Determining how to efficiently convert cellulose into smaller molecules is vital for harnessing this abundant biopolymer as a renewable source of chemicals and fuels. Understanding the molecular-level chemistry can aid the rational design of improved processes. This knowledge had remained elusive, despite decades of research into the chemical mechanisms governing its conversion. To solve these mysteries, we have created multiscale models of thermochemical and enzymatic conversions of cellulose that allow us to investigate complex reaction networks, determine elementary steps, calculate kinetic parameters, and compare model results with experimental data. Our thermochemical investigations focused on revealing key mechanisms in the cellulose pyrolysis reaction network. The results of these studies have been used in the first mechanistic model of cellulose pyrolysis, providing a valuable tool for process design and optimization. The enzymatic investigation revealed the previously elusive detailed mechanism of an industrially important cellulase, revealing targets for protein engineering. Together, this work highlights how advanced computational tools can uncover notoriously complex carbohydrate chemistry that we can use to advance renewable chemicals and fuels.