Thermal Hydrogenolysis of Polyaromatic Hydrocarbons and Activated Carbon at Elevated Temperatures and Pressures

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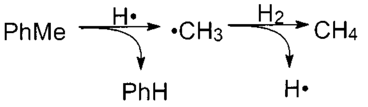
Vaporised polyaromatic hydrocarbons (indene, naphthalene, biphenyl, phenanthrene, anthracene) admixed with benzene, have been processed in flow reactors at 1–35 bar H_2 at temperatures between 500 and 990 °C. Smooth gasification to methane on a 4–20 s timescale occurs, nearing completion at the higher T and P values. Relative rates at 977 °C (benzene/naphthalene/anthracene ca. 0.1:1:2.5) are interpreted on the basis of the mechanism advanced earlier for benzene: (reversible) addition of $H^\bullet$ and opening of target aromatic rings. Activated carbon reacts analogously, but on a per C basis its rate is about 500 times smaller than that of naphthalene. Resistance to ring-opening hydrogenolysis in highly condensed entities and limited accessibility for $H_2/H^\bullet$ together account for this difference.

1. Introduction

Thermal, noncatalytic processing of organic materials is a longstanding practice in the petrochemical industry. Cracking and hydrotreatment of crude oil or fractions thereof are straightforward and robust technologies and therefore remain attractive next to advanced catalytic processes. In the thermal conversion of complex (hydrocarbon) mixtures a multitude of radical and molecular reactions takes place; a detailed computer programme is required to cover the kinetics of ethylene production, for example.[1] Ingredients for these computer models are rate and product data on individual reactions. One good example is the thermal hydrogenolysis (TH) of toluene, key steps of which are represented by Equation (1) and Equation (2).

$$H_2 \rightleftharpoons 2\,H^\bullet \qquad (1)$$

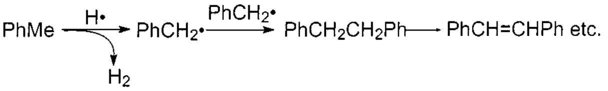


$$\mathrm{PhMe} \xrightarrow[\mathrm{PhH}]{H^\bullet} {}^\bullet CH_3 \xrightarrow[H^\bullet]{H_2} CH_4 \qquad (2)$$

This reaction proceeds smoothly on a timescale of seconds in the temperature region of 700−800 °C.[2−4]

Compared with pyrolysis (no H_2 added, model reactions in nitrogen, for example) the hydrogen acts as a mediator, suppressing condensation reactions to PAH and, eventually, soot. Hence, from benzene, (reversible) formation of biphenyl does occur, but at a percent level only, Equation (3).

$$\begin{aligned} &H^\bullet + \mathrm{PhH} \rightleftharpoons H_2 + \mathrm{Ph}^\bullet\ ;\\ &\mathrm{Ph}^\bullet + \mathrm{PhH} \rightleftharpoons \mathrm{Ph\text{-}Ph} + H^\bullet \end{aligned} \qquad (3)$$



$$\mathrm{PhMe} \xrightarrow[H_2]{H^\bullet} \mathrm{PhCH_2}^\bullet \xrightarrow{\mathrm{PhCH_2}^\bullet} \mathrm{PhCH_2CH_2Ph} \longrightarrow \mathrm{PhCH{=}CHPh}\ \text{etc.} \qquad (4)$$

Even in the TH of this relatively simple system with toluene and benzene, many more reactions occur at a lower level, but with increasing importance at more elevated temperatures. One is condensation by combination of two stabilized radicals, as in Equation (4). Another is the degradation of benzene itself: traces of methane are already being produced at 500 °C,[5] while its yield passes the percent level (based on total carbon) in 8 seconds at 1 bar of H_2 at 900 °C.[6]

We have recently reported on the TH of benzene in a flow reactor under pressure, with up to 36 bar of hydrogen.[4] Methane was the only important product, and its output was as high as 70% of total C at, for example, 985 °C/30 bar/21 s dwell time. Quantitative thermokinetic analysis led us to conclude that the ring-opening hydrogenolysis occurs through reversible addition of a H atom, reversible isomerisation of $C_6H_7^\bullet$ radical species, H transfer from H_2 to give, for example, methylcyclopentadiene, which decomposes into ${}^\bullet CH_3$ and cyclopentadienyl radical (see Scheme 1 of ref.[4]) − which is further hydrogenolysed into methane. Under these conditions the conversion of toluene to benzene [Equation (2)] is ca. 400 times faster than the breakdown of the benzene ring.[4]

In a way, the gasification of benzene to methane is the reverse of condensation to aromatics beyond benzene and biphenyl: naphthalene or PAHs in general. Said higher homologues are expectedly also susceptible to hydrogenolysis, but as yet with unknown rates, products, and mechanisms. We considered it worthwhile to investigate the behaviour and fate of some representatives − naphthalene, indene, anthracene, and phenanthrene − under conditions in between those for mild TH and total gasification,[7] to compare the results with the known features of benzene.[4] The 'methanisation' of a representative (activated) carbon, 'the ultimate PAH' is also described.

