ELUCIDATING N-PROPANOL AND ISOPROPANOL DISSOCIATION PATHWAYS USING A TABLE-TOP BRIGHT, COHERENT VUV LIGHT SOURCE AND ELECTRONIC STRUCTURE THEORY

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Alcohols are common additive in fuels due to their high-octane content that allows higher compression ratio to be achieved. While other alcohols such as ethanol and the butanols have been extensively studied, n-propanol and isopropanol have received far less attention in the literature. A possible reason for this is that resolving the chemistry of the propanols and their radical pyrolytic products requires overcoming significant experimental and theoretical challenges, especially at the high temperatures involved for combustion. In order to help resolve the chemistry of these alcohols for combustion conditions, we studied the pyrolysis of both n-propanol and isopropanol under varying pyrolytic conditions using experimental and theoretical approaches in tandem. The decomposition pathways of n-propanol and isopropanol were experimentally probed using a silicon carbide microreactor, which is resistively heated to temperatures ranging over 300 - 1500 K. Speciation products were detected using a table-top line-tunable VUV light source in combination with a Photoionization Mass Spectrometer, enabling selective ionization followed by detection of ionization masses. Owing to the availability of multiple spectra lines, this tool allows us to selectively ionize acetaldehyde and vinyl alcohol at their corresponding ionization energies to separate the contribution of the two species with equal mass-to-charge ratio in isopropanol. To further confirm experiment, we employed different levels of electronic structure theory—Density Functional and Coupled Cluster theory—in combination of various basis sets to accurately compute the potential energy surfaces and thermal chemical properties of the pyrolytic products and the associated transition states. The potential energy surface calculations, along with the associated predicted ro-vibrational frequencies, rotors, etc., were employed to calculate rate constants and branching ratios for reaction to confirm the experimentally observed mechanisms for n-propanol and isopropanol.