Thermal Hydrogenolysis of Nitrogen-Containing (Hetero)arenes at Elevated Temperature and Pressure

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The behaviour of the aromatic nitrogen derivatives pyridine **P** and quinoline **Q** – and for comparison benzonitrile and azobenzene – was studied under elevated pressure (20 to 30 bar) in a flow reactor with an atmosphere of hydrogen at temperatures ranging from 773 to 1173 K. Compounds were introduced into the reactor admixed with benzene. Efficient removal of the heteroelement was observed, accompanied by deep gasification of the carbon skeletons, at higher temperatures. **P** reacts much faster than benzene, while **Q** is a little less reactive than **P**. The main products were methane, hydrogen cyanide and ammonia. Mechanisms are discussed based on induced decomposition by hydrogen atoms. The facile reaction of **P** is explained by hydrogen abstraction to give the 2-pyridyl radical followed by ring opening, a reaction with much better thermochemistry than that for benzene and the phenyl radical. Reaction via (partially) hydrogenated intermediates may also play a part. "Exocyclic" nitrogen – such as in benzonitrile – is readily displaced by hydrogen, while for azobenzene spontaneous fission of the rather weak C–N bond is the major rate- (and product-) determining step.

Introduction

Recently, the hydrogenolysis of benzene (**B**) and its homologues has been discussed.[1,2] Benzene (**B**) reacts readily at around 1200 K in a quartz tubular flow reactor with 20−30 bar of hydrogen to give high yields of methane on a second timescale. This process appears to proceed via (reversible) hydrogen atom addition and isomerisation, that is, hydrogenation to the C_6H_8 species and subsequent splitting into $\cdot CH_3$ and $\cdot C_5H_5$ (e.g. cyclopentadienyl) radicals.[1] Naphthalene (**N**) reacts about 10 times faster; this is understood − also on a thermokinetic basis − overall to be an easier ring-opening hydrogenolysis reaction.[2] Anthracene (**A**) reacts only marginally faster than N; this is explained by the extra energy barrier required to split the central ring, leaving degradation of a side ring as the only effective channel for the reaction.[2]

Activated carbon (**AC**), "the ultimate PAH" is considerably more resistant; its lifetime in its gasification to methane is over an hour at 1250 K (970 °C).[2] This highly condensed structure is less reactive with $H\cdot/H_2$, and effective breakdown of the aromatic rings is slow. Nevertheless, in the vapour phase even quite complex PAHs can be ultimately degraded to methane, and therefore this "dry" gasification has potential applications in waste management technology. Halogens can be tolerated even at high concentrations, as these − and other − substituents are displaced by hydrogen at much higher rates than arene rings are degraded.[1] Under reductive conditions, organic chlorine derivatives exclusively give HCl, unlike combustion, which also produces free chlorine. Furthermore, "dioxins" (polychlorinated dibenzo-*para*-dioxins and -furans, PCDD/Fs) cannot form, and if present, will be detoxified, at least by hydro-dechlorination to their parent compounds, dibenzo-*p*-dioxin (**DD**) and dibenzofuran (**DF**).

The reactivity of **DD** and **DF** has also been dealt with recently.[3] **DD** is relatively easily converted in a hydrogen atmosphere at around 1000 K; this reaction is about a factor of 10 faster than that of chlorobenzene, which gives benzene and HCl. Interestingly, in addition to CO, **DF** is an important product. Both processes are sensitive to the concentration of hydrogen atoms, which appear to react by addition to (−Cl or −O) substituted carbon atoms as a first step.

DF is much more resistant to degradation. Moreover, rates do not seem to depend on the hydrogen (atom) concentration, as hydrogenolysis with 1−35 bar of H_2 and a recent report[4] on the thermolysis in argon show. Naphthalene is an important product throughout, and a thermolysis mechanism for **DF** involving C−O fission and isomerisation has been advanced.

