A Fundamental Study of the Fragmentation of Small Molecules related to Lignin via Collision-Activated Dissociation (CAD)

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In the search for a replacement for fossil fuels and other valuable chemicals which are currently obtained only from crude oil, lignocellulosic biomass and its catalytic transformation and degradation products have become of particular interest as a renewable alternative. In order to study the degradation and catalytic transformation products of lignin, a large component of lignocellulosic biomass, negative-ion mode electrospray ionization, (-)ESI, tandem mass spectrometry has been utilized as it allows for the structural elucidation of the complex product mixtures created. However, the fundamental mechanisms by which many of these negative ions fragment upon collision-activated dissociation (CAD) are very poorly understood. In order to study the fragmentation pathways of lignin degradation products several model compounds relevant to these products were selected. These compounds were introduced into a linear quadrupole ion trap (LQIT) mass spectrometer via (-)ESI with a sodium hydroxide dopant and subjected to CAD. The model compounds studied exhibited unique fragmentation patterns that allow for their identification in complex mixtures. Common fragmentation products (and the functionality present) formed upon CAD include: methyl radical (methoxy), ethyl radical (ethoxy), carbon monoxide (phenol), and carbon dioxide (carboxylic acid). In order to better understand the mechanisms by which these compounds fragment via CAD several interesting fragmentation pathways were studied in more depth using additional model compounds and isotopic labeling. One of these observed pathways that proved to be of particular interest was the formation of neutral methanol upon fragmentation of several of the selected model compounds, which contained both carboxylic acid and methoxy functionalities. This particular fragmentation pathway was examined using isotopic labeling as well as through the study of model compounds with differing methoxy and carboxylic acid functionalization. Based upon these studies 4-hydroxy-3,5-dimethoxybenzoic acid (one of the studied compounds) is believed to form the 5-methoxy-1,3-didehydrophenoxide anion following the loss of carbon dioxide and methanol. The fragmentation pathways and proposed fragmentation mechanisms will be presented for this compound as well as many others studied. Future work will focus on the integration of these fragmentation pathways into a searchable library for the identification of compounds in unknown complex mixtures.