

# Lignin Model Pyrolysis: A Computational Approach

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A great amount of insight can be obtained by the computational study of the thermal decomposition of  $\beta$ -O-4 model compounds, representing the most common linkage in lignin. While experimental work determines overall product distributions and total rates of reaction, kinetic parameters of individual reactions and details of substituent effects on equilibrium and transition state structures are difficult to obtain experimentally. Computational methods allow the location of transition states and the calculation of activation barriers and entropical pre-factors for targeted chemical reactions. We launched a systematic computational study of the kinetic details of the pyrolysis of phenethyl phenyl ether (PPE) and various oxygen substituted derivatives, which are model compounds for the  $\beta$ -O-4 linkage in lignin. Using density functional methods, we investigate relevant reaction steps including homolytic cleavage, competitive hydrogen abstraction, radical rearrangement, and  $\beta$ -scission reactions. Electronic structure analysis of reactants, intermediates, products, and transition states is used to explain the effect of naturally occurring substituents, which can perturb multiple steps of the pyrolysis mechanism. We calculate relative rate constants using transition state theory, apply analytic kinetic models and kinetic Monte Carlo techniques to obtain experimentally observed product selectivities and monitor reaction progress as a function of time.

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