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Thermolysis of Benzo[*c*]phenanthrene-5,6-dicarboxylic Anhydride and 6*H*-Benzo[*cd*]pyren-6-one. Entries to the Combustion Effluents Benzo[*ghi*]fluoranthene and Cyclopenta[*cd*]pyrene.

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***Abstract*:** Thermolysis of the oxy-PAH benzo[*c*]phenanthrene-5,6-dicarboxylic anhydride (**3**) and 6*H*-benzo[*cd*]pyren-6-one (**4**) gave the abundant $C_{18}H_{10}$ CP-PAH combustion effluents benzo[*ghi*]fluoranthene (**1**) and cyclopenta[*cd*]pyrene (**2**). © 1997 Elsevier Science Ltd.

It was recently observed that concomitant with the abundant formation of oxygen-containing polycyclic aromatic hydrocarbons (oxy-PAH) in samples from fullerene (C_{60} and C_{70}) forming benzene/oxygen flames, externally cyclopentafused-PAH (CP-PAH), *viz.* the primary products of fullerene deficient ethene/oxygen flames, are absent.[1] This suggests that in benzene/oxygen flames CP-PAH are oxidized into oxy-PAH, and that the latter are also involved in growth reactions leading ultimately to C_{60} and C_{70}. In this context, elucidation of the *intrinsic* thermal properties of relevant oxy-PAH is important to gain insight in the factors controlling the build up of larger PAH structures under flame conditions. It has been shown that simple aromatic dicarboxylic anhydrides, aromatic ketones and quinones are converted *via* benzyne-, ethynyl- and radical-like intermediates into CP-PAH *via* CO_2 and CO,[2] and CO elimination,[3] respectively, under Flash Vacuum Thermolysis (FVT) conditions, *i.e.* at combustion temperatures. More recently the formation of the $C_{18}H_{10}$ CP-PAH combustion effluent cyclopent[*hi*]acephenanthrylene upon FVT of various triphenylenedicarboxylic acid derivatives has been reported.[4]

Herein we report that the oxy-PAH benzo[*c*]phenanthrene-5,6-dicarboxylic anhydride (**3**, $C_{20}H_{10}O_3$)[5] and the carbon black as well as flame constituent 6*H*-benzo[*cd*]pyren-6-one (**4**, $C_{19}H_{10}O$)[6] are precursors providing entries to the $C_{18}H_{10}$ PAH potential energy surface under high temperature conditions. It is shown that the ubiquitous $C_{18}H_{10}$ CP-PAH combustion effluent benzo[*ghi*]fluoranthene (**1**)[7] is the primary product, which subsequently rearranges into cyclopenta[*cd*]pyrene (**2**),[8] *viz.* another abundant $C_{18}H_{10}$ CP-PAH identified in combustion samples. Since **1** has been proposed to play an important role with respect to the point of divergence in growth reactions during soot formation and in incomplete combustion, *viz.* the build up of planar *versus* non-planar CP-PAH,[9] elucidation of efficient high temperature routes towards **1** is a topical issue.

Upon FVT (unpacked quartz tube 40 cm, 0.01 Torr, subl. temp. 150 °C, 50 mgh^{-1}) of **3** in the temperature range 800-1100 °C analysis of the pyrolysates (^{1}H-NMR, GC-MS) revealed complete conversion of starting material; products with molecular formulas $C_{18}H_{12}$, $C_{18}H_{10}$ and $C_{16}H_{10}$, respectively, were found. Whereas at 800 °C benzo[*ghi*]fluoranthene (**1**, 33%, $C_{18}H_{10}$), benzo[*c*]phenanthrene (**5**, 65%, $C_{18}H_{12}$) and fluoranthene (**6**, 2%, $C_{16}H_{10}$) were identified, at T ≥ 900 °C cyclopenta[*cd*]pyrene (**2**) and above 1000 °C minute amount of pyrene (**10**) were additional products (Scheme 1). Despite the occurrence of carbonization in the hot zone above 900 °C, the mass recoveries remained good throughout the whole temperature range (Table 1). The temperature conversion data show that **3** is converted mainly into $C_{18}H_{10}$ CP-PAH. It is assumed that

