Ring-Closure Scheme for the Formation of Large Polycyclic Aromatic Hydrocarbons from the Supercritical Pyrolysis of Methylcyclohexane

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In the Nineteenth ISPAC, we reported our initial results on the supercritical pyrolysis of methylcyclohexane, a candidate "endothermic" fuel for future high-speed aircraft. Having used high pressure liquid chromatography (HPLC) with diode-array ultraviolet-visible (UV) absorbance detection, we reported the identification of 34 individual PAH in the products of methylcyclohexane pyrolysis at 570 °C, 140 sec, and pressures of 20-100 atm. Among these 34 PAH were several methylated PAH as well as the following 6- to 10-ring benzologues of perylene: benzo[*ghi*]perylene, coronene, benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene, benzo[*a*]coronene, naphtho[8,1,2-*abc*]coronene, and ovalene.

Since that initial report, we have used HPLC/UV to identify 4 additional PAH (7- to 8-ring perylene benzologues) in the supercritical methylcyclohexane products: dibenzo[*e*,*ghi*]perylene, dibenzo[*cd,lm*]perylene, tribenzo[*a,cd,lm*]perylene, and phenanthro[5,4,3,2-*efghi*]perylene. Gas chromatographic analyses have also revealed high amounts of C_1 to C_4 light hydrocarbons among the methylcyclohexane products. In order to account for the presence of all of the observed perylene benzologues in our methylcyclohexane products (and the absence of certain other large PAH), we propose a modification of Sullivan *et al.*'s scheme that makes use of Clar's Naphthalene Zigzag Series. Sullivan *et al*.'s scheme is based on two types of ring closures: Peri-Ring Closure and Ortho-Ring Closure. The steps of the modified scheme are the following: formation of an initial PAH molecule, methylation of that molecule at an outside carbon, and formation of an additional ring either by addition of C_2 at a 4-carbon bay (Peri-Ring Closure) or by addition of C_3 at the 3-carbon bay created by the methylation (Modified Ortho-Ring Closure).

Moreover, it is important to note that due to the similar products obtained during the supercritical pyrolysis of other fuels such as toluene, *n*-octane and jet fuel, we can infer that the same scheme may be applicable in the formation of large PAH from other fuels in similar contexts.