Since nitrogen is a fairly common ingredient in organic materials, especially those related to biomass or crude oil,

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it is worth investigating the fate of N-containing benzene derivatives under the same conditions. In addition to heteroaromatic nitrogen compounds − pyridine (**P**) and quinoline (**Q**) − our investigation includes benzonitrile (**BN**) and azobenzene (**AB**) as examples of "exocyclic" N derivatives.

Results and Discussion

Pyridine

Five runs with pyridine were performed employing a molar inflow ratio of **P**/benzene/hydrogen of 0.05:1:12 at 20 bar with a residence time of about 4.5 s. The recoveries of **P** are depicted in Figure 1. The main products were methane and ethane in a ratio of around 2. The formation and survival of ethane can be ascribed to the relatively mild conditions under which the conversion of **P** occurred: benzene is essentially inert at $T < 1100$ K.[1] Higher molecular-weight products included traces of (in decreasing order) pyrrole, methylpyridine and quinoline (**Q**), but only in the experiment performed at the lowest temperature. The nitrogen atom of pyridine ended up almost exclusively in the form of HCN, reaching "synthetic" yields; at 1013 K, with 60% conversion of **P**, 55% of the pyridine input was found as HCN.

Quinoline

Analogously, runs were performed with about 4.6 mol% **Q** in benzene under a pressure of 20 bar. The recoveries of **Q** have been plotted in Figure 1; it appears that **Q** reacts only marginally slower than **P**. Several nitrogen-containing compounds were identified in the liquid product mixtures (see Figure 2).

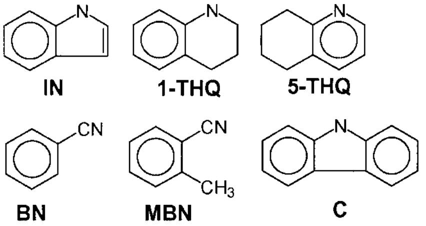


Figure 2. Observed by-products in the hydrogenolysis of quinoline

The yields were low, less at higher degrees of conversion, and never exceeded 1−2 mol% of the quinoline input. Indole (**IN**) and benzonitrile (**BN**) were relatively prominent. In one case (at the lowest temperature) traces of carbazole (**C**), 1,2,3,4- (**1-THQ**) and 5,6,7,8-tetrahydroquinoline (**5-THQ**) and *o*-methylbenzonitrile (**MB**) were also found.

To compare the relative stability of **N** and **Q** several runs were performed using a 1:1 mixture, again diluted in benzene (ca. 5 mol% each), with a H_2 pressure of 30 bar and a residence time of about 6 s. The recoveries of both substrates are depicted in Figure 3, which shows that **Q** appears to react several times faster than **N**.

Quinoline: HCN and NH_3 Formation

HCN and NH_3 were identified in the outflowing gases of the reaction of **Q**. Figure 4 shows that the HCN yield reaches about 70 mol% of the inflow of **Q** under a pressure of 20 bar and at 1173 K. Parallel to this, a 10−15% yield of ammonia was observed. Under a pressure of 30 bar yields of NH_3 increased to about 35 mol% (dotted line in Figure 4).

Benzonitrile and Azobenzene

As mentioned in the previous section, **BN** is a by-product of the reaction of **Q**. Four experiments were performed to

