Simple and competitive catalytic hydrogenation of nitrobenzene, allyl benzyl ether and benzyl crotyl ether in alkaline alcoholic media

E. Lamy-Pitara [a,*], B. N'Zemba [a], J. Barbier [a], F. Barbot [b], L. Miginiac [b]

[a] *Catalyse en Chimie Organique, LACCO, U.M.R. 6503, Université de Poitiers, 40, avenue du Recteur Pineau, 86022 Poitiers, France*
[b] *Chimie Organométallique appliquée à la synthèse organique, U.R.A. C.N.R.S. 574, Université de Poitiers, 40, avenue du Recteur Pineau, 86022 Poitiers, France*

Abstract

The catalytic hydrogenation of nitrobenzene into aniline, in ethanolic solutions modified by different additions of KOH, was studied. Platinum catalysts supported on graphite were used. In ethanolic solutions, different dimer reaction intermediates (azoxybenzene, azobenzene, hydrazobenzene), strongly adsorbed on the catalyst, were formed thus inducing a decrease of selectivity in aniline. The best selectivity in aniline was obtained in a neutral or slightly alkaline solution. The competitive hydrogenation of nitrobenzene with benzylic ethers (allyl benzyl ether: $C_6H_5-CH_2-O-CH_2-CH=CH_2$ and benzyl crotyl ether: $C_6H_5-CH_2-O-CH_2-CH=CH-CH_3$) was also studied in the same experimental conditions, as a function of the acidity of the solution (obtained by addition of KOH or H_2SO_4). In an acid solution the group C=C was more easily hydrogenated than the NO_2 group whereas in an alkaline solution the opposite result was obtained. The hydrogenation rate of the crotyl group was lower than that of the allyl group and became equal to zero in strong alkaline solutions. This result can be explained by a steric effect and/or an electronic donor effect of the methyl group. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

An abundant literature is devoted to the catalytic hydrogenation of nitrobenzene into aniline.

Metals used as catalysts include nickel, platinum, palladium, rhodium and ruthenium. The order of activities is as follows: $Pd/C > Rh/C > Rh/Al_2O_3 > Raney\ Ni$ [1]. Although, platinum and palladium catalysts are largely studied because of their good reactivity and selectivity in mild experimental conditions [2–4], nickel, copper or chrome (often used in the state of sulfides or oxides) are the most commonly used catalysts in the industry [1,5,6].

---

* Corresponding author. Tel.: +33-49-45-39-56; Fax: +33-49-45-34-99

It is known that in liquid phase hydrogenation of nitrobenzene the mechanism and the obtained products depend strongly on the acidity of the solution [2].

In an acid solution aniline is obtained through consecutive reactions involving phenylhydroxyl-amine as an intermediate product [7]. Furthermore, the produced aniline can also be further hydrogenated thus decreasing the yield in aniline [8].

In a basic solution a more complex mechanism occurs leading first to the formation of different dimers (azoxybenzene, azobenzene and hydrazobenzene) [7], which are generally slowly converted to aniline.

Debus and Jungers [9] showed that, in an alcoholic solution with a Raney nickel catalyst, dimers (such as azoxybenzene, azobenzene and hydrazobenzene) accumulated before being converted to aniline. They also found that the hydrogenation of these intermediates needs more severe experimental conditions. This conclusion has been confirmed by other authors [6,10,11].

On the other hand, with Raney nickel catalysts, which were previously treated with chloroplatinic acid, the reduction of nitrobenzene leads directly to aniline without formation of intermediates [12]. Similar results were obtained by Wisniak and Klein [1] with rhodium and palladium catalysts supported on alumina and carbon, whereas Ru/C catalysts were not active in the same experimental conditions ($T = 373–483$ K, $p(H_2) = 5.6–56$ atm). The results above confirm the important influence of the acidity on the mechanism of the reaction.

Concerning the competitive hydrogenation between two aromatic compounds having a nitro group and a C=C group respectively very few works have been reported in the literature [13–15]. The hydrogenation of an equimolar mixture of 2-phenylpropene and 4-nitrotoluene in different solvents on 5% Pt/SiO_2, leads to the preferential hydrogenation of 2-phenylpropene [13,14]. Similar results were obtained in the case of competitive hydrogenation of phenylacetylene and nitrobenzene (in 96% ethanol and with nickel catalysts), where the triple bond was first hydrogenated selectively to the double bond [13,15].

In the first part of this paper the hydrogenation of nitrobenzene in a basic alcoholic solution is presented. It is followed by a study of the competitive hydrogenation between this compound and two benzylic ethers having a lateral chain: the allyl benzyl ether ($C_6H_5–CH_2–O–CH_2–CH=CH_2$) and the benzyl crotyl ether ($C_6H_5–CH_2–O–CH_2–CH=CH–CH_3$), as a function of the acidity of the solution, allowing to compare the reactivities of the $–NO_2$ function and of the C=C function. The purpose of this work was to define the conditions and in particular the role of the acidity of the solution, allowing to hydrogenate selectively the NO_2 function of an aromatic compound bearing a lateral chain with a C=C bond [16].

