JOURNAL OF CATALYSIS 112, 411–417 (1988)

Hydrodenitrogenation of Benzo(f)quinoline and Benzo(h)quinoline over a Sulfided $NiO-MoO_3/\gamma-Al_2O_3$ Catalyst

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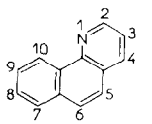
Received May 1, 1987; revised January 18, 1988

The hydroprocessing of benzo(f)quinoline and benzo(h)quinoline was studied by a batch method at 340°C and 70 bar H_2 over a commercial sulfided $NiO-MoO_3/\gamma-Al_2O_3$ catalyst. The hydrogenation of the N ring occurs at similar rates for the two isomeric benzoquinolines but is slower than the hydrogenation of the N ring of quinoline. On the other hand, an important and unusual percentage of $C_{sp^2}-N$ bond cleavage is observed from the two intermediates 1,2,3,4-tetrahydrobenzo(f)quinoline and 1,2,3,4-tetrahydrobenzo(h)quinoline. These two main reactions, hydrogenation of N rings and cleavage of C–N bonds, are then discussed in terms of aromaticity; a decrease in aromaticity favors both the hydrogenation of N rings and the cleavage of $C_{sp^2}-N$ bonds.

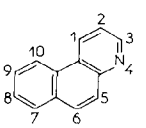
INTRODUCTION

We have recently reported (*1*, *2*) results on the hydrogenation of N heteroaromatics such as pyridine, quinoline, and acridine and have clearly shown the existence of a correlation between the ease of hydrogenation of the N ring and the aromatic character of this ring: the rates of hydrogenation increase with a decrease in the aromatic character of the ring to be hydrogenated.

Our continuing interest in acquiring better knowledge of the factors affecting hydrotreating reactions, particularly those concerning removal of N atoms (hydrodenitrogenation), has led us to investigate the hydroprocessing of the two isomeric benzoquinolines, benzo(h)quinoline (**1.A**) and benzo(f)quinoline (**2.A**) over a commercial



1.A



2.A

sulfided $NiO-MoO_3/\gamma-Al_2O_3$ catalyst, HR 346, used in all our series, at 340°C and 70 bar H_2. These two benzoquinolines can be regarded as representative models for N compounds present in heavy fuels (*3*). However, there is only one recent paper (*4*) devoted to the hydrodenitrogenation of these two compounds over a supported catalyst (Ni–W), and no kinetic data were given. Vierhapper and Eliel (*5*) have performed the hydrogenation of benzo(h) quinoline over noble metal catalysts in an acidic aqueous medium, but again no kinetic data are available. Nevertheless, the possible implications of this work will be considered in the discussion.[1]

EXPERIMENTAL

The catalyst used was Procatalyse HR 346, which had the following composition: 3% NiO, 14% MoO_3, and 83% Al_2O_3. It was sulfided at atmospheric pressure using a fluidized-bed technique with a gas mixture of 15% H_2S and 85% H_2 by volume. The catalyst (5 g; particle size 0.100–0.125 mm) was heated in flowing H_2/H_2S (gas flow 120 ml/min) from 20 to 400°C (8°C/min) and held at 400°C for 4 h, then cooled and finally swept with nitrogen for 30 min.

[1] We thank one of the referees for drawing this work to our attention.

0021-9517/88 $3.00

Experiments were carried out in a 0.3-liter stirred autoclave (Autoclave Engineers type Magne-Drive), operating in a batch mode and equipped with a system for sampling of liquid during the course of the reaction without stopping the agitation.

Typical procedure was as follows. A 0.1 *M* solution of organic reactant in 80 ml of decane (analytical grade) was poured into the autoclave. The sulfided catalyst (0.8 g) was rapidly added to this solution under nitrogen to avoid contact with air. After it was purged with nitrogen, the temperature was increased under nitrogen until it reached 340°C. Nitrogen was then removed and hydrogen was introduced at the required pressure (70 bar). Zero time was taken when the agitation began.

Benzo(h)quinoline was commercially available; benzo(f)quinoline was a generous gift from I.F.P.

