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# SUPERCritical FUEL PYROLYSIS

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## SUMMARY/OVERVIEW:

The fuels used in the next generation of hypersonic aircraft will have to operate under very high pressures (beyond the critical pressures of most hydrocarbons) and will have to sustain very high heat loads in order to meet aircraft cooling requirements [1-3]. Critical to the development of the fuel systems in these aircraft is an understanding of the fuel pyrolysis reaction mechanisms under the conditions that the fuels will be operating. Of particular interest are the reactions leading to polycyclic aromatic hydrocarbons (PAH), which can serve as precursors to fuel-line deposits [3,4], a problem of critical importance to avoid, for safe aircraft operation. In order to better elucidate the mechanisms and kinetics of the reactions of fuel pyrolysis and PAH formation under supercritical conditions, pyrolysis experiments are being conducted, under the present research program, with model fuels at temperatures of 300-600 °C, pressures of 20-100 atm, and residence times of 30-1000 sec. The model fuels include the jet fuel components toluene, 1-methylnaphthalene, and mixtures of toluene and *n*-heptane—as well as the "endothermic" fuel methylcyclohexane. The supercritical pyrolysis experiments are conducted in an isothermal silica-lined stainless-steel coil reactor specially designed [4,5] for such experiments, and PAH reaction products are analyzed by high-pressure liquid chromatography with diode-array ultraviolet-visible absorbance and mass spectrometric detection (HPLC/UV/MS), an isomer-specific technique ideally suited for the analysis of PAH [6]. It is anticipated that the results from this research will provide information of critical importance to the design and development of fuel systems for high-speed aircraft.

## TECHNICAL DISCUSSION

Acquisition of the new HPLC/UV/MS instrument this past year, through DURIP funds, has facilitated the identification of many new PAH products from our supercritical pyrolysis experiments with toluene, methylcyclohexane, and 1-methylnaphthalene. In the cases of toluene and methylcyclohexane, several new eight-ring PAH products have been recently identified [6], and the reaction schemes responsible for their formation are the subject of a paper in preparation. In the case of 1-methylnaphthalene, 17 additional PAH products have been recently identified, and a paper describing the reactions responsible for the formation of PAH from the supercritical pyrolysis of 1-methylnaphthalene has just been accepted [7]. This report thus focuses on the results of 1-methylnaphthalene (critical temperature, 499 °C; critical pressure, 36 atm), a two-ring aromatic component of jet fuels [8].

Figure 1 presents the HPLC chromatogram of the aromatic products of 1-methylnaphthalene pyrolysis at 585 °C, 110 atm, and 140 sec. In addition to that of 1-methylnaphthalene itself (unreacted fuel), Figure 1 displays the structures of the 37 individual two- to seven-ring PAH

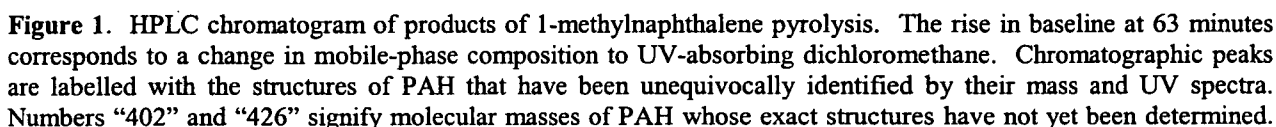
products that have been identified by HPLC/UV/MS, as well as the molecular masses of the eight- and nine-ring PAH products whose exact identities are not yet known. Fifteen of the PAH of  $\geq 5$  rings in Figure 1 have never before been identified as products of 1-methylnaphthalene pyrolysis or combustion. The structures of the earliest-eluting products of Figure 1—naphthalene, 2-methylnaphthalene, the dimethylnaphthalenes, and the bi-naphthyls—reveal that within the supercritical 1-methylnaphthalene pyrolysis environment, it is possible to break the methyl C-H bond (bond dissociation energy, BDE, 85.1 kcal/mole [9]), the methyl-aryl C-C bond (BDE, 103.8 kcal/mole [9]), and the aryl C-H bond (BDE, 112.2 kcal/mole [9]). Since we find no single-ring aromatics among our products and since the gaseous hydrocarbon products we observe (90 % methane, 5% ethane, and the balance  $C_3$  to  $C_4$  alkanes, with only a trace of ethylene—and no acetylene) can all come from methyl and hydrogen—we see that the only kind of bond that appears not to be broken in this reaction environment is the aromatic C-C bond (BDE, 122.3 kcal/mole [10]). We could thus expect the larger aromatic products in this reaction environment to be formed by different combinations of methyl, hydrogen, naphthalene, and 1-methylnaphthalene radicals and molecules—forming bonds in ways that preserve the 2-ring aromatic units of the reacting naphthalene and methylnaphthalene entities.

