Preparative flash vacuum thermolysis. Conversion of triphenylene to cyclopent[*h*,*i*]acephenanthrylene. A significant reaction for environmental science and combustion research

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Cyclopent[*h*,*i*]acephenanthrylene is selectively formed upon flash vacuum thermolysis at 1000 °C of triphenylene; the reaction represents a novel mechanistic route in combustion, giving rise to a cyclopentapolyaromatic compound.

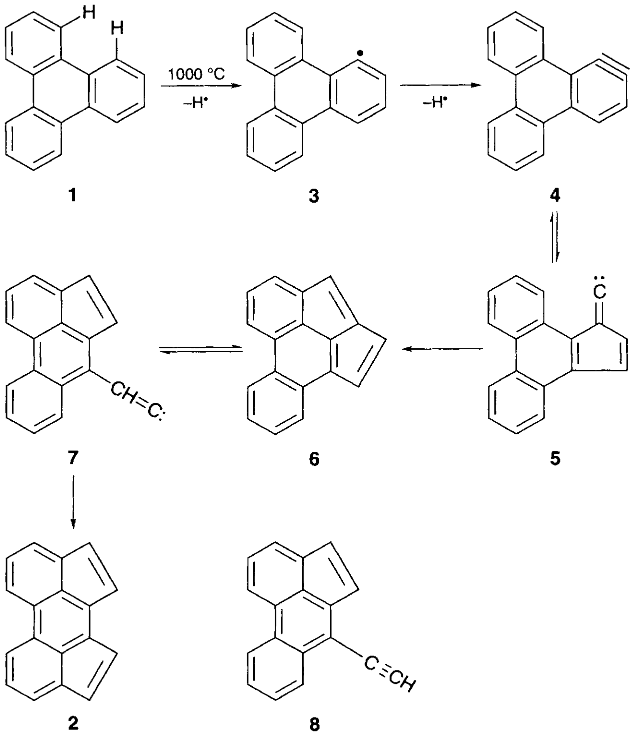
The possible occurrence of cyclopentafused polycyclic aromatic hydrocarbons (CP-PAH) in combustion emitants, attracts increasing interest because of the growing awareness that CP-PAH are potential mutagens and/or carcinogens. Cyclopenta-[*c*,*d*]pyrene (CPP) is a notable example.[1] CPP and other CP-PAH were for example found as major products in soot of methane–dichloromethane flames.[2] Despite the environmental threat, many CP-PAH are still unknown and not available as reference compounds for routine monitoring in *e.g.* diesel exhaust, incineration effluents and cigarette smoke.[3] CP-PAH are very thermodynamically stable at high temperature,[4] explaining their survival during combustion. The build-up at high temperature of [60]fullerene (C_{60}) is also an example of thermal CP-PAH formation.[5] Some CP-PAH, made *via* thermolysis, *e.g.* corannulene[6] and pyracylene[7] are referred to as prefullerene structures, because they fit on the curved surface of C_{60}.[5]

Convenient synthetic methodology for CP-PAH, based on high temperature gas-phase chemistry, was recently developed *via* flash vacuum thermolysis (FVT) of PAH with (masked) ethynyl substituents.[1,6] Another thermal pathway to CP-PAH was found in recent FVT work with biphenylene, which yields acenaphthylene and cyclopent[*a*]indene, without retro-cleavage to benzyne.[8] The next benzyne homologue triphenylene ranks, according to the empirical stability rules of Clar,[9] as one of the most stable PAHs. The observation that **1** remains unchanged in the molten phase up to 600 °C, and that it is often monitored as a combustion emmitant,[10] is in line with this thermal stability.

