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OH-formation in the α- and β-hydroxyethyl + O_2 reactions

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Ethanol is becoming an increasingly important component in fuel blends for automotive engines, and many countries have introduced ethanol as a compulsory component of gasoline. Understanding the low temperature and high pressure ignition properties of ethanol is crucial, especially for new engine technologies relying on chemical kinetics to time the ignition. The most important primary radicals produced during the combustion of ethanol are the α- and β-hydroxyethyl radicals (CH_3CHOH and CH_2CH_2OH, respectively). Their reactions with O_2 create highly reactive OH radicals amongst other species. Despite the importance of this process, the available experimental and theoretical work is sparse, especially at elevated pressures.

We have explored the potential energy surfaces corresponding to reactions $CH_2CH_2O + O_2$ and $CH_3CHOH + O_2$. Geometries were optimized using the 6-311++G(d,p) Gaussian basis set and density functional theory with the B3LYP functional. Accurate energy barriers were obtained by the QCISD(T) method. When the multireference character was significant multireference methods were also applied. Thermal rate coefficients and product branching ratios were calculated by master equation calculations.

Experimentally the Cl-initiated oxidation of ethanol was studied in a heatable high pressure (up to 50 bar) flow cell between 500 and 800 K. Cl atoms were generated in situ by oxalyl chloride photolysis. C_2H_5O radicals were rapidly produced by the reaction of Cl atoms and ethanol. Subsequent reactions were probed by means of a time-delayed tunable dye laser detecting the laser induced fluorescence signal of OH.

The experiments were modeled with a detailed chemical reaction mechanism assuming homogeneous and isothermal conditions. The model was used to select the optimal conditions for extracting information on the elementary reactions as well as to simulate the obtained OH–time curves. Effect of the newly-derived rate coefficients on calculated ignition delay times was also investigated.

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