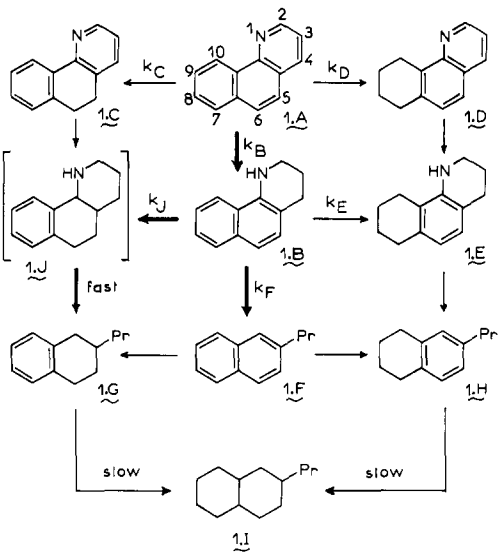
Analyses were performed on a Girdel 30 gas chromatograph equipped with a flame ionization detector using hydrogen as carrier gas. The wall-coated open tubular fused silica capillary columns used were Chrompack CP Sil 5 CB (0V1) or CP Sil 19 CB (0V17), 10 m × 0.22 mm i.d. Products were identified by GC-MS analysis.

The rate constants were deduced from the experimental curves by curve fitting and simulation using an HP 9820 computer with an HP 9826 A tracing table, assuming all the reactions to be first order in the organic reactant. The calculated reaction rate constants (in min^{-1}) depend on the weight of catalyst and are then referred to 1 g of catalyst.

RESULTS

Hydrodenitrogenation of Benzo(h)quinoline (1.A)

The products identified during the overall HDN of benzo(h)quinoline (**1.A**) are shown in Scheme 1. These are 1,2,3,4-tetrahydrobenzo(h)quinoline (**1.B**); 5,6-dihydrobenzo (h)quinoline (**1.C**); 7,8,9,10-tetrahydrobenzo(h)quinoline (**1.D**); 1,2,3,4,7,8,9,10-octahydrobenzo(h)quinoline (**1.E**); 2-propylnaphthalene (**1.F**); 2-propyl-1,2,3,4-tetrahydronaphthalene (**1.G**); 6-propyl-1,2,3,4-tetrahydronaphthalene (**1.H**); and 2-propyldecalin (**1.I**). Most of these products have been identified by GC-MS analysis.



SCHEME 1. Reaction network for hydroprocessing of benzo(h)quinoline over sulfided $NiO-MoO_3/\gamma-Al_2O_3$ at 340°C and 70 bar H_2.

The structure of the two isomeric tetrahydro derivatives (**1.B**) and (**1.D**) was definitely attributed by trapping these intermediates as their hydrochloride salts, removing solvent and neutral compounds, and regenerating the free bases in basic medium. The analysis of the ^{13}C NMR spectrum of the resulting mixture reveals a peak at δ 42.2 ppm characteristic of a saturated C–N bond. The most abundant (M + 4) intermediate is therefore (**1.B**) in agreement with the preceding findings (*4*). It should be noted that most of these intermediates were also observed on the $Ni-W/Al_2O_3$ catalyst used by Shabtai *et al.* (*4*), thus illustrating similar behavior in the activity of sulfided $Ni-Mo/Al_2O_3$ and $Ni-W/Al_2O_3$ catalysts.

The concentration vs time plots for the hydroprocessing of benzo(h)quinoline are given in Fig. 1. It can be seen in this figure that (**1.B**) is rapidly formed compared with