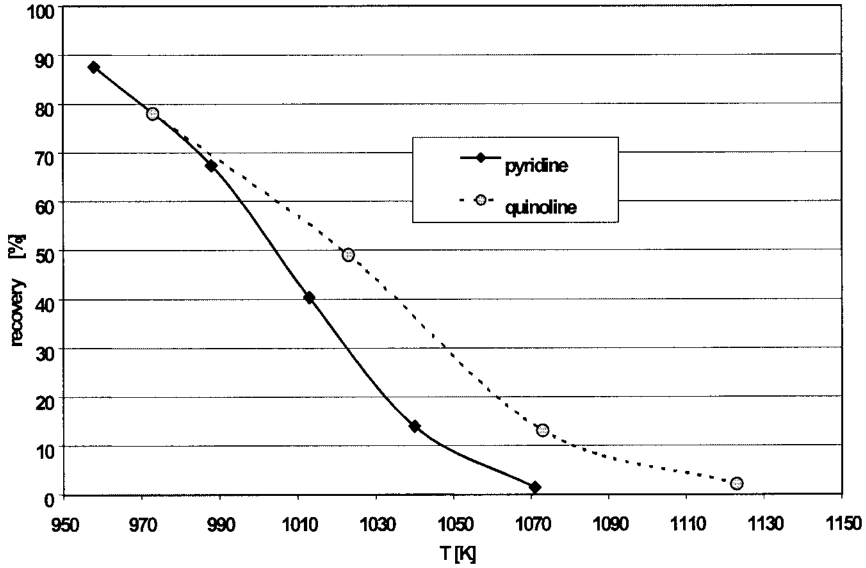


Figure 1. Recoveries of pyridine and quinoline

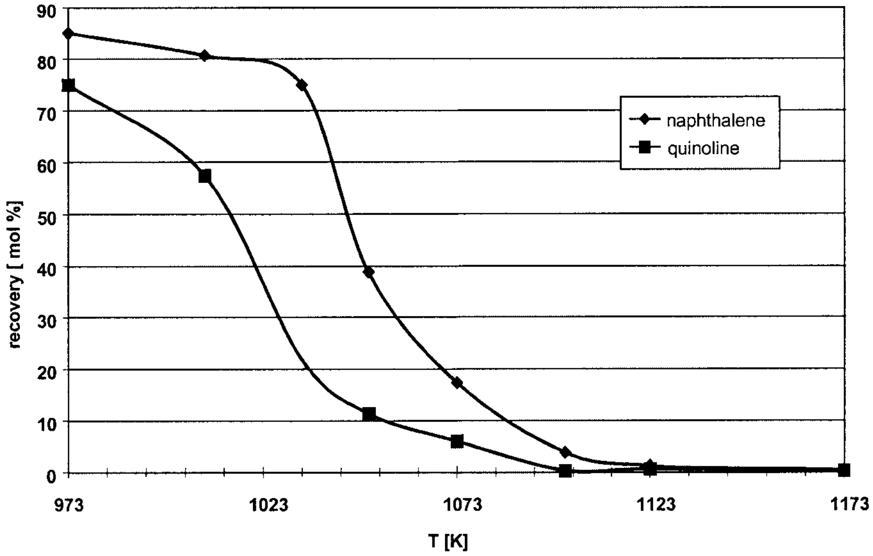


Figure 3. Naphthalene and quinoline recoveries at 30 bar H_2

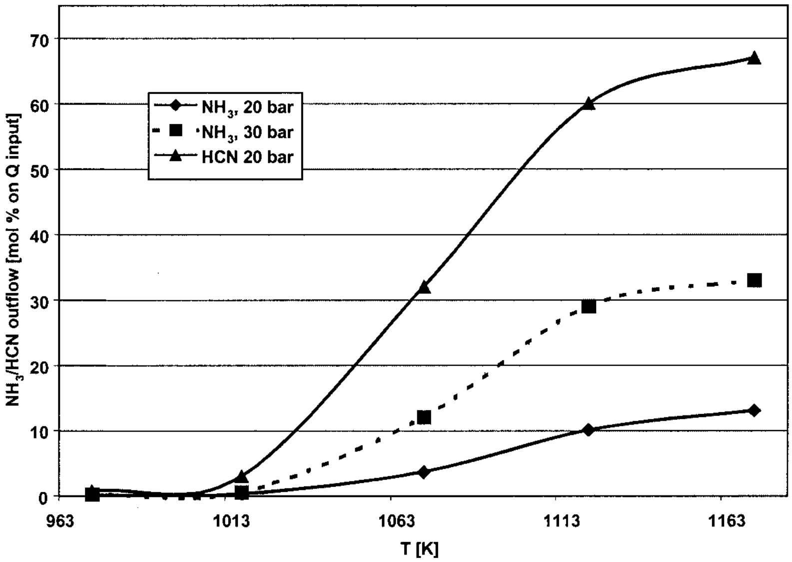


Figure 4. HCN and NH_3 formation from the reaction of quinoline

see if – and how rapid – the cyano group could be removed under the thermal hydrogenolysis (TH) conditions used. The results show that this very strong Ar–CN bond, BDE 131 kcal·mol^{-1},[5] can be hydrogenolysed with some 70% efficiency under relatively mild conditions (1123 K, 20 bar H_2). The only gaseous N-containing product was found to be HCN.

