions: Reaction of CH_3 Radical with Submicron Hydrocarbon Droplets

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Understanding the fundamental chemical processes that govern combustion phenomena offer the opportunity to optimize combustion for improved engine efficiency and minimization of pollutant formation. The elementary reactions that govern the performance of a combustion system range from direct H-atom abstraction reactions to more complex reactions involving competing addition-elimination mechanisms. In order to understand these elementary processes, less complicated model systems are required that can successfully reproduce the primary characteristics of larger molecules involved in the combustion reactions.

There is currently a growing shift away from gasoline towards less volatile fuels such as tar sands, oil shale and biofuels derived from plant matter.[1] In this context, the role of heterogeneous chemistry in the combustion process is very important since low volatility oxygenated fuels are directly injected into combustion chambers, coating cylinder walls, valves, and injectors with a liquid fuel films.

Hydrocarbon molecules such as squalane, oleic acid, linoleic acid, linolenic acid and squalene are similar in structure to the long chain alkyl (methyl, ethyl, or propyl) esters found in biodiesel fuel and represent model systems to examine the fundamental heterogeneous reactions between hydrocarbon droplets and gas phase radicals and molecules.

An atmospheric pressure flow tube reactor system composed of a droplet generation system, a flow tube reactor, and an analysis system is used in order to investigate for the first time the heterogeneous reaction of model system saturated and unsaturated hydrocarbon aerosol droplets with carbon-based radical species such as CH_3. The CH_3 radicals are created along the length of the flow tube by photolysis of CH_3I. The methyl radical reaction with hydrocarbon droplets may proceed *via* hydrogen atom abstraction or in the presence of C=C double bond *via* addition to the double bond. Preliminary results show no evidence of product formation after the reaction of CH_3 radicals with saturated hydrocarbon squalane droplets. In contrast, the reaction of CH_3 radical with the unsaturated squalene droplets reveal the appearance of new peaks at higher masses, attributed to methylated squalene. In addition, the mass spectrum shows evidence of squalene H loss. Peaks corresponding to $SqI(CH_3)_n$ (n=0–3) were also identified. In this context, detailed investigations were performed in order to understand the influence of I atoms on the reaction mechanism.

References

(1) Zador J.,Taatjes C. A. and Fernandes R. X., Prog. Energy Combust. Sci. **2011**, 37, 371-421.