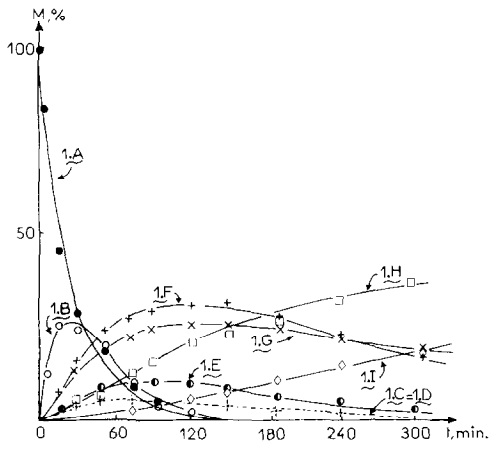


FIG. 1. Product distribution vs time for hydroprocessing of benzo(h)quinoline over sulfided $NiO-MoO_3/\gamma-Al_2O_3$ at 340°C and 70 bar H_2. Benzo(h)quinoline (●); 1,2,3,4-tetrahydrobenzo(h)quinoline (○); 5,6-dihydrobenzo(h)quinoline and 7,8,9,10-tetrahydrobenzo(h)quinoline (⊣⊢); 1,2,3,4,7,8,9,10-octahydrobenzo(h)quinoline (◐); 2-propylnaphthalene (+); 2-propyl-1,2,3,4-tetrahydronaphthalene (×); 6-propyl-1,2,3,4-tetrahydronaphthalene (□); 2-propyldecalin (◇).

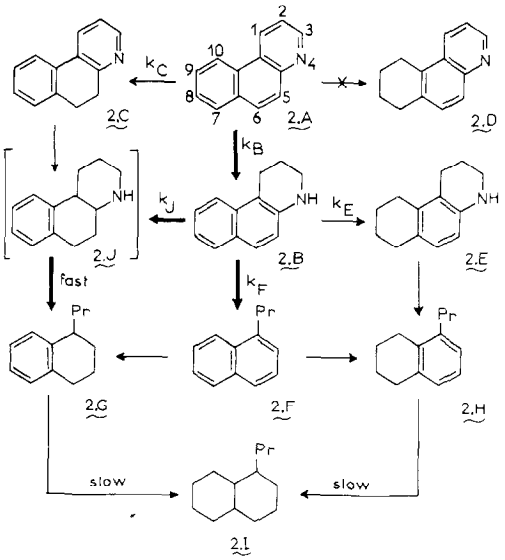
(**1.C**) and (**1.D**), thus confirming the easier hydrogenation of the N ring, as also observed for quinoline itself under the same operating conditions (*1*). The curves drawn in Fig. 1 are computer-simulated based on the reaction network shown in Scheme 1. The rate constants which will deserve some comments are those for the disappearance of both benzo(h)quinoline (**1.A**) and 1,2,3,4-tetrahydrobenzo(h)quinoline (**1.B**): $k_B = 30 \times 10^{-3}$, $k_C = k_D = 3 \times 10^{-3}$, $k_E = 7 \times 10^{-3}$, $k_F = 22 \times 10^{-3}$, and $k_J = 18 \times 10^{-3}$ $min^{-1} \cdot (g \cdot cat.)^{-1}$. 2-Propyl-1,2,3,4-tetrahydronaphthalene (**1.G**) was assumed to result from hydrogenation of (**1.B**) through a fast decomposition of the postulated intermediate (**1.J**). This assumption seems to be valid because 2-propylnaphthalene (**1.F**) should have given (**1.G**) and (**1.H**) in nearly identical amounts, as shown in the hydrogenation of 1-alkyl- or 2-alkylnaphthalenes (*6*). It should be noted finally that (i) denitrogenation is almost complete after 2 hr and (ii) a relatively unusual amount of aromatic hydrocarbons is observed for this period as due to C_{sp2}–N bond cleavage and not to dehydrogenation of 2-propyldecalin. These points will be discussed later.

Hydrodenitrogenation of Benzo(f)quinoline (*2.A*)

The reaction network for the hydroprocessing of benzo(f)quinoline (**2.A**) is not very different from that proposed for the HDN of its isomer, benzo(h)quinoline (**1.A**), except that 7,8,9,10-tetrahydrobenzo (f)quinoline (**2.D**) was not detected.

The products identified during the hydrodenitrogenation of benzo(f)quinoline (**2.A**) are shown in Scheme 2. These are 1,2,3,4 tetrahydrobenzo(f)quinoline (**2.B**), whose structure was determined in a manner similar to that of its isomer (**1.B**); 5,6-dihydrobenzo(f)quinoline (**2.C**); 1,2,3,4,7,8,9,10-octahydrobenzo(f)quinoline (**2.E**); 1-propylnaphthalene (**2.F**); 1-propyl-1,2,3,4-tetrahydronaphthalene (**2.G**); 5-propyl-1,2,3, 4-tetrahydronaphthalene (**2.H**); and 1-propyldecalin (**2.I**).