Azobenzene, when co-fed into the reactor with BN, was completely converted at 973 K. The azo-function is very likely converted to N_2, but this has not been checked. Neither NH_3 nor N-containing organics could be detected, except for traces of aniline at lower temperatures.

Rates

Table 1 summarises the available literature data on the thermolytic reactions of **P** (Entries 1–8) and **Q** (10–12). The calculated (extrapolated) first-order rate constants for **P** at 1250 K have a range of over 2 orders of magnitude. However, when leaving out data extrapolated from measurements taken at much higher temperatures (Entries 2,6–8) the *k* values are around 1–2 s^{-1}. The value (also extrapolated) determined in this work (Entry 9) is decidedly larger; depending on its temperature dependence, $k \approx 5$ s^{-1} (for an experimental E_a of 40 kcal·mol^{-1})[4] to even 200 (assuming E_a = 75 kcal·mol^{-1}).[6] If we accept the shock-tube data of Entries 6 and 7 as representative for unimolecular homolysis of the (weakest) C–H bond in **P**, the (extrapolated) rate constant is some 20 times less than those for thermolysis, and is essentially negligible compared with our value for hydrogenolysis.[7–13]

The limited data on **Q** (Entries 10–12) show similar *k* values for shock-tube and regular thermolysis (despite a

Table 1. Summary of kinetic data for the reactivity of **P** and **Q**

Entry/[Ref.]/Technique Reaction	A [s^{-1}]	E_a [kcal·mol^{-1}]	k (at 1250 K) [s^{-1}]	T range [K]
1/[4]/static vs. time in Ar (0.012 bar) pyridine → products	7.3×10^{12}	73.8	0.88	1135−1200
2/[7]/shock tube in Ar (0.2−4 bar) pyridine → products	1.6×10^{16}	100.3	0.044	1700−2000
3/[6]/stirred flow reactor, bath: pyridine pyridine → products	6.3×10^{6}	39.5	0.77	1173−1273
4/[8]/static vs. time in He pyridine → products	3.8×10^{12}	70.0	2.12	1223−1323
5/[9]/static vs. time, bath: pyridine (0.08−0.13 bar) pyridine → 2-pyridyl + H·	1.26×10^{15}	85.1	1.60	1100−1220
6/[10]/shock tube in Ar pyridine → 2-pyridyl + H·	7.94×10^{15}	98.0	0.055	1300−1800
7/[11]/shock tube in Ne (0.1−0.5 bar) pyridine → 2-pyridyl + H·	7.69×10^{14}	95.0	0.018	1711−2415
8/[12]/shock tube in He (2.2−3.4 bar) pyridine → products	$6.54 \times 10^{9}/8.1 \times 10^{10}$	52.5/63.5	5.50/0.620	1615−2032/1725−2335
9/this work: pyridine (see text)	rate constant k_P for hydrogenolysis (20 bar)	−	>5 (−200)	1073−1103
10/[13]/shock tube in Ar (0.93 bar) quinoline → products	1.00×10^{13}	75.5	0.61	1275−1700
11/[4]/static vs. time in Ar (0.012 bar) quinoline → products	1.59×10^{13}	77.9	0.37	1135−1200
12/[8]/static vs. time in He quinoline → products	2.1×10^{8}	44.9	2.9	1130−1273
13/this work: quinoline (see text)	rate constant k_Q for hydrogenolysis (30 bar)	−	ca. 0.6 k_P	1073−1103

large variation in rate parameters), but not unlike those for the thermolysis of **P**. Whatever their significance, our observed rate (constant) for hydrogenolysis (compare Figure 1) is about a factor of 1.5−2 less than that for **P**, although the hydrogen pressure used was higher (30 rather than 20 bar). Note that Bruinsma et al.[4] have reported a comparable relative rate for static pyrolysis (Entries 1 and 11).