In earlier work we have shown the utility of FVT, both for the study of the thermal persistence of a species and to observe equilibration with isomeric structures on its thermal energy surface.[3] Here we report the thermal fate of triphenylene **1** under FVT.[11] When **1**, $C_{18}H_{12}$, was sublimed into the hot quartz tube (rate 0.5 g h^{-1}, at 0.05 Torr), it passed virtually unchanged below 950 °C and was redeposited at the exit of the furnace, without causing carbonisation in the tube. At 950, 975 and 1000 °C, the sublimate turned orange, due to selective formation of a new compound, deposited in a 10, 25 and 35% admixture respectively, with unchanged **1**. The orange coloured component was isolated by preparative HPLC and identified with ^1H NMR and ^{13}C NMR as cyclopent[*h*,*i*]acephenanthrylene **2** ($C_{18}H_{10}$ CPAP, mp 170–171 °C). It was identical with CPAP, synthesized *via* a nine step liquid phase route.[12,13] Above 1000 °C the recovery of aromatic products at the furnace exit decreased and progressive carbonisation occurred in the pyrolysis tube†. CPAP, like corannulene,[6] is one of the few CP-PAH structures available, that fit on the C_{60} surface.

Our rationalisation for the conversion of **1** to **2** is shown in Scheme 1. The reaction is thought to involve selective thermal cleavage of the weakest CH bond in the peri position of symmetrical **1**, to the triphenylyl radical **3**. The radical, as a high energy species, then 'stabilizes' in the high temperature pyrolysis condition, by losing another hydrogen, entering into the $C_{18}H_{10}$ energy surface, to form 1,2-dehydrotriphenylene **4**. As a benzyne homologue, **4** must undergo ring-contraction and 1,2 H-shift,[15] to the vinylidenecarbene **5**, that is intramolecularly trapped to cyclopent[*f*,*g*]acephenanthrylene **6**. Sequential ring-opening of **6**, to carbene **7** allows for a second ring-closure of the latter to form CPAP, which is deep enough on the $C_{18}H_{10}$ energy surface to escape from the hot tube. Our pyrolysate does not show an ethynyl ^1H NMR signal. Instead, orange coloured **2** is selectively formed.‡ This H-abstraction–carbene rearrangement process has to our knowledge not been invoked in any thermal PAH interconversion scheme.

This paper, like the previous one in this series on CCP,[1] serves two goals. The first one is to show the preparative strength of FVT towards CP-PAH. Secondly, it is a model experiment to emphasize that PAH may interconvert during combustion, normally at temperatures between 800–1200 °C, with a tendency to form CP-PAH. The latter are stable enough to escape to the environment. There is ample evidence that in combustion the imperious H-abstraction reaction *via* OH radical attack, is a major process.[17] For generation of PAH radicals like **3**, this abstraction reaction may even be more efficient than the purely thermal cleavage. Thus when triphenylene is monitored as a combustion emitant, CPAP is likely present.§



Scheme 1

Formation of ethynyl and CP-PAH derivatives by direct addition of C_2 units has been proposed as a fundamental process for the PAH build-up under forceful thermal conditions.[2,3,18] Recent studies on the build up of C_{60} in the carbon arc in the presence of hydrogen,[19] and in controlled flames,[20] revealed formation of smaller intermediate CP-PAH condensation products.

Footnotes

† Although **2** survives at very high temperatures in the gas-phase, it undergoes, in contrast with triphenylene, rapid exothermal decomposition on TGA analysis, just above its melting point. This phenomenon is also apparent with acenaphthylene, which remains stable in pyrolysis above 900 °C,[9] but dimerizes and polymerizes rapidly in its molten phase.[14]

‡ Ethynyl acephenanthrylene **8**, is not an unlikely product, because in the FVT preparation of CPP,[1] ethynylpyrene was observed and in an FVT attempt towards cyclopent[*b*,*c*]acenaphthylene, ethynylacenaphthylene came out as the final product.[16]

§ In a recent study of the high temperature pyrolysis of pyrene, C_2 insertion to the $C_{18}H_{10}$ series was postulated and the simultaneous appearance of **1** and **2** was observed for the first time.[18] CPP was also present in this study.

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Received, 7th September 1995; Com. 5/05811B