The concentration vs time plots for the hydroprocessing of benzo(f)quinoline are given in Fig. 2. From this figure it can be seen that the hydrogenation of the N ring is



SCHEME 2. Reaction network for hydroprocessing of benzo(f)quinoline over sulfided $NiO-MoO_3/\gamma-Al_2O_3$ at 340°C and 70 bar H_2.

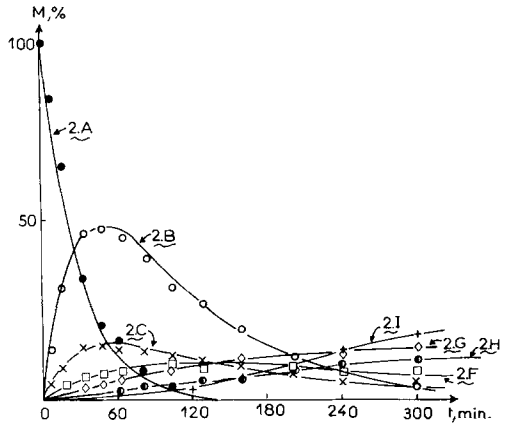


FIG. 2. Product distribution vs time for hydroprocessing of benzo(f)quinoline over sulfided NiO–MoO_3/γ-Al_2O_3 at 340°C and 70 bar H_2. Benzo(f)quinoline (●); 1,2,3,4-tetrahydrobenzo(f)quinoline (○); 5,6-dihydrobenzo(h)quinoline (×); 1-propylnaphthalene (□); 1-propyl-1,2,3,4-tetrahydronaphthalene (◇); 5-propyl-1-2,3,4-tetrahydronaphthalene (◐); 1-propyldecalin (+).

easier than the hydrogenation of the other two aromatic rings; however, the intermediate (**2.D**) was not detected by GC-MS analysis.

The curves drawn in Fig. 2 are derived from the reaction network shown in Scheme 2. From the total disappearance rate constant for benzo(f)quinoline (**2.A**) it was possible to calculate the corresponding appearance rate constants for (**2.B**) and (**2.C**), $k_B = 31 \times 10^{-3}$ and $k_C = 8 \times 10^{-3}$ $min^{-1} \cdot (g \cdot cat.)^{-1}$ respectively. These constants are of the same order of magnitude as those measured in the equivalent steps of hydrogenation of benzo(h)quinoline.

The comparison of Figs. 1 and 2 for the disappearance of the tetrahydro derivatives is most significant: (**1.B**) and (**2.B**) are formed at similar rates (30×10^{-3} and 31×10^{-3} $min^{-1} \cdot (g \cdot cat.)^{-1}$, respectively) but their rate of disappearance is somewhat different ($k_E + k_F + k_J = 47 \times 10^{-3}$ $min^{-1} \cdot (g \cdot cat.)^{-1}$ for (**1.B**) and 12×10^{-3} $min^{-1} \cdot (g \cdot cat.)^{-1}$ for (**2.B**). The lower reactivity of (**2.B**) does not allow the calculation of the individual rate constants k_E, k_F, and k_J with good accuracy. Nevertheless, from the experimental data plotted in Fig. 2, it can be seen that the first denitrogenated intermediate is 1-propylnaphthalene (**2.F**), followed by 1-propyl-1,2,3,4-tetrahydronaphthalene (**2.G**) and 5-propyl-1,2,3,4-tetrahydronaphthalene (**2.H**), so that the explanations given in the case of HDN of benzo(h)quinoline are still valid for benzo(f)quinoline, namely (i) a relatively unusual percentage of C_{sp2}–N bond cleavage is observed from (**2.B**) as compared with the hydrogenation of rings leading to (**2.G**) or (**2.H**), and (ii) (**2.G**) is more rapidly formed than its isomer (**2.H**), so that, for the same reasons given in the case of (**1.F**), (**2.G**) is assumed to result mainly from the decomposition of the highly reactive intermediate (**2.J**) as well as from the hydrogenation of (**2.F**).

