

Isomer-Dependent Selectivities in the Pyrolysis of Anisaldehyde

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Identifying the reactive intermediates, such as radicals, carbenes and ketenes, can provide direct evidence to elucidate the underlying reaction mechanisms. As a multiplexed, sensitive, selective, and universal detection tool photoelectron photoion coincidence spectroscopy (PEPICO) has proven to be very powerful in identifying stable species and fleeting reaction intermediates in the gas phase.[1-2] The thermal decomposition of the three anisaldehyde isomers was studied utilizing PEPICO. The pyrolysis intermediates and products were identified isomer-selectively by their photoion mass-selected threshold photoelectron spectrum (ms-TPES) in comparison with reference spectra. C–O bond fission in the methoxy group generates methyl and aldehyde phenoxy radicals in the initial fragmentation step for all anisaldehyde isomers. For *para*- and *meta*- isomers, these radicals can produce either 1-formyl-2,4-cyclopentadiene-1-yl radical or phenoxy radicals by low-energy removal of CO from the phenoxy radical (Ph–O) or aldehyde (–CHO) groups, respectively. The 1-formyl-2,4-cyclopentadiene-1-yl radical channel then generates cyclopentadienyl radicals by decarbonylation or fulvenone (c-C₅H₄=C=O), a reactive ketene species in lignin valorization, by hydrogen atom loss. In contrast, the phenoxy radicals only generate cyclopentadienyl radicals by decarbonylation. The *ortho*-anisaldehyde isomer shows high selectivity towards the phenoxy radical channel due to sterically enhanced fast H transfer from the aldehyde to phenoxy groups, which significantly lowers the decarbonylation energy barrier from the aldehyde group and fully suppresses the fulvenone channel. This contrasts with pyrolysis reactions of other bifunctionalized benzene compounds, such as benzenediol and salicylaldehyde, in which only the *ortho* isomer yields fulvenone. In general, cyclopentadienyl formation is unwanted in catalytic processes, as it is a coke precursor, responsible for catalyst deactivation.

[1] Steglich, M.; Custodis, V. B.; Trevitt, A. J.; daSilva, G.; Bodi, A.; Hemberger, P., Photoelectron spectrum and energetics of the meta-xyllylene diradical. *J. Am. Chem. Soc.* **2017**, *139* (41), 14348-14351.

[2] Hemberger, P.; Bodi, A.; Bierkandt, T.; Köhler, M.; Kaczmarek, D.; Kasper, T., Photoelectron Photoion Coincidence Spectroscopy Provides Mechanistic Insights in Fuel Synthesis and Conversion. *Energy Fuels* **2021**, *35* (20), 16265-16302.