

High-Temperature Unimolecular Decomposition of Some Esters

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In recent years, there has been a growing interest in the production and utilization of renewable biofuels due to diminishing petroleum reserves, fluctuating energy prices, increasing demand of energy, and environmental concerns. Biofuels can be derived from lignocellulosic biomass, vegetable oils and animal fats. A typical biodiesel fuel is a mixture of saturated and unsaturated methyl and ethyl esters having a carbon chain length of 12 or more. These oxygenated biofuels have benefits on soot-reduction, a low impact on global warming, and they can be readily used in advanced diesel engines and diesel-hybrids. Understanding the combustion behavior of these fuels is crucial to accurately predict emissions such as CO, particulate matter, unburnt hydrocarbons and NO_x. There are only a few studies dedicated to understand the combustion chemistry of these large esters due to their chemical complexity. To understand the kinetic behavior of these practical biofuels, a detailed knowledge of smaller molecular chain esters is important.

This work reports thermal unimolecular dissociation of esters with varying functionalities, such as ethyl levulinate, ethyl propionate and diethyl carbonate. Experiments were performed behind reflected shock waves over temperature range of 920 – 1320 K and pressures of 1.0 – 2.5 bar. We employed laser absorption technique to follow the reaction kinetics by quantitatively measuring ethylene near 10.532 μm using CO₂ gas laser. We determined the rate coefficients for the formation of C₂H₄ from the initial slope method and further ascertained the rate constants by a complete kinetic model. Our data exhibited no noticeable pressure dependence under the current experimental conditions. Furthermore, we carried out high-level quantum chemical and master equation calculations to assess the pressure- and temperature- dependence of the reactions. Our results present evidences that the mechanism of ethylene elimination from these esters occurs via a six-center retro-ene transition state. The systematic effect of the acid group on the kinetics of alkyl esters decomposition will be discussed.