2. Experimental

The platinum catalysts, used in this work, were prepared by impregnation of pure granular graphite (Lonza KS-15), of a specific area equal to 14 m^2/g, with an aqueous solution of chloroplatinic acid (0.2 to 5%) and reduction at 573 K. The graphite support was pretreated in a hydrogen stream at 1273 K and in the air at 573 K [8].

The obtained Pt/graphite catalysts were characterized in situ by cyclic voltammetry and also by hydrogen and oxygen chemisorption (by pulsed chromatography) and by transmission electron microscopy. A glass cell was used for their characterization by cyclic voltammetry. This cell, used also as reactor for the hydrogenation reactions, has five holes allowing to introduce three electrodes (working, counter and reference electrodes) and also the inlet and outlet of gases (N_2 or H_2) [17,18].

The granular Pt/graphite catalyst (200 mg) was deposited on a glass frit; it was stirred and maintained in suspension during the hydrogenation reaction by a counter current hydrogen flow (of a rate: 180 ml/min).

The hydrogenation experiments were carried out in an alcoholic solution (95% ethanol) of different acidities (obtained by addition of KOH or H_2SO_4), at 299 K, with $p(H_2) = 1$ atm and small concentrations in organic compound ($2.5 \cdot 10^{-3}$ M) allowing to avoid a limitation of the reaction rate by the diffusion rate of hydrogen.

Most of organic compounds used in this work were of commercial origin (Fluka, pro analysis, purity $\geq 99.5\%$). The benzyl ethers ($C_6H_5CH_2OR$, with R=CH_2=$CHCH_2$, CH_3CH=$CHCH_2$, $CH_3CH_2CH_2$ and $CH_3CH_2CH_2CH_2$) were synthesized by reaction of benzylbromide with the corresponding saturated or unsaturated alcohol, according to the method of Cookson and Wallis [19].

The progress of the reaction was followed by HPLC (Waters 486) using a Bondapak C18 column, with a 50:50 volumetric ratio of methanol–water eluent and a UV detector, allowing to detect benzenic compounds.

The initial selectivities of different reaction products, reported in Table 2, are defined as the ratios of formation rates of these products to the consumption rate of the reactant at a reaction time $t = 0$. The maximum selectivity in aniline indicates the maximum quantity of produced aniline divided by the corresponding quantity of converted reactant.

3. Results

3.1. Characterization of catalysts

The platinum catalysts supported on graphite, prepared by impregnation of different platinum amounts (0.2% to 5%) as described in the experimental part, were characterized in situ by cyclic voltammetry [18,20] and by gas phase chemisorption of hydrogen and oxygen following the method of 'pulsed chromatography' [21].

The metallic surface area was obtained by integration of the anodic or cathodic parts of the voltammograms corresponding to the desorption or the adsorption of a monolayer of hydrogen, according to the reaction: $H^+ + e^- \Leftrightarrow H_{ads}$ [18,20].

The platinum surface area values, measured by cyclic voltammetry (with an uncertainty of the order of 10%) are given in Table 1, for different platinum loadings. From these surface area values and taking into account the platinum loadings, the dispersion and the average size of platinum particles were evaluated (Table 1).

Table 1
Characterization of Pt/graphite catalysts by cyclic voltammetry

	Metal loading (% Pt/gr)					
	0.2	0.5	1	2	3	5
Metallic surface area (cm^2/g)	2130	3070	7110	8710	11400	12000
Dispersion (%)[a]	34 (30)[a]	20.5 (20)[a]	22 (22)[a]	17 (20)[a]	12 (12)[a]	8 (6)[a]
Metal particle size (nm)	2.5	4	3.9	5	7	10

[a] Dispersion measured by hydrogen chemisorption (by pulsed chromatography).

The metal dispersion was also measured by chemisorption of hydrogen pulses. It can be remarked that the dispersion values, evaluated by this technique, are about equal to those found by cyclic voltammetry (Table 1).

Three catalysts, corresponding to 0.2%, 0.5% and 3% platinum loadings, were also analysed by TEM and the related histograms were traced (Fig. 1). Different particle size distributions were obtained for these platinum catalysts:

- for 0.2% Pt/g the particle size varies between 10 Å and 70 Å, with the highest particle density, d, being: $20 \leq d \leq 40$ Å.
- for 0.5% Pt/g the particle size varies between 20 Å and 130 Å, with the highest particle density, d, being: $35 \leq d \leq 65$ Å.
- for 3% Pt/g, the particle size varies between 40 Å and 175 Å, with a wide repartition of the different particle sizes.