Whereas **Q** reacts a bit more slowly than **P** and faster than **N**, by far the largest rate difference is that between **P** and benzene **B**. At 20 bar H_2, 50% benzene is converted at a temperature of about 1250 K,[1] while **P** reaches the same degree of conversion at about 1000 K (Figure 1). In free energy terms, this suggests that the hydrogenolysis of **P** is about 13 kcal·mol^{-1} less "costly" than that of **B**. Since the C−H bond neighbouring the nitrogen of **P** is (only) about 5 kcal·mol^{-1} weaker than a benzene C−H bond,[14] the major contribution to the difference in rates must be from rate determining steps other than C−H bond scission − a conclusion consonant with the observed overall rates (rate constants) given in Table 1.

Mechanisms

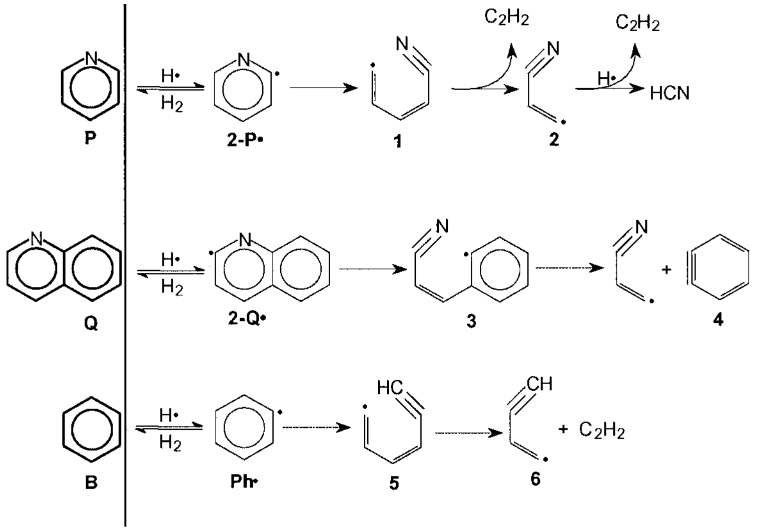
The proposed reaction rationales are presented in Schemes 1 and 2. Also aimed at understanding the formation of the detected products these schemes illustrate a (major part of) the TH pathways of **P** and **Q**.

In Scheme 1 the (reversible) hydrogen abstraction from **P/Q/B** by hydrogen atoms to give the radicals **2-P·**, **2-Q·** and phenyl **(Ph·)** is considered. This "assisted pyrolysis" with fragmentation of **Ph·** is important in the high temperature pyrolysis of benzene,[14] but insignificant under our conditions of hydrogenolysis. For **P** (and **Q**) the situation is different due to different thermochemistries. The heats of formation of **Ph·** and **2-P·** (78 and 86.5 kcal·mol^{-1}, respectively) differ by 8.5 kcal·mol^{-1}. For the ring-opened species **5** and **1** (with estimated heats of formation of 142 and 113 kcal·mol^{-1}, respectively),[5] only 26 kcal·mol^{-1} is required for the isomerisation of **2-P·** compared with 64 kcal·mol^{-1} for **Ph·**. This allows a facile reaction of **P**, via **2-P·**, **1** and **2** − and/or their closed-shell hydrogenation products − to, for example, acetylene and HCN. To put this on a more quantitative kinetic basis, consider equilibrium (1):

$$\mathbf{P} + \mathrm{H}\cdot \rightleftarrows \mathbf{2\text{-}P}\cdot + \mathrm{H}_2 \qquad (1)$$

$$\mathbf{2\text{-}P}\cdot \rightarrow \text{products} \qquad (2)$$

The value of K_1 can be estimated as follows. The reaction, based on a C−H bond strength[14] of about 106 kcal·mol^{-1}, is endothermal by about 3 kcal. On the other hand, the entropy term (at 1000 K) is about 8 cal·mol^{-1}·K^{-1} positive,[15] leading to log $K_1 \approx 1$. The logarithm of the equilibrium ratio [H·]/[H_2] in 20 bar hydrogen is −9.3 at 1000 K