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As will be shown in our subsequent paper,[8] TH also enables heteroaromatics containing nitrogen, sulfur or oxygen to be converted into NH_3, HCN, H_2S, and water. Furthermore, TH is an attractive alternative for the disposal of organohalogen compounds,[9] since HX (HCl, HBr) is formed under the reductive conditions without any X_2, and 'dioxins' (PCDD/Fs) neither arise nor survive.

2. Results

2.1 PAH

First, a short series of experiments (A1) was performed with naphthalene in benzene at 1 bar, to obtain insight into the relative rates of conversion. Next, anthracene was included (A2). Reactions of benzene/naphthalene were then conducted at elevated pressure (series B), followed by runs (C) with a more complex feed, also including biphenyl, indene, dibenzofuran, and phenanthrene. Representative data on each series − with conditions and key observations − are collected in Table 1.

At 1 bar, the methane output at 900 °C in series A1 is below 1% (mol) based on benzene, but the level is twice that of a comparable run without added **N**(aphthalene). If (only) 1 mol of CH_4 is formed per mol of **N** converted under these relatively very mild conditions (see also Scheme 1), the conversion of **N** must have been ca. 4%. GC analysis of the liquid product mixture, after correction for a modest recovery loss as seen by comparison with 'blank' runs conducted at 500 °C, produced a value of ca. 6%. The respective numbers for 950 °C are 12 and 20%. While on the basis of the methane output in absence of **N**, the conversion of **B**(enzene) could have been about 1−2%, a rough value for the relative rate for **N** vs. **B** (at 950 °C) is 10−20.

With a little **A**(nthracene) added (series A2), methane levels are comparable. The measured output levels of both **N** and **A** imply relative rates (assuming plugflow and first-order disappearance) for **A** vs. **N** of ca. 2.7 at 950 °C and 2.3 at 974 °C, respectively. That **A** reacts faster than **N** is also reflected by the change in **A/N** ratio, from 0.0118 in the feed, to 0.0084 (950 °C) and 0.0072 (974 °C). In a 'blank' run at 500 °C the **A/N** output ratio was 0.0112, showing that recoveries of both PAHs were adequate.

Using a 1:10 molar ratio of **N** in **B** as a feed, a number of experiments were conducted in the high pressure facility (series B). With hydrogen in at least a twelvefold molar excess, residence times were varied by changing inflow rates of H_2 and/or the organic feed. At the lowest *T* used (760 °C, with residence time $\tau = 22$ s), recoveries were ≈ 93% for **B** and 82.5% for **N**. The output of methane (**M**) was 10% (mol) on the benzene input. Ethane (**E**) was also formed, at a level of 56% based on methane. Note that ethane is long-lived at this mild temperature. Because of the rather high but still incomplete catch of the volatile benzene it is not possible to derive accurate (relative) rate data from this experiment (exp. i). Analysis of the combined liquid catch showed formation of small amounts of toluene and biphenyl, and traces of a number of PAHs, such as indene, acenaphthene, fluorene, and pyrene. At 885 °C (exp. ii), the **N** output comprised only ca. 5% of the **N** input, with a 46% recovery of benzene **B**, confirming that **N** reacts much more rapidly than **B**. Methane comprised 330% based on **B**, with an **E/M** molar ratio down to 0.030.

With the residence time reduced to 4.1 s (exp iii), recoveries were now 43% for **N** and 82% for **B**. The CH_4 output went down to ≈ 40% M on **B**, with an **E/M** molar ratio of 0.097. With τ at about 22 s again, a further increase of *T* to 990 °C (exp. iv) resulted in an essentially complete conversion of **N**, with output levels well below 1%. Benzene recoveries were around 23%, showing that **B** was now also being converted to a major extent. The output of methane was over 400%, based on inflowing **B**, and the **E/M** ratio ca. 0.002−0.003.

Table 1. Summary of experimental conditions and results

Series	Conditions P H_2 [bar]	T range [°C]	τ [a] [s]	Feed description	Results
A1	1.0	903−950	4.3±0.1	H_2/**B** = 6.0; **N/B** = 0.052	CH_4: 0.4−1.0% mol on **B** (twice the amount from runs without **N**[4]); C_2H_4 + C_2H_6 (ratio ≈ 4:1) ca. 40% mol on CH_4; conversion of **N**: calculated[b]: 4−12%; measured (≈6)-20%
A2	1.0	903−974	4.2±0.1	H_2/**B** = 6.0; **N/A/B** = 0.074:0.00055:1	CH_4: 0.3−1.6% mol on **B**; C_2H_4 + C_2H_6 as above; conversions: (**N** measured: 29% at 950 °C; 35% at 974 °C); (**A** measured: 43% at 950 °C; 61% at 974 °C)
B	32±4	760, 885−990	4−23	H_2/**B** = 12.5−30; **N/B** ≈ 0.10	see Figure 1[17]
C	32±4	925, 940, 990	21±2	H_2/**B** = 33; other (mol % on **B**)[a]: **N**(6.9); biph(1.05); ind(1.59); phe(0.78), DBF[c] (1.9)	

