

## Low-temperature oxidation chemistry of 1-butanol: A combined photoionization mass spectrometry and quantum-chemical/master-equation study

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The efficient use of novel biofuels in internal combustion engines, particularly those relying on compression ignition, depends critically on an understanding of their fundamental autoignition chemistry. 1-Butanol is a particularly promising candidate as a next-generation biofuel. Whereas its high-temperature ( $T > 1000$  K) oxidation has been the subject of substantial experimental and modeling effort, the oxidation chemistry of 1-butanol in particular, and medium-chain alcohols in general, remains underexplored in the low-temperature region ( $T < 800$  K), where fuel-chemistry effects on the autoignition behavior are important.

We present a combined experimental and theoretical approach to gain detailed insight into the fundamental low-temperature oxidation chemistry of 1-butanol. On the experimental side, we employ the technique of pulsed laser-photolytic chlorine initiation in a slow-flow reactor between 300 and 700 K at low pressure ( $\sim 4$  Torr). Four different ( $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -) 1-hydroxybutyl radicals are prepared via H-abstraction by Cl atoms at the different CH sites from 1-butanol. The chemistry of these 1-hydroxybutyl radicals in an excess of  $O_2$  is interrogated using multiplexed time-resolved synchrotron photoionization mass spectrometry. By employing synchrotron radiation as the ionizing source, branching ratios between the observed primary products are obtained on an isomer-resolved level. Relevant stationary points on the potential energy surfaces for the four 1-hydroxybutyl radicals reacting with  $O_2$  have been computed using the CBS-QB3 method, and time-dependent master-equation calculations have been performed based on these surfaces. From the master-equation calculations, product branching ratios for the four 1-hydroxybutyl radical isomer +  $O_2$  reactions are obtained, which are compared to the experimentally derived values.

Our experimental and theoretical results show that the reactions of all four 1-hydroxybutyl radicals with  $O_2$  are dominated by alcohol-specific product channels. We will highlight this observation and the differences from the oxidation chemistry of alkanes. Furthermore, we will discuss the competition between channels associated with chain-propagating formation of OH and essentially chain-terminating channels associated with  $HO_2$  formation.

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