

4F07: POLYCYCLIC AROMATIC HYDROCARBONS FROM THE CO-PYROLYSIS OF CATECHOL AND 1,3-BUTADIENE.

Shiju Thomas, Mary J. Wornat, Louisiana State University, USA

Comment by Katharina Kohse-Hoeinghaus, Bielefeld University, Germany

kkh@pc1.uni-bielefeld.de

Do you know anything about the history of the oxygen function in your system? Would the effect be the same if you had the OH function on the butadiene molecule (i.e. an alcohol)?

Reply by Mary Judith Wornat

mjwornat@lsu.edu

Yes, we can account for the history of the oxygen function in our system. Since the carrier gas in our pyrolysis experiments is pure nitrogen and since there are no oxygen-containing species in the products of our 1,3-butadiene-only pyrolysis experiments, we know that the only source of oxygen in our reactor system is the oxygen that is introduced in the feed catechol in the catechol-only pyrolysis and catechol/1,3-butadiene co-pyrolysis experiments. (This oxygen is present as the hydroxyl groups in the catechol, *i.e.*, *ortho*-dihydroxybenzene, structure.) In all of our experiments, our measurements of the amounts of the fuel(s) fed to the reactor, the amounts of the unreacted fuel(s) exiting the reactor, and the amounts of the speciated products exiting the reactor permit us to close both C-atom and O-atom balances on the reactor. Even though the catechol-only pyrolysis and catechol/1,3-butadiene co-pyrolysis experiments produce tiny amounts of oxygen-containing aromatics—as evidenced by the brown structures associated with minor peaks in Figure 1 in the paper—virtually all of the oxygen fed to the reactor as OH in catechol can be accounted for by three major constituents in the reactor exit stream: unreacted catechol and the two major products CO and phenol. Our companion paper ([26] in the paper) demonstrates that for any given temperature, the percentages of catechol's oxygen that end up as oxygen in unreacted catechol, CO, and phenol are the same for catechol-only pyrolysis as they are for catechol/1,3-butadiene co-pyrolysis, so the apportionment of the oxygen among the unreacted catechol and the products CO and phenol is unaffected by whether or not 1,3-butadiene is present. The apportionment is very dependent on temperature, however. As the catechol conversion plot of Figure 3 in the paper and our yield/temperature plots ([14] in the paper) for CO and phenol show: Almost all of the oxygen remains tied up in the catechol structure at temperatures ≤ 750 °C. Between 750 and 850 °C, catechol rapidly converts, and the oxygen formerly bound in catechol appears as oxygen in phenol (whose yield peaks at 850 °C) and, more principally, as oxygen in CO. As temperature is raised above 850 °C, catechol conversion quickly proceeds to completion and phenol yields sharply drop so that at temperatures above 900 °C, all of the oxygen fed to the reactor (as catechol) exits the reactor as CO. Therefore the general progression of the oxygen is from catechol-associated hydroxyl at lower temperatures to CO at higher temperatures, but with some involvement of phenol at intermediate temperatures.

The second question concerns whether our findings would be different if we were to use a hydroxyl-substituted 1,3-butadiene instead of 1,3-butadiene itself. To answer this question, we need to consider the structure and the bond dissociation energies (BDEs) of the proposed hydroxyl-substituted 1,3-butadiene molecule, in comparison to those of 1,3-butadiene. In the case of 1,3-butadiene, the easiest-to-break bond, as stated in the paper, is the C-H bond of an internal carbon, having a BDE of 87.5 kcal/mole [34]. We would not expect that value to be significantly altered if one of the carbons of the 1,3-butadiene molecule was bonded to an OH group instead of an H. However, if the OH group was present, we would no longer expect that C-H bond to be the bond with the lowest BDE. The theoretical studies of Ribeiro-Claro [1] indicate that the BDE of the O-H bond in a hydroxyl-substituted 1,3-butadiene would be very close to that of the O-H bond in vinyl alcohol, which is 85 kcal/mole ([33] in the paper). Since 85 kcal/mole is lower than 87.5 kcal/mole, we would expect the conversion-versus-temperature curve for the hydroxyl-substituted 1,3-butadiene to be a little to the left of the 1,3-butadiene conversion curve of Figure 3. Since scission of the O-H bond would also lead to oxygen-containing radicals—which, in the case of catechol, have been shown to greatly accelerate fuel conversion and pyrolysis reactions—we would also expect: (1) the conversion/temperature curve of the hydroxyl-substituted 1,3-butadiene to be more steep than the one for 1,3-butadiene in Figure 3, and (2) for any given temperature, the yields of 1- and 2-ring aromatic hydrocarbons and PAH to be higher for the hydroxyl-substituted 1,3-butadiene than for 1,3-butadiene. However, because C-O bonds in alcohols are strong (having BDEs generally > 93 kcal/mole), we would also expect high CO production from a hydroxyl-substituted 1,3-butadiene, especially at the highest temperatures of our experiments. This “tying up” of one-fourth of the molecule’s C atoms into CO greatly reduces the hydroxyl-substituted 1,3-butadiene’s capacity to produce the small hydrocarbon growth species that 1,3-butadiene so abundantly produces—especially the C₄ species, which our paper has shown to be the most effective PAH growth species in the catechol/1,3-butadiene co-pyrolysis environment. Therefore we would expect PAH yields from the co-pyrolysis of catechol and hydroxyl-substituted 1,3-butadiene to be lower than those from co-pyrolysis of catechol and 1,3-butadiene.

Reference:

[1] P.J. Ribeiro-Claro, *Journal of Molecular Structure* 283 (1993) 141–149.