Scheme 1. TH of **P**, **Q** and **B** − comparison of the hydrogen abstraction pathways

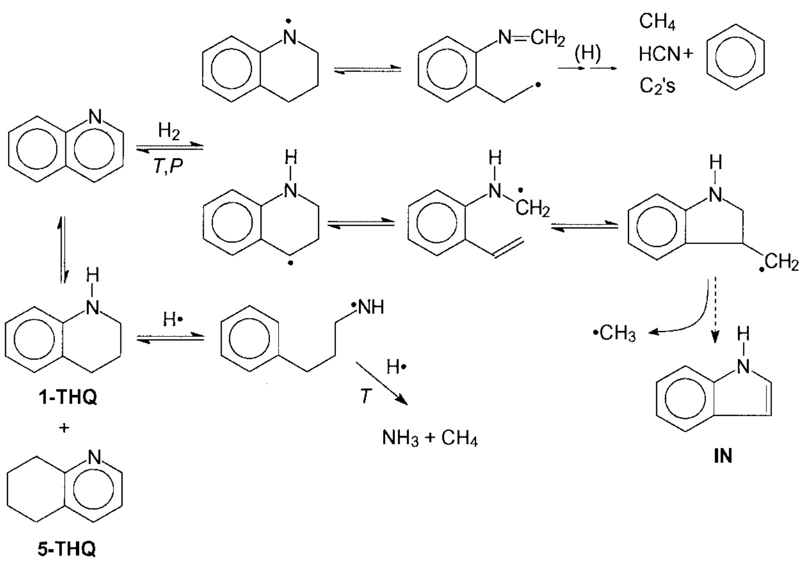
(about −8.3 at 1100 K, and about −7.3 at 1200 K).[16] Consequently, the (log) ratio of [**2-P·**]/[**P**] is − 8.3. For log k_2, reasonable parameters [15] are log A_2 = 14 and E_2 = 30, hence log k_2 = 7.4 at 1000 K. This leads to an overall first-order rate constant of about 0.1 s^{-1} for the conversion of **P** at 1000 K, which is very close to the observed rate (Figure 1): ca. 50% reaction in 4.5 s implies a unimolecular rate constant of about 0.15 s^{-1}. By applying this approach to the reaction of **P** at 1100 K using the same parameters, a rate constant of about 5 s^{-1} is obtained (compare Table 1).

In the case of quinoline the reaction via the ring-opened isomer **3** is not as straightforward as it is for pyridine; the splitting off of benzyne **(4)**, requires much more energy (some 30 kcal·mol^{-1}) than the loss of acetylene in the case of pyridine. A possible mechanism for this process is the hydrogenation of **3** to the substituted benzene, which is then subject to simple and rapid "desubstitution".

In Scheme 2 another possibility is presented based on the addition of hydrogen atoms, leading to hydrogenation of the aromatic rings; the resulting intermediates are easily degraded further, either by spontaneous (C−C, C−N) bond homolysis or via radical species derived therefrom, as illustrated next.

Inasmuch as this scenario is relevant, the same should hold for **P**, which reacted only a bit more quickly than **Q**.