3.2. Catalytic hydrogenation of nitrobenzene in neutral and alkaline alcoholic solutions

A previous study concerning the hydrogenation of nitrobenzene in aqueous acid media has shown that the acidity of the solution favours the further hydrogenation of aniline, produced at a first step, into cyclohexylamine mainly, thus decreasing the yield in aniline [8].
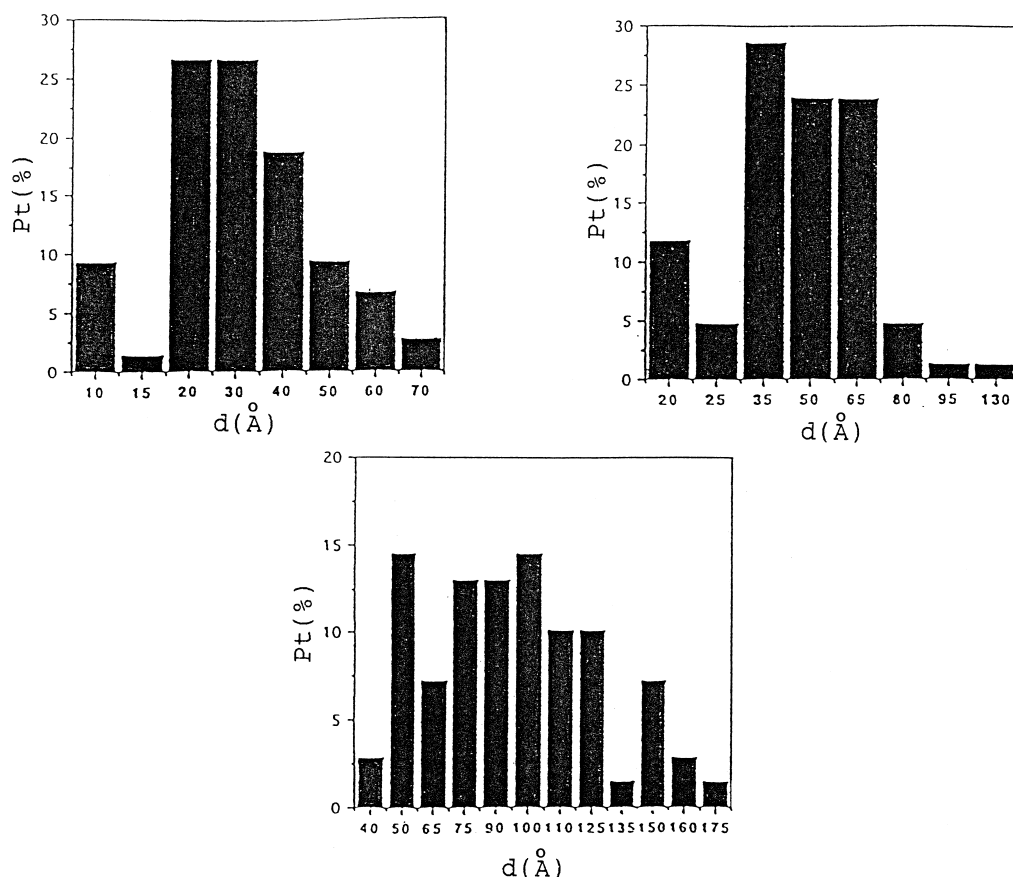

Fig. 1. Distribution of particle size of platinum catalysts supported on graphite. (A) 0.2% Pt/graphite, (B) 0.5% Pt/graphite, (C) 3% Pt/graphite.

Otherwise, in order to compare the hydrogenation of nitrobenzene with the hydrogenation of allyl benzyl ether and of benzyl crotyl ether in the same experimental conditions, it was necessary to achieve this reaction in an alcoholic solution, since these two unsaturated benzylic ethers are soluble only in ethanol and not in water.

Therefore, this study was carried out in a 95% ethanol solution in the absence and in the presence of different concentrations of KOH allowing to vary the basicity of the solution.

3.2.1. Hydrogenation of nitrobenzene in ethanol—Effect of the dispersion of the catalyst

The hydrogenation of nitrobenzene in a 95% ethanolic solution ($C = 2.5 \cdot 10^{-3}$ M), at 299 K, with $p(H_2) = 1$ atm, was carried out with platinum/graphite catalysts. A preliminary study with different Pt loadings (0.2–0.5–1–2–3–5%), corresponding to different Pt dispersions varying from 8% to 34%, (Table 1) showed that the intrinsic hydrogenation activity of platinum increases slightly from $2 \cdot 10^{-9}$ mol. min^{-1} cm^{-2} for a dispersion equal to 8%, to $3 \cdot 10^{-9}$ mol min^{-1} cm^{-2} for a dispersion equal to 34%. Moreover, the maximum selectivity in aniline was independent of the dispersion of the catalyst This reaction leads to the formation of phenylhydroxylamine, as an intermediate product, and of aniline as a final product (Fig. 2). A maximum selectivity in aniline, equal to 100%, is attained after the complete conversion of nitrobenzene (Fig. 2).