[a] τ: average residence time; **B**: benzene, **N**: naphthalene, **A**: anthracene, biph: biphenyl, phe: phenanthrene, DBF: dibenzofuran, ind: indene. − [b] On the basis of 1 mol CH_4/mol of **N** converted. − [c] Features will be discussed in a subsequent paper.[8]

At this highest *T* used, the organic product mixture contained only very small amounts of biphenyl (ca. one quarter of the recovered **N**), and traces (order of magnitude less) of other PAHs. In exp (iii) at 885 °C, on the other hand, more substantial amounts of by-product hydrocarbons were found; in mol % on the benzene input these were: toluene (0.17), indene (0.09), biphenyl (0.70), acenaphthene (0.05), fluorene (0.07), and pyrene (0.03). These values were also the highest measured throughout the whole series of experiments. In other cases reported, the PAH by-product yields rarely exceeded the detection limit (ca. 0.01% on benzene input).

Under these conditions, mainly of kinetic control, intermediately formed arenes are also subject to hydrogenolysis, presumably with rates at least as high as those of naphthalene. At *T* approaching 1000 °C, such hydrocarbons, just like naphthalene, will be essentially completely ‘gasified’ to methane. As already briefly discussed before,[4] ethane is still quite stable at 760 °C, will exist for seconds at 885 °C and is very short-lived at 990 °C. Thus, only (very) small equilibrium proportions of ethane, toluene, and biphenyl can exist next to methane and − remaining − benzene.[4]

Results with the series C cocktail were consonant with this: at 925 °C the recovery of **B** was 36%, that of **N** 4.2%. An apparent level of 21% of the starting biphenyl amount was found, but it is equivalent to 0.57% (mol) based on the remaining benzene (or 0.20% on **B** input); an important proportion of the remaining biphenyl must have been (reversibly) formed from the benzene. Other recoveries were: phen (7.2%), indene (0.3%), DBF (3.0%).

At 941 °C, degrees of reaction were of course higher; only 18.5% of **B** was recovered, with 1.5% of **N**, 8.5% of biph, 3.0% of phen, 1.4% of DBF, and 0.3% of indene. At 990 °C, the expected ‘final’ picture was observed: a minor proportion of the benzene was recovered, and the other compounds were seen only at trace levels. The output of methane was 575% (mol)[17] based on inflowing benzene, and the ethane/methane ratio was only 0.0012.

An overview of methane formation in series B and C (normalised to the residence time of 20s), also taking − modest − differences in [H_2] into account, is given in Figure 1.[17]

As far as hydrocarbons are considered (dibenzofuran will be evaluated together with other heteroatomic analogues in a forthcoming paper[8]), relative rates of conversion appear to be:

indene >> anthracene > naphthalene > phenanthrene >> benzene.

Mechanistic consequences are discussed in the next section. Of these compounds, indene and also naphthalene − together with biphenyl − are clearly already formed as intermediate or side products from the hydrogenolysis of benzene itself.[4] Anthracene and phenanthrene served here merely as model compounds, to provide information about the (differences in) stability compared with benzene or naphthalene. The conclusion that the higher homologues of benzene all react considerably more rapidly than benzene itself is valid. When reactions are performed under relatively mild conditions, even simple starting compounds and mixtures, may/will produce quite complex product compositions. However, when the goal is a high degree of conversion, that of benzene is a proper yardstick. Its full conversion − and consequently that of other hydrocarbons − is possible at temperatures not much above 1000 °C,[4] pressures in the range of 30−40 bar on a tens-of-seconds timescale, with methane as essentially the only product.

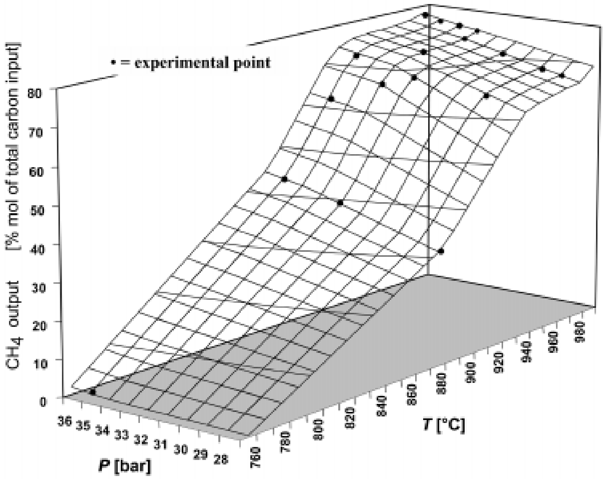


Figure 1. Methane formation from PAH mixtures (series B and C, reaction time 20s) (see ref. [17])

To verify the relative rate of reaction of naphthalene vs. benzene [provisionally set at 10−20 at 950 °C from the experiments at 1 bar (vide supra)], we critically analysed all pertinent data from the runs in series B and C. Smoothing of conversion data by interpolation to one residence time of 4 s, assuming first-order behaviour of hydrocarbons, resulted in the conclusion that a benzene conversion level of 30% is reached at 970 °C (1243 K) − tallying with the previously reported 977 °C (1250 K) in 25 bar of H_2.[4] The same degree of conversion of naphthalene should occur at about 860 °C. The ca. 110 °C difference at this *T* level is equivalent to a relative rate of 10 at 977 °C, as outlined in Section 3.1b.