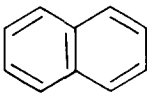
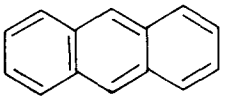
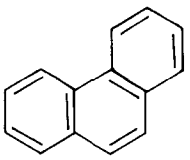
DISCUSSION

Hydrogenation of N Rings

The N rings of benzo(h)quinoline (**1.A**) and benzo(f)quinoline (**2.A**) are hydrogenated at similar rates and about ten times more slowly than the N ring of quinoline. The arguments developed in our recent papers (*1, 2*) to explain the large differences in the rates of hydrogenation of N heteroarmatics are based on the more or less important aromatic character of the ring to be hydrogenated compared with hydrogenation of the corresponding hydrocarbon rings. This is illustrated in Table 1 where the rates of hydrogenation increase with the decreased character of the ring to be hydrogenated. The angularity of phenanthrene compared to its isomer anthracene leads to an increased resonance energy and, as a consequence, to a decreased hydrogenation rate. The relative hydrogenation rates of N rings are given in Table 2 using the same source of data for resonance energies for the two series of hydrocarbons and N heterorings. As seen in this table, the rates of hydrogenation closely parallel those of the corresponding hydrocarbons and it was concluded that factors invoked in one series are readily transposable to the other.

TABLE 1

Resonance Energies and Relative Rate Constants for Hydrogenation of Hydrocarbons

Hydrocarbon	RE[a]	RE[b]	RE[c]	RE/ring[d]	k_{rel}
	36	0.38	39	40	1
	61	0.59	75	28	10
	84	0.71	105		36
	92	0.89			4

[a] Data from Ref. (*7*), in kilocalories per mole.
[b] Data from Ref. (*8*), in β units.
[c] Data from Ref. (*9*), in kilocalories per mole.
[d] Data from Ref. (*10*), in kilocalories per mole.

For angular systems like phenanthrene and phenanthridine, the resonance energy is increased compared with their "linear" isomers anthracene and acridine, thus leading to a decrease in the rates of hydrogenation (*7, 11*). A similar angular structure is present in the two isomeric benzoquinolines (**1.A**) and (**2.A**) and that could account for their low hydrogenation rates compared to quinoline.

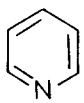
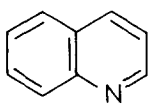
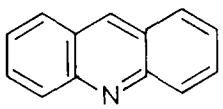
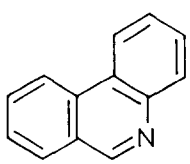
By comparison with the work of Vierhapper and Eliel (*5*), hydrogenation of pyridine, quinoline, acridine, and benzo(h) quinoline over a PtO_2 catalyst was shown to proceed through selective hydrogenation of N rings in a weakly acidic aqueous medium and through selective hydrogenation of benzene rings in a strongly acidic one. This could mean that sulfided Ni–Mo/Al_2O_3 or Ni–W/Al_2O_3 catalysts would be weakly acidic in their nature, in agreement with recent IR measurements (*12*). However, one must be careful when considering such an analogy because of the different operating conditions, hydrogen pressure, solvent and catalyst.

Decomposition of 1,2,3,4-Tetrahydro Derivatives [(***1.B***) *and* (***2.B***)]

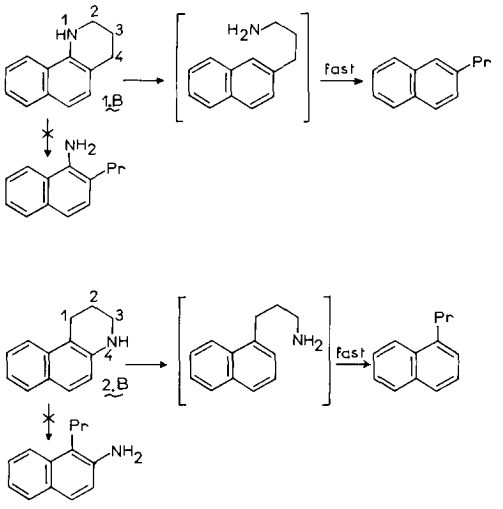
As already mentioned, the important feature to be noted here is the high percentage of C_{sp^2}–N bond cleavage to yield 2-propylnaphthalene or 1-propylnaphthalene through a fast decomposition of (2-naphthyl)-3-propylamine or (1-naphthyl)-3-propylamine (Scheme 3) as is generally observed for aliphatic amines under operating conditions such as those used in this work. It should also be noted that the cleavage of the C_{sp^3}–N bonds (C_2–N_1 in (**1.B**) and C_3–N_4 in (**2.B**)) should have given 2-propyl-1-naphthylamine and 1-propyl-2-naphthylamine, respectively, which would have been detected if present. This possibility can therefore be ruled out, in agreement