That this hypothesis is indeed the case is borne out by the structures of the five- to seven-ring PAH products of supercritical 1-methylnaphthalene pyrolysis, shown in Figure 1 and listed in the left-most column of Table 1. All of the product PAH structures in the left column of Table 1 reveal the intactness of the two two-ring naphthalene or 1-methylnaphthalene units required in their construction. This finding, along with consideration of BDEs and relative abundances of reactant species, has been used to construct [7] radical reaction pathways responsible for the five- to seven-ring product PAH—reaction pathways that involve species plentiful in the supercritical 1-methylnaphthalene pyrolysis environment: 1-naphthylmethyl radical, methyl radical, 1-methylnaphthalene, naphthalene, and (to a lesser extent) 2-methylnaphthalene. Examples of such pathways are given in the middle column of Table 1.

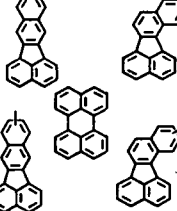
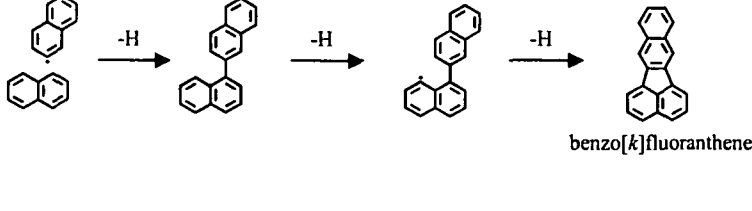
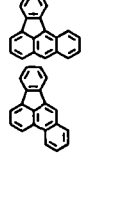
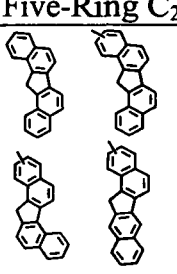
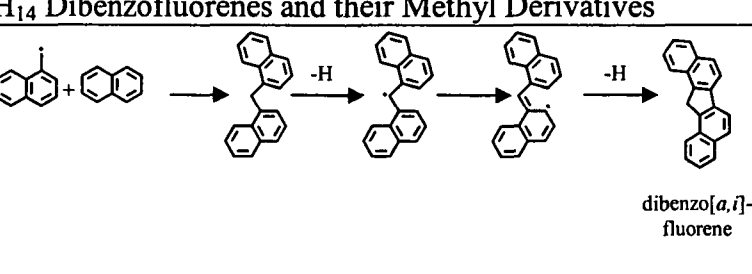
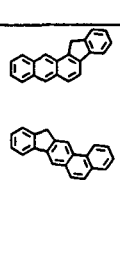
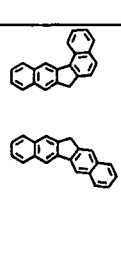
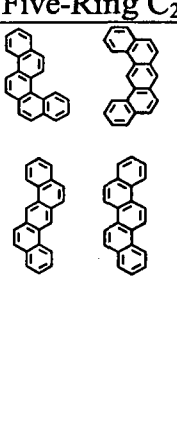
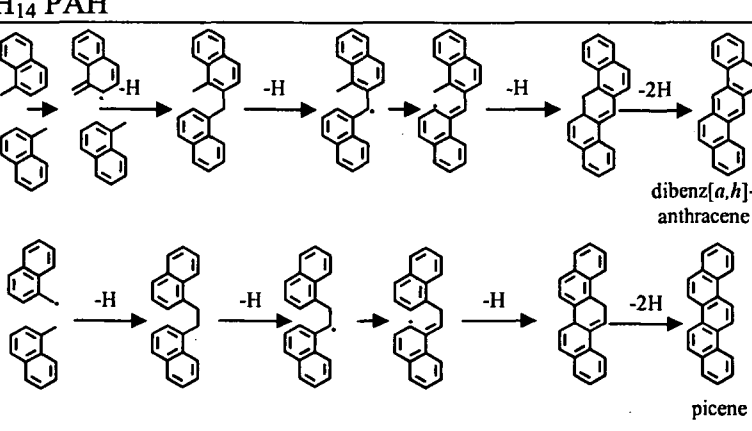
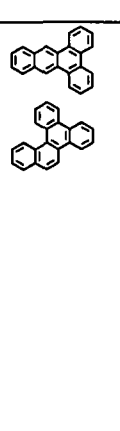
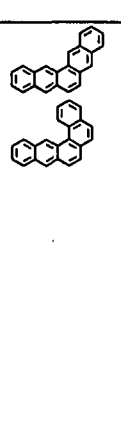
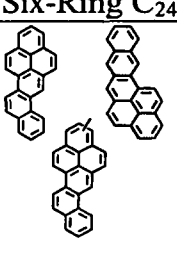
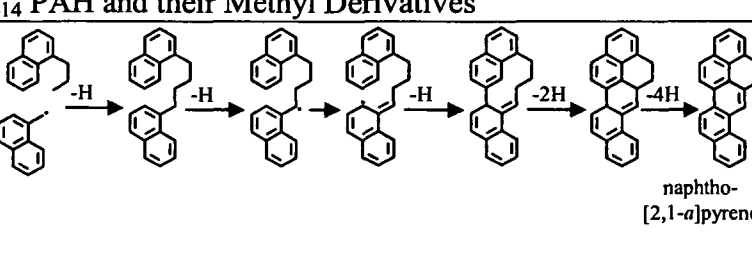
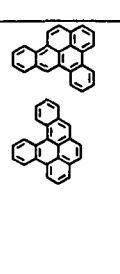
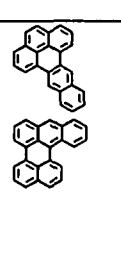
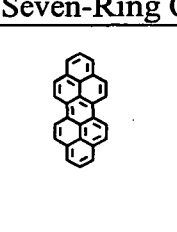
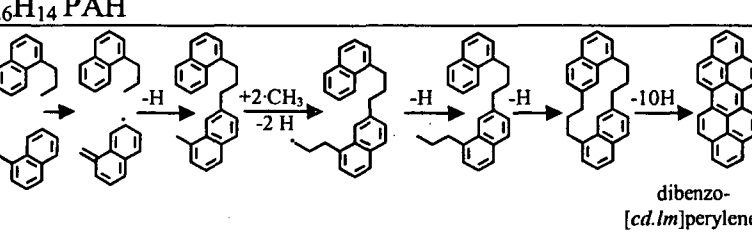
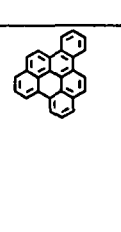
Because the HPLC/UV/MS analysis technique affords such isomer specificity, we can say with certainty that the 5- to 7-ring PAH listed in the left column of Table 1 definitely are products of 1-methylnaphthalene pyrolysis, and all other isomers of those particular PAH classes (some of which are listed in the two right-most columns of Table 1) are not. This ability to distinguish which particular PAH isomers are products and which are not has revealed that the 5- to 7-ring PAH products that form are those whose structures preserve the intactness of the parent two 2-ring naphthalene units, whose reaction pathways involve the species most abundant in the reaction environment, and whose formation involves bond breakage at the sites of lowest BDE.