2.2 Activated Carbon: the Ultimate PAH

Hydrogenolysis of benzene and other (semi)volatile hydrocarbons in a large excess of hydrogen will be a relatively clean reaction, with minimal formation (underway) of tar and soot. This will no longer be true with high-boiling materials and/or with insufficient hydrogen. It is therefore of interest to know about the (rates of) hydrogenolysis of such nonvolatile compounds/materials. Recalling the widely studied ‘coal liquefaction’[16] − a very mild, partial hydrogenolysis, in comparison with our conditions, to obtain liquid fuels − we thought it worthwhile to conduct a brief study into the ‘gasification’ of an activated carbon.

A portion of 1.00 g Norit ROW 0.8 Supra carbon was placed in the middle section of the quartz tubular reactor and kept in place by a plug of quartz wool. After preconditioning overnight at 750 °C under a slow stream of nitrogen (to remove water and oxygen), it was subjected to ca. 35 bar of H_2 flowing at a rate of ca. 400 mmol/h.

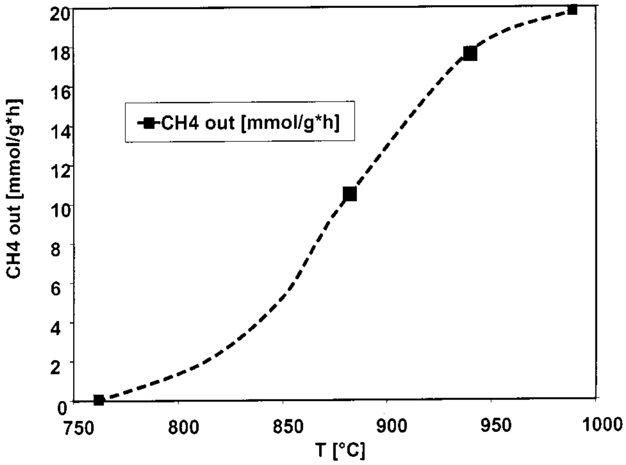


Figure 2. Methane formation from AC

Reaction was followed by analysis of methane, but at 750 °C this was below 0.001 mmol/h. The temperature was raised to 885 °C, and now the output of methane, followed over 30 min, comprised ca. 11 mmol/h (this also means a calculated weight loss of nearly 7% of the AC). This procedure was repeated at two still higher temperatures; accounting for further weight losses, the results shown in Figure 2 were obtained.

Obviously, the 'lifetime' of the (remaining) AC at 985 °C, with respect to conversion into methane, is still over an hour (when a fresh sample of AC was processed at that temperature overnight it was totally gasified, however). Compared with **N**(aphthalene) this is at least two orders of magnitude less. When comparing lifetimes on a per C basis at 885 °C, 'methanisation' of the AC appears to be ca. 500 times slower than that of **N**. Reasons for this are discussed in the next section.

3. Discussion

3.1 Kinetic Features

3.1.a Effect of Hydrogen Pressure

If the degree of conversion of **N** is set at 885 °C (1158 K) in 32 bar of H_2, $\tau = 4$ s, at 50%, and first-order dependence on [**N**] is assumed, the experimental rate constant $k = 0.17$ s^{-1}. If as a first approximation, a first-order situation in $[H_2]$ is also accepted, this k at 1 bar should be down to $0.17{:}32 = 0.0053$, meaning $\approx 2\%$ conversion. This is to be compared with an observed − or at least indicated − 4−6% at 900 °C.

If an overall Arrhenius activation energy of 60 kcal/mol is applied (see next section), the 32 bar value will go up to $k = 0.8$ s^{-1} at 950 °C (equivalent to 96% conversion in 4 s, if plugflow conditions apply); a corresponding value of $0.8{:}32 \approx 0.025$ s^{-1} at 1 bar would mean ca. 10% reaction, while the experiment gave 10−20%.

These admittedly fragmentary data are an indication, but not a proof, of a (close to) first-order dependence on $[H_2]$. In any event, the effect of increasing $[H_2]$ is large: with other things equal, the step from 1 to 30 bar results in the same degrees of conversion at temperatures 130−160° lower.