Scheme 1

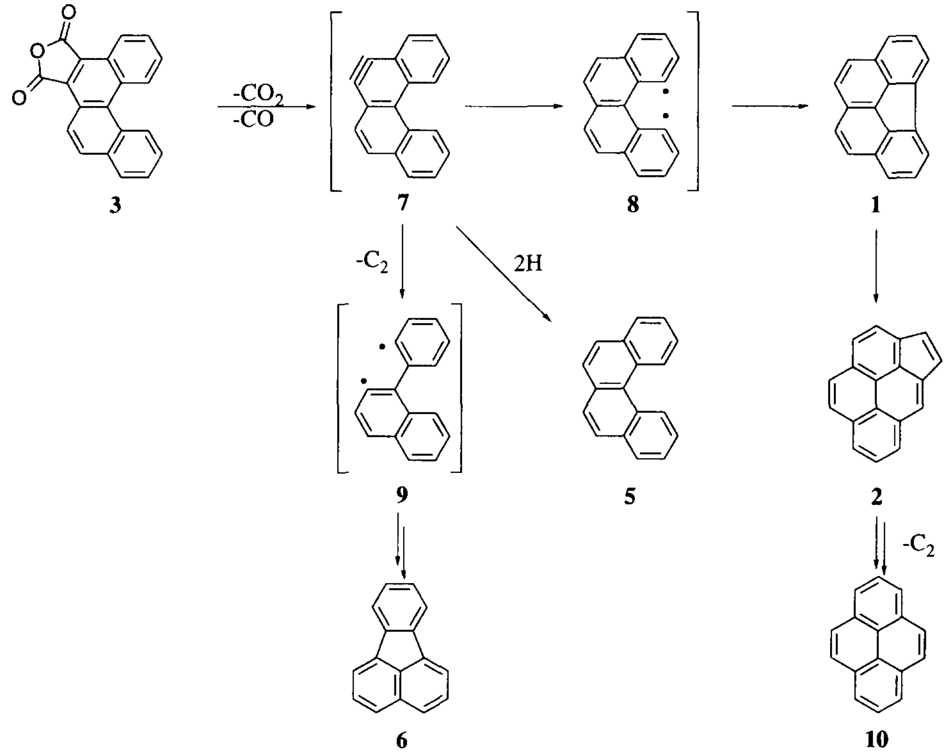

Table 1. Pyrolysate Product Composition obtained upon FVT (0.01 Torr) of **3**.[a]

T (°C)	**1** (%)	**2** (%)	**5** (%)	**6** (%)	**10** (%)	**Mass Recovery** (%)
800	33	-	65	2	-	70
900	60	10	28	2	-	71
1000	63	20	15	2	-	56
1100	51	39	6	2	2	52

[a] ^1H NMR, cap. GC and GC-MS analysis.

the primary aryne intermediate **7** is susceptible to undergo hydrogen migrations furnishing **8**, which upon ringclosure gives **1**. The presence of **5** suggests that in the lower temperature range, besides hydrogen migrations, hydrogen abstraction,[4] is a competitive process (Scheme 1). It should be stipulated that we have found earlier[10] that for the direct conversion of **5** into both **1** and **2** a high temperature ($T \geq 1050$ °C) as well as elevated pressures (0.5-1.0 Torr) are a prerequisite, *i.e.* under the present FVT conditions **5** is recovered intact! The temperature conversion data obtained for **3** indicate that the yield of **5** decreases in favour of that of **1**. The latter subsequently rearranges into **2** presumably *via* a ring-contraction/ring-expansion mechanism[11,12] at $T \geq$ 900 °C (Table 1). The minute amount of the $C_{16}H_{10}$ CP-PAH **6** found in all pyrolysates as well as the identification of **10** at 1100 °C indicates that another process, *viz.* C_2 extrusion[13] from both **7** and **2**, respectively, takes place.[14]

Our second $C_{18}H_{10}$ precursor 6*H*-benzo[*cd*]pyren-6-one (**4**)[6] was found to be much more stable than **3** under high temperature conditions in the gas phase. FVT (unpacked quartz tube 40 cm, 0.01 Torr, subl. temp. 150 °C, 50 mgh^{-1}) of **4** at 1100 °C gave pyrolysates containing only starting material. However with increasing pressure (range 0.01-1.0 Torr), a smooth conversion of **4** into **1** and **2** was observed (Scheme 2 and Table 2).[15] Despite the fact that elevated pressures are required, the conversion data concomitant with increasing pressure indicate that **4** is transformed selectively into **1**, which subsequently rearranges into **2**; at 1.0 Torr **2** (58%) is the primary product (Table 2). Interestingly, benzo[*c*]phenanthrene (**5**) is absent in all pyrolysates. This suggests that CO elimination from **4** occurs *via* a concerted process;[3] apparently no intermediates, such as **7** and **8**, are involved in the formation of **1** (compare Scheme 1).

Scheme 2

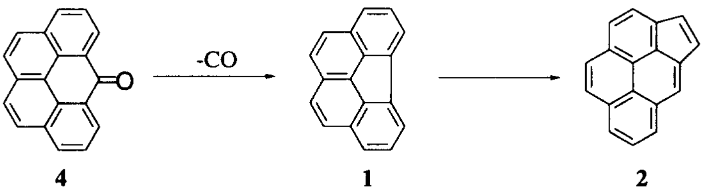

Table 2. Pyrolysate Product Composition upon Thermolysis of **4** at 1100 °C and different pressures.[a]

p (Torr)	**1** (%)	**2** (%)	**4** (%)	**10** (%)	**Mass Recovery** (%)
0.01	-	-	100	-	82
0.1	2	1	97	-	75
0.5	12	13	75	-	48
1.0	19	58	19	4	23

[a] ^1H NMR, cap. GC and GC-MS

In summary, oxy-PAH **3** and **4** are selective precursors for the abundant $C_{18}H_{10}$ CP-PAH combustion effluents **1** and **2** under high temperature conditions in the gas phase. Hence, although the identification of oxy-PAH in combination with a paucity of CP-PAH in fullerene forming benzene/oxygen flames is in line with the occurrence of CP-PAH oxidation,[1] our results unequivocally reveal that under appropriate thermal conditions oxy-PAH decarboxylate and decarbonylate to CP-PAH. Subsequently, these CP-PAH may then contribute to the growth reactions ultimately leading to fullerene formation under flame conditions.[16]

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14. Similar observations were made during independent FVT (1100 °C, 0.01 Torr) experiments with **2**; a pyrolysate (mass recovery 87 %) consisting of **1** (2%), **2** (97%) and **10** (1%) was obtained. It is noteworthy that upon FVT of **1**,[11] **2**,[8,11,12] **3**, **4** and **5**[10] no evidence for the formation of the combustion effluent cyclopent[*hi*]acephenanthrylene even in trace amounts was found.
15. The pressure was increased by leaking in N_2 giving rise to larger contact times and more rigorous thermolysis conditions; carbonization in the hot zone becomes a competitive process leading to a decrease in mass recoveries (Table 2). See also: Brown, R.F.C. *Pyrolytic Methods in Organic Chemistry*, Organic Chemistry Monographs, Academic Press, Vol. 41, New York **1980**.
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