

1D12: A CHEMICAL KINETIC STUDY OF *n*-BUTANOL OXIDATION AT ELEVATED PRESSURE IN A JET STIRRED REACTOR.

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Comment by Ben Akih-Kumgeh, McGill University, Canada

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In the first part of your talk, you said pyrolysis studies suggest that *n*-butanol consumption occurs by the cleavage of the c-c bond close to the alcohol group but in your model you focus on H-abstraction. Is that a contradiction or different pathways dominate depending on whether *n*-butanol is pyrolyzed or oxidized? It does seem that H-abstraction would indeed be a dominant fuel consumption pathway. You have illustrated abstraction by OH radical, does the extended mechanism also account for abstraction by H, HO₂, etc?

Reply by Murray Thomson

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As mentioned in our literature review, C-C cleavage was suggested to be dominant in pyrolysis studies of *n*-butanol and co-flow flames of methane doped with *n*-butanol. The current JSR experiments are experimentally much different than the previous studies, as the fuel concentration is premixed with oxidizer and the fuel concentration is very low. Under these conditions, H atom abstraction dominates over C-C fission. To answer the second question; our mechanism includes abstraction of H atoms by a number of radical species, which are mentioned in the manuscript (e.g. OH, H, HO₂, HCO, O, etc.).

Comment by Grainne Black, NUI, Galway, Ireland

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In your mechanism, the two main sites for hydrogen abstraction are at the gamma and the OH positions. The prominence of the OH route would seem to be unlikely, given the stability of the resulting radical relative to the alpha radical, for example. Computational work that we have carried out for H-abstraction from *n*-butanol by hydroxyl and hydroperoxyl finds that the OH is in fact the least preferred route.

Reply by Murray Thomson

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As shown in Figure 4 (in the paper) of the published manuscript ($\pi = 1$, $T = 1000$ K), the primary sites for hydrogen abstraction are from the alpha, beta, and gamma carbons, with each pathway contributing to approximately 22% of butanol consumption. The fourth leading pathway is via abstraction of hydrogen from the OH group, which accounts for approximately 20% of butanol consumption. At higher temperatures (e.g. $T = 1220$ K), the proposed model predicts that hydrogen abstraction from the OH site is the least

prominent (12%), while abstraction of hydrogen from the alpha (29%) and gamma (31%) sites are predominant.