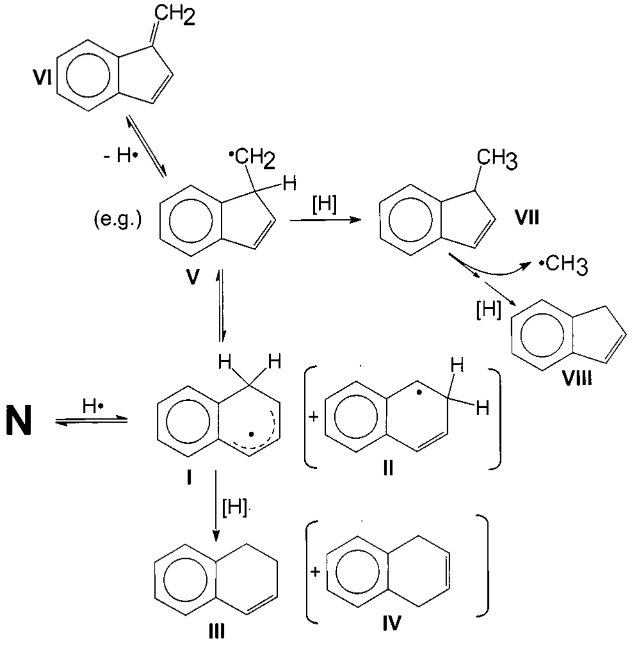
3.1.b Relative Rate of N vs. B

For benzene **B**, 30% conversion at 970 °C (1243 K), $\tau = 4$ s, implies a k value of 0.09, which is satisfactorily covered by the experimental Arrhenius parameters reported earlier,[4] $\log A = 10.6$, $E = 66$ kcal/mol. To obtain the same rate constant for **N** at ≈ 110° lower temperature, its E value must be lower by 5.5 kcal/mol; this in turn translates into a ca. tenfold faster rate for **N** at 977 °C (1250 K).

3.2 Mechanisms

3.2.a Naphthalene

That **N** reacts (ca. 10 ×) faster than benzene (**B**) is no surprise; whatever the mechanistic details, (partial) hydrogenation of one ring of **N** − whether kinetically or thermodynamically governed − will be easier than that of benzene itself. By analogy with **B**, the first step(s) are again a reversible addition of $^{\bullet}$H, with a preference for species **I** over **II** (see Scheme 1), which will be intermediates in the formation of dihydronaphthalene **III** (and to a smaller extent, **IV**). If **III** and **IV** are in equilibrium with **N**, the [**III**]/[**N**] ratio will be linearly dependent on $[H_2]$.



Scheme 1. Proposed naphthalene (**N**) TH mechanism; [H] denotes a hydrogen transfer − by a hydrocarbon, a hydrocarbon radical, and/or H_2

Alternatively, radical **I** (or **II**) can isomerise, along the pathways discussed earlier for $C_6H_7^{\bullet}$ from **B**,[4] to species such as **V**, which can in turn equilibrate with the benzofulvene **VI**. The concentration of this isomer of **N**, when equilibrated with **N**, will adopt a concentration independent of $[H_2]$.

Both types of derivatives of **N**, exemplified by **III** and **VI**, will be subject to ring-opening reactions; examples of those involving hydrogen (atoms) are illustrated in Scheme 2 and Scheme 3. Whatever the exact pathways, these will result − ultimately − in benzene and methane, with alkylated benzenes (plus indene) and C_2-C_4 hydrocarbons (or radicals) as short-lived or relatively stable intermediates.

For methane, the key product, the methyl radical will be the immediate precursor. It can arise from methyl-arene entities (if present or formed as intermediate products) through ipso-addition of $^{\bullet}H$[4] and − more importantly − by homolysis of weaker, and hence short-lived, sp^3 C-methyl bonds, as in methylindene **VII** or compound **XI** (1-but-1-enylbenzene).

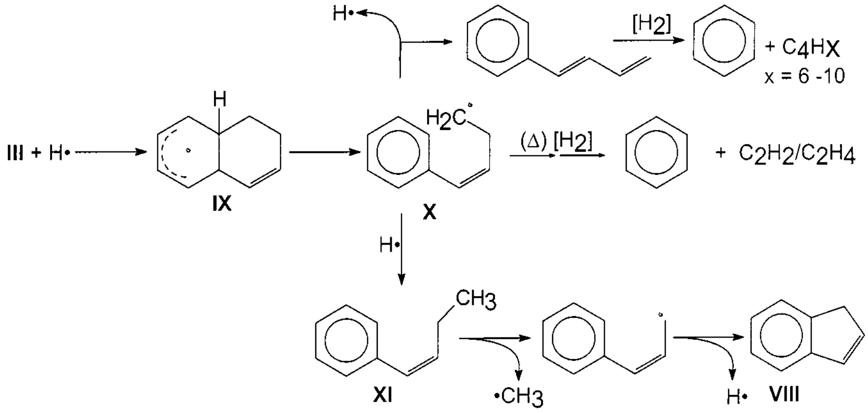
Taking thermochemistry into account,[10] it appears that under our 'standard' conditions [977 °C (1250 K), 30 bar] the equilibrium concentrations of **III** and **VI** are not much different, and are both around 10^{-4} relative to **N**. This may explain why the overall order in $[H_2]$ is neither zero (expected for reaction through an **N** isomer without any hydrogen assistance) nor 3/2 (or even 2), which would apply for reaction through **III**/**IV** or further hydrogenated **N** derivatives.