The remaining PAH products of Figure 1 are the six 8-ring  $C_{32}H_{18}$ , whose peaks are labelled “402” in Figure 1, and the 9-ring  $C_{34}H_{18}$ , whose peak is labelled “426.” As there are hundreds of possible structures in these latter two families, the fact that certain peaks of these molecular formulas exhibit some prominence suggests that a high degree of product selectivity is in effect for these 8- and 9-ring products, just as it has been demonstrated in the 5- to 7-ring PAH products of supercritical 1-methylnaphthalene pyrolysis. The  $C_{32}H_{18}$  PAH can be constructed from 1-naphthylmethyl radical reacting with naphthalene and 1-methylnaphthalene; the  $C_{34}H_{18}$  PAH can be constructed from 1-naphthylmethyl radical, methyl, and two 1-methylnaphthalenes. Even though the exact identities of these 8- and 9-ring products have not yet been determined, their presence, along with their suggested selectivity, serve as evidence that the types of reaction mechanisms outlined in Table 1—for the combination of two naphthalene and methylnaphthalene entities in the formation of 5- to 7-ring PAH—are likely to apply to the combination of three and more such entities in the formation of larger-ring-number PAH and eventually carbonaceous solids.

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7. Somers, M. L., McClaine, J. W., and Wornat, M. J., "The Formation of Polycyclic Aromatic Hydrocarbons from the Supercritical Pyrolysis of 1-Methylnaphthalene," accepted to *Proceedings of the Combustion Institute* 31 (2006).
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10. R.T. Sanderson, *Chemical Bonds in Organic Compounds*, Sea and Sand, Scottsdale, AZ, 1976, Chapter.



**Table 1. Five- to Seven-Ring PAH Products of Supercritical 1-Methylnaphthalene Pyrolysis**

| Observed Products                                                                       | Reaction Pathways Responsible for Formation of Observed Products                                                                | Examples of Isomers not Observed*                                                     |                                                                                       |
|-----------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| Five-Ring C <sub>20</sub> H <sub>12</sub> PAH and their Methyl Derivatives              |                                                                                                                                 | A                                                                                     | B                                                                                     |
|        |  <p>benzo[k]fluoranthene</p>                  |    |    |
| Five-Ring C <sub>21</sub> H <sub>14</sub> Dibenzofluorenes and their Methyl Derivatives |                                                                                                                                 |                                                                                       |                                                                                       |
|        |  <p>dibenzo[a,i]-fluorene</p>                 |    |    |
| Five-Ring C <sub>22</sub> H <sub>14</sub> PAH                                           |                                                                                                                                 |                                                                                       |                                                                                       |
|       |  <p>dibenz[a,h]-anthracene</p> <p>picene</p> |   |   |
| Six-Ring C <sub>24</sub> H <sub>14</sub> PAH and their Methyl Derivatives               |                                                                                                                                 |                                                                                       |                                                                                       |
|      |  <p>naphtho[2,1-a]pyrene</p>                |  |  |
| Seven-Ring C <sub>26</sub> H <sub>14</sub> PAH                                          |                                                                                                                                 |                                                                                       |                                                                                       |
|      |  <p>dibenzo[cd,lm]perylene</p>              |                                                                                       |  |

\*Examples of PAH isomers not observed in 1-methylnaphthalene products: Those in Column A do not preserve the intactness of two 2-ring naphthalene units; those in Column B require involvement of one or more 2-methylnaphthalene entities in their construction.