An analysis of available thermochemical data does not lead to clear-cut "advantageous" pathways for the hydrogenolysis of these or analogous (partially hydrogenated) N derivatives. Whereas the full hydrogenation of **P** to piperidine is exothermal by 45 kcal·mol^{-1} − about 4.5 kcal less than that of B to cyclohexane − N−H or N−C bonds, on the other hand, are about 6−8 kcal·mol^{-1} weaker than the corresponding C−C and C−H bonds.[5] The same can be said for dihydroarene-based pathways as discussed for **N**.[2]



Scheme 2. TH of **Q** by hydrogenation

In the competition reaction involving **Q** and **N**(aphthalene), the latter appeared to react only several times more slowly, and compared with rates observed in our earlier study, at least an order of magnitude more rapidly, by a comparable hydrogenation/ring opening/fragmentation scenario.[2] The reason for this difference is as yet unknown. For similar reactivities, the hydrogenolysis would be expected to occur on both rings of **Q**. However, no aliphatic pyridine derivatives, except the earlier mentioned **5-THQ**, were detected in the liquids produced in the experiments with quinoline, whereas products arising from hydrogenolysis of the "pyridine" ring were clearly present. One explanation could be that the aliphatic pyridine derivatives are even more vulnerable to TH, and get readily converted even at mild temperatures.

In the proposed rationale (Scheme 2) both HCN and ammonia are direct products from the hydrogenolysis of **Q**. The question of whether HCN can be hydrogenolysed to form ammonia (observed at high degrees of conversion of **Q**), which seems very unlikely on thermodynamic grounds, cannot yet be answered on the basis of the present results.

Azobenzene reacted completely at the lowest temperature of this study (973 K), with no intermediate products formed. One reason for this is the character of the azo bond. Reaction by addition of hydrogen to the nitrogen double bond appears to be energetically unfavourable. Hydrogenolysis by *ipso*-addition of a hydrogen atom may well occur, but spontaneous homolysis of the rather weak C−N bond is the most likely first step.

Also, benzonitrile reacted for a great part under relatively mild conditions. Similar to the results of earlier studies,[17,18] the facile removal of the −CN functionality under hydrogenolysis conditions, despite the very strong arene−CN bond, can be understood in terms of the (reversible) addition of a hydrogen atom to the carbon of the cyano function, followed by fragmentation to HCN and the phenyl radical.

Conclusions

High-pressure thermal hydrogenolysis has proven to be an efficient way to convert (hetero)aromatics. Basic product patterns are common for all compounds studied and can be briefly described as "mineralization" and, at sufficiently high temperatures, "gasification". The nitrogen atoms of pyridine **P** and quinoline **Q** are converted into HCN and NH_3 in reactions which are (much) faster than the degradations of benzene or naphthalene. Decomposition is induced by hydrogen atoms. Thermochemical considerations show that reversible formation of 2-pyridyl radicals followed by ring opening to a cyano-pentadienyl radical − **1** in Scheme 1 − is much easier than the analogous process with benzene. Alternatively, (partial) hydrogenation of **P** and **Q** may occur, also followed by ring opening and further fragmentation.

Experimental Section

Setup: The high-pressure set-up as well as the experimental procedures have been described elsewhere.[1]

Sampling and Analyses of Inorganic Products: Inorganic products were trapped in an ice-cooled, magnetically-stirred water trap. Upon detection, by treating the solution obtained with a standard solution of Fe^{II}/Fe^{III} (0.1 mol each as chlorides), hydrogen cyanide was quantified by potentiometric titration (0.1 mol $AgNO_3$, Titrisol standard solution) on an automatic Mettler 25 titrator.
Addition of HCl to the aqueous solution obtained followed by evaporation in a rotavap gave a white, subliming crystalline product. The substance was analysed by IR spectroscopy and the spectrum matched that of analytically pure ammonium chloride. Ammonia was quantified by pH-metric titration with a 0.01 M HCl solution (Titrisol).

Chemicals: The following chemicals were utilised (purity given in %): benzene (Merck p.a., 99%, distilled), monobromobenzene (Baker, > 99.5%), naphthalene (Janssen Chimica, > 99%), benzonitrile (Merck, > 99%), azobenzene (> 99%, recrystallised), *n*-pentane (Baker Analysed, > 99%), quinoline (> 99%, distilled in vacuo), pyridine (Merck, > 99%), hydrogen (Air Products, 99.995%), methane (Air Products, 99.995%), nitrogen (Air Products 99.995%).

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