If various pathways and intermediates together determine the overall rate of disappearance, it is not possible to interpret the relative rate of **N** vs. **B** in a simple way. The factor 10 is (at 977 °C) equivalent to a ca. 5.7 kcal/mol difference in overall (free) energy of activation. Note that the difference in the heats of reaction for formation of **III** from **N** and for C_6H_8 from benzene is much larger: 11 kcal/mol.[11] Whereas for **B**, reaction through cyclohexadiene as an intermediate seems to be unimportant,[4] reaction through **III** for **N** may not be ruled out a priori.

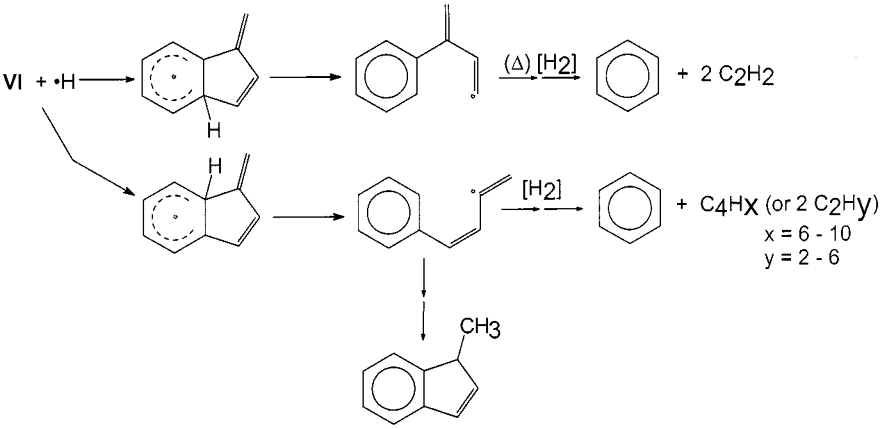
Note also that whereas fulvene has a 34 kcal/mol higher heat of formation than **B**,[4] our estimate for **VI** vs. **N** is 22 kcal/mol:[10] a difference of 12 kcal/mol. Furthermore, about the same difference will hold for comparison of formation of radical species **I** from **N**, and of cyclohexadienyl radical $^{\bullet}C_6H_7$ from **B**.[12] This merely shows that several different pathways involving H addition to naphthalene can result in higher rates than with benzene; at the same time it suggests that to proceed (irreversibly) from hydrogenated intermediate(s) to ring-opened products is more difficult to achieve from **N** (through **I**, **III**, and/or **VI**) than from **B** (through C_6H_7 radical species).

3.2.b Other PAHs

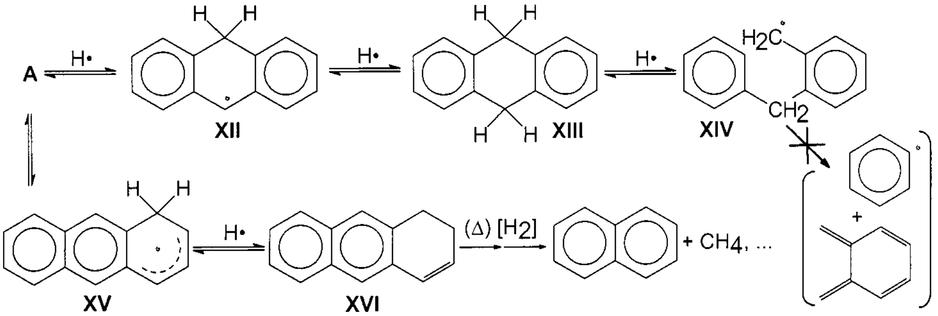
That **A**(nthracene) reacts (only) 2−3 times more rapidly than **N** (implying a ca. 2 kcal/mol lower overall free energy of activation) is at first sight rather surprising: compared with formation of radical **I** or dihydroarene **III** from **N**, the analogous conversions of **A** to 9-hydroanthryl radical **XII**



Scheme 2. Proposed dihydronaphthalene (**III**) TH mechanism



Scheme 3. Proposed benzfulvene (**VI**) TH mechanism



Scheme 4. Proposed anthracene (**A**) TH mechanism

(see Scheme 4) or dihydroanthracene **XIII** are each ca. 12 kcal/mol more exothermal.

Although, in an equilibrated environment, both **XII** and **XIII** will be present in proportions up to two orders of magnitude larger than with the **N** system, and although, for example, ring-opening in **XII** by a H atom (Scheme 4) is straightforward, we do not see how fragmentation of the resulting radical species **XIV** is possible without a high energy barrier. This disfavours breakdown of **A** through its central ring. Instead, **A** is subject to hydrogenolysis of a side ring, comparable to the conversion of **N**. The thermochemistry (heats of addition, for example, for **A** to give radical **XV** or dihydroanthracene **XVI**) is now only marginally different from that of **N**/**I**/**III**.

Naphthalene is an expected product from this degradation pathway, but this has not been verified in the competition experiments − with **N** − described.

Phenanthrene appears to react more slowly than **N**, by a factor of about 2. As a brief comment, we wish to point out that it is an annelated biphenyl system, which will make fragmentation through hydrogenation of the central ring at least as difficult as with **A**.

