

KINETIC INVESTIGATIONS OF THE INITIAL STEPS OF ETHANOL AND CYCLOHEXANE OXIDATION RELEVANT TO IGNITION CHEMISTRY

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Ethanol and cyclohexane are both important compounds for understanding real motor fuels. Many countries have introduced ethanol as a compulsory blend component for gasoline. Cyclohexane is a simple representative of naphthenes (cyclic alkanes), which are present in significant amounts in gasoline with even higher contents in fuels such as those derived from non-traditional heavy petroleum sources. These components are gaining prominence in the fuel stream at the same time that detailed ignition chemistry is increasingly important due to the emergence of advanced combustion strategies such as HCCI operating at higher pressures and lower temperatures. These engines rely on chemical kinetics to time the ignition, making autoignition chemistry central to their performance.

Alkyl and substituted alkyl radicals are of primary importance for the initiation of low temperature combustion, and the key reaction steps controlling auto ignition are the reactions of alkyl/substituted alkyl radicals with oxygen. However, these reactions present a very complex kinetic behavior involving competing steps of stabilization, dissociation and elimination as a function of temperature and pressure. Detailed characterization of these initial steps is desired at wider temperature and pressure ranges. The present work focuses on critical processes for the reactions of primary radicals of ethanol and cyclohexane (hydroxyethyl and cyclohexyl respectively) with oxygen at intermediate temperatures and elevated pressures supported by comparison with detailed modeling.

Experiments were performed in a heatable flow reactor wherein gas samples are exchanged every laser pulse. Hydroxyethyl and cyclohexyl radicals are generated by pulsed-photolytic Cl initiated oxidation of ethanol and cyclohexane respectively. Time resolved formation of OH was monitored by OH-laser induced fluorescence between 500 K and 800 K at pressures varying from 3 to 50 bar. Comparison with kinetic models that employ rigorous multiwell master equation calculations of rate coefficients for the hydroxyethyl + O₂ and cyclohexyl + O₂ reactions shows that “formally direct” chemical activation pathways are needed to successfully model the experimental data even at elevated pressure. Furthermore, the effect of chemical activation pathways on calculations of higher level observables such as ignition delay times is also discussed.

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