TABLE 2

Resonance Energies and Relative Rate Constants for Hydrogenation of *N*-Heteroaromatics

N heteroring	RE[a]	RE/ring[b]	k_{rel}
	43	42	1
	69	30	22
	106		24
			2

[a] Data from Ref. (*9*), in kilocalories per mole.
[b] Data from Ref. (*10*), in kilocalories per mole.



SCHEME 3. Illustration of C_{sp^2}–N bond cleavage in the decomposition of 1,2,3,4-tetrahydrobenzo(h) quinoline (**1.B**) and 1,2,3,4-tetrahydrobenzo(f)quinoline (**2.B**).

with the findings of Shabtai *et al.* over a Ni–W catalyst (*4*). In addition, 1-naphthylamine has been shown to be decomposed with a rate constant of the same order of magnitude as the rate constant k_F (*13*).

As already mentioned in the text, unusual amounts of 1- and 2-propylnaphthalenes are formed through cleavage of the C_{sp^2}–N bonds of 1,2,3,4-tetrahydrobenzo(f) quinoline and 1,2,3,4-tetrahydrobenzo(h) quinoline, respectively. This route represents about 40% in the case of 2-propylnaphthalene as deduced from the rate constant ratio $k_F/(k_E + k_F + k_J)$ and is estimated at about 30% in the case of 1-propylnaphthalene. These results contrast sharply with those reported for aniline used as a reference model where hydrogenolysis of the C_{sp^2}–N bond represents only 10% (*14*). This unusual degree of C_{sp^2}–N bond rupture was not completely unexpected from our considerations on the role of the aromaticity on both hydrogenation of aromatic rings and cleavage of C_{sp^2}–N bonds (*2, 15*).

From our kinetic results it can be seen that (**2.B**) reacts more slowly than its isomer (**1.B**). In order to explain their own results, Shabtai *et al.* (*4*) have invoked steric interactions due to the peri-position of the N atom in (**1.B**) relative to the H atom at C_8. There would result some displacement of the N atom out of coplanarity with the aromatic system. These explanations find recent support from ^{13}C NMR measurements which show the influence of steric effects on the NMR displacement of chemical shifts at the peri-position (*16*). Nevertheless, it should be added that these steric considerations may also have direct consequences on the aromaticity. Depending on the ability of the lone pair on the nitrogen atom to conjugate with the aromatic ring differences would result in the aromatic character of the molecule which would lead to differences both in the reaction rates and in the partitioning for hydrogenation vs hydrogenolysis.

CONCLUSION

From the present studies we can draw the following conclusions:

(i) As for other N heteroaromatics, N rings of the two isomeric benzoquinolines must be hydrogenated prior to any C–N bond cleavage. The ease of hydrogenation is related to the aromatic character of the ring to be hydrogenated, thus confirming our previous assumptions.

(ii) The presence of an important and unusual degree of C_{sp^2}–N bond cleavage, up to 30–40%, from the two isomeric 1,2,3,4-tetrahydrobenzoquinolines is particularly relevant and is also related to the aromatic character of the ring adjacent to the C_{sp^2}–N bond to be cleaved. A low aromatic character favors both hydrogenation of N rings and cleavage of C_{sp^2}–N bonds in compounds with aniline-like structure.

ACKNOWLEDGMENTS

This work was supported by the Groupement Scientifique "Hydrotraitement Catalytique" CNRS, related to the industrial partners of the G.I.E. ASVAHL (TOTAL., ELF, and I.F.P.). M. H. Toulhoat of I.F.P. is gratefully acknowledged for his generous gift of benzo(f)quinoline.

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