On the other hand, the five-membered ring of indene would be expected to be much more vulnerable to hydrogenation and subsequent degradation (to benzene), and this is borne out by experiment.

If these results and insights are extrapolated to higher PAH analogues, it is to be expected that − next to side chains and singly bound aryl groups − accessible 'terminal' (annelated) benzene rings − as in anthracene − and certainly analogous five-membered rings (cf. indene) will be smoothly hydrogenolysed, the fragments essentially ending exclusively in methane if a sufficiently high T is chosen − to limit, for example, the half-life of ethane to < 1 second.

More condensed systems, or regions in a PAH, may be rapidly and reversibly converted into dihydro-type entities and hydroaryl radical sites, but pathways to fragmentation are hardly accessible, if not blocked. Through degradation of outer rings, however, any PAH will ultimately be fully 'gasified' to methane, at 977 °C or less, given enough time − and hydrogen.

3.3. Activated Carbon

The formation of methane from the employed **A**ctivated **C**arbon (AC) at 885 °C (1158 K), Figure 2, comprises about 10 mmol/g carbon/h; this is equivalent to a rate constant of about $3 \cdot 10^{-5}$ s^{-1}, accepting that the AC is pure C(arbon).

The rate constant, on a per mol basis, for the conversion of **N** at this temperature is 0.17 s^{-1} (Section 3.1a). Expressed on a per C basis as well (treating all C's as equal), this rate constant is 0.017. Interestingly, that for the AC is some 500−600 times smaller, which we ascribe to the poor accessibility of this solid material.

A simple model approach can illustrate this better. The AC used has a surface area of 1250 m^2/g, and a particle density of about 0.8 g/cm^3 (ca. 40% of the real density of 2.1). Shaping it as identical cubes results in edges of ca. 230 nm and an average of about 850 C atoms per piece, or about 10 × 10 × 10 atoms in a rocksalt-like configuration (if it is pure carbon). A model with relatively large platelets results in a thickness of about 80 nm. As a rough estimate, up to 10% of these C centres are at the surface and in principle within reach for gasification. The highly condensed structure must then be the major reason for the low rate, by another factor of (at least) 50: because of unreactive surface atoms, and those hidden and bound in lower layers. Yet another factor may be that, should a hydrogenolytic attack − in (micro)pores − be successful in the first instance, a radical (esp. $^{\bullet}CH_3$) may be created that does not become 'free' as a gas-phase species, but is trapped again and reintegrated in the carbon matrix.

4. Final Conclusions

In a flow reactor, with ca. 30 bar of H_2, aromatic hydrocarbons − from benzene to PAHs such as anthracene and phenanthrene − are smoothly converted into methane at around 850 °C and on a 4−20 seconds timescale. Activated carbon reacts analogously, but − on a per C basis − at a rate ca. 500 times lower than that of naphthalene. In terms of the mechanistic framework discussed before for benzene,[4] ring-opening hydrogenolysis is less easy with more condensed PAH structures; with AC the limited accessibility is also an important factor.

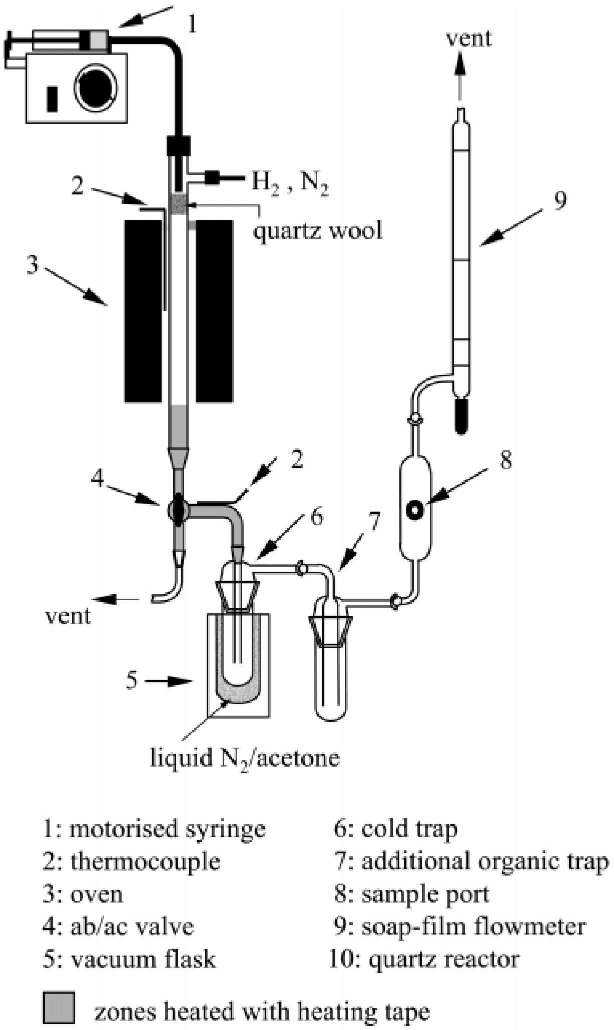


Figure 3. Atmospheric pressure set-up

Experimental Section

Apparatus and Methods: The set-up used for experiments at 1 bar is depicted in Figure 3. Substrates were introduced in benzene solution by means of a motorised syringe (Perfusor VI) (1) onto a piece of quartz wool placed in the electrically heated zone of the reactor tube, to ensure proper evaporation. The quartz reactor, of ca. 45 cm^3 (10), was placed vertically in the Heraeus oven (3) electronically controlled by an RKC REX C10 device.
After a stabilization time of ca. 30 min, products were conducted through a heated glass tap (4) to a cold trap (6) and a second trap (7), both also filled with acetone. The collecting time (CT) was measured from the moment that the products entered the cold trap, visible by aerosol formation in the top of the trap. Switching of valve (4) marked the end of the CT. The two obtained samples were joined and analysed collectively.

Gaseous samples were taken through the port (8) of a glass sampling bulb. The total gaseous outflow was measured by means of an HP 0101−0113 soap film flowmeter (9).

The high-pressure set-up and the experimental procedure applied in this study have been described previously.[4]

During each high-pressure experiment, two liquid (organic) samples were collected: one in the pressurised trap of the high-pressure system and one in the cold trap. Each sample was analysed by GC/FID (HP5890, quantification) and GC/MS (HP5890/HP5972 scan mode, MM range 30−350, with a standard NIST NBS75 spectra library − for identification). Standard method: init. temp. 50 °C; init. time 5 min; rise 10 °C/min; final temp. 280 °C, final time 10 min; column: Chrompack CP-SIL 5CB/MS, 50 m × 0.32 mm × 0.4 μm; carrier gas: H_2 (GC/FID), He (GC/MS); column head pressure 90 kPa. Co-injection standard: monobromobenzene, ca. 0.1 g per sample.

In both parts of the study, eight to twelve 500 μL samples were taken during each run from the exit gas flow. C1/C2 compounds were quantified on a Packard 428 gas chromatograph equipped with a packed column (Alltech, Carbosphere, 86−100 MESH), an FID detector and a methaniser. Peak areas were compared to those of a standard mixture[17] (CO, CO_2, methane, acetylene, ethylene, ethane, each 1% vol in nitrogen).

Cumulative results were divided by the CT, in order to express the amounts of products in time-dependent units (mmol/h).

Chemicals: The following chemicals were available and used as such: benzene (Merck p.a., 99%; distilled), monobromobenzene (Baker, > 99.5%), naphthalene (Janssen Chimica, > 99%), biphenyl (>99% by GC), indene (> 99% by GC), anthracene (> 99% by GC), and phenanthrene (> 99% by GC)

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[1] For instance, KTI/SPIRO® software for the KTI ethylene production unit.
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[10] The standard heat of formation for gaseous **III** is ≈ 31 kcal/mol (≈ 12.5 kcal above the reported value for liquid **III**).[15] Δ_fH^0(**IV**) will be ca. 3 kcal/mol higher.[15] For the equilibrium **N** + $H_2 \rightleftarrows$ **III**, ΔS^0 [unit fugacity, 977 °C (1250 K)] ≈ 30 cal/mol/K, by analogy with known data for comparable situations. This implied ΔG^0 (977 °C; 1250 K) ≈ 32.5 kcal/mol, hence $\log K \approx -5.7$. In 30 bar H_2, the [**III**]/[**N**] equilibrium ratio will then be about $10^{-4.2}$. For benzofulvene **VI** Δ_fH^0 is estimated starting from Δ_fH^0(**VIII**) = 39 kcal/mol;[15] for the exocyclic methylene group an increment of +19 kcal/mol is added (ca. 2.5 kcal less than that for cyclopentane → methylenecyclopentane[15] to account for extra resonance energy). Hence, isomerisation of **N** to **VI** is about 22 kcal/mol endothermal and, ignoring a small difference in entropy, the equilibrium ratio [**VI**]/[**N**] will be about $10^{-3.9}$ at 977 °C (1250 K), independent of [H_2].
[11] With Δ_fH^0(**N**) = 36, and Δ_fH^0(**III**) = 31, addition of H_2 to **N** is ca. 5 kcal/mol exothermal. Conversion of benzene (Δ_fH^0 = 20) to cyclohexadiene ($\Delta_fH^0 \approx 26$) is 6 kcal/mol endothermal, however.
[12] The heat of addition of $^{\bullet}$H to **B** is 22 kcal/mol,[13] meaning that an allylic C−H bond in cyclohexadiene is ca. 77 kcal/mol. If

the same value holds for the appropriate C−H bond in **III** to give radical **I**, $\Delta_f H^0$(**I**) = 56 and the addition of $^\bullet$H to **N** becomes 32 kcal/mol exothermal. The same value has been found by DFT calculations.[14]

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[17] At higher temperatures (larger degrees of conversion), the methane concentrations in the outflow are quite large (> 5%), causing some overloading and nonlinearity of the FID signal. In reality the outputs in Figure 1 at $T > 960$ °C are 5−15% higher than reported, as was verified afterwards by comparison of signals from 500 and 250 μL samples.

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