These results are similar to those obtained in a neutral aqueous solution and also in a neutral alcoholic solution with a different graphite support (Carbone Lorraine EG) [8]. However, the catalytic activity obtained in a neutral alcoholic solution was lower than that obtained in a neutral aqueous solution.

The following results (see Sections 3.2.2, 3.3, 3.4 and 3.5), related to the effect of the basicity of the solution on simple and competitive hydrogenations, were obtained with a 0.5% Pt/graphite catalyst corresponding to a dispersion of 20%.

3.2.2. Hydrogenation of nitrobenzene in alcoholic alkaline media

The hydrogenation of nitrobenzene ($C = 2.5 \cdot 10^{-3}$ M, $p(H_2) = 1$ atm), at 299 K, in alcoholic solutions (95% ethanol), in presence of different concentrations of KOH, was studied.
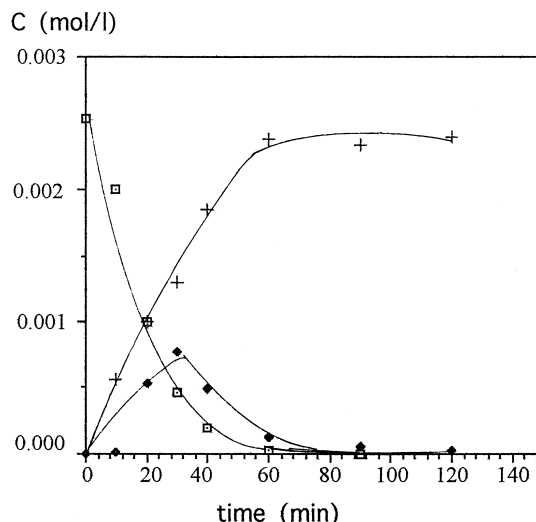

Fig. 2. Catalytic hydrogenation of nitrobenzene in a 95% ethanol solution with a 0.5% Pt/graphite catalyst ($C_{nitrobenzene} = 2.5 \cdot 10^{-3}$ M, $p(H_2) = 1$ atm, 299 K): □ nitrobenzene, ◆ phenylhydroxylamine, + aniline.
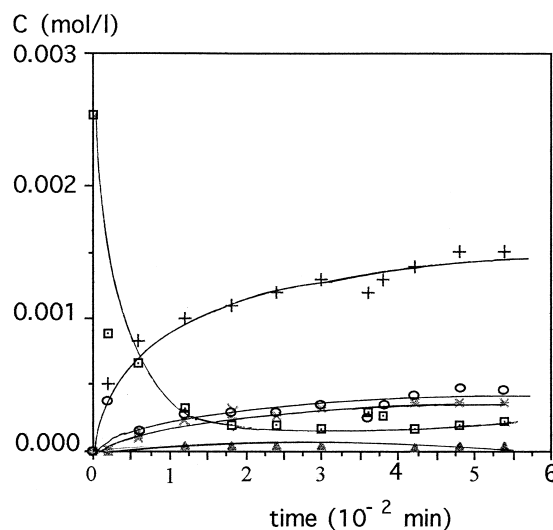
Fig. 3. Catalytic hydrogenation of nitrobenzene in a 95% ethanol $+ 10^{-1}$ M KOH solution with a 0.5% Pt/graphite catalyst. ($C_{\text{nitrobenzene}} = 2.5 \cdot 10^{-3}$ M, $p(H_2) = 1$ atm, 299 K): □ nitrobenzene, ○ nitrosobenzene, + aniline, ∗ hydrazobenzene, ▲ azobenzene.

In such experimental conditions the following products were obtained: nitrosobenzene, aniline and heavier products (dimers) such as azoxybenzene, azobenzene and hydrazobenzene (Fig. 3 and Table 2). No trace of hydroxylamine was observed in alkaline media.

The selectivity in nitrosobenzene depends on the concentration of KOH: in a 10^{-3} M KOH solution the initial selectivity in nitrosobenzene is important (67%), but it decreases strongly with increasing KOH concentrations (Table 2).

On the other hand, when the basicity increases, an increase of heavy products and a decrease of the maximum selectivity in aniline was observed (Table 2).

The composition of heavy products (dimers) depends on the basicity of the solution: in solutions of a high basicity (10^{-2} M to 1 M KOH) azobenzene and hydrazobenzene are produced, when in 10^{-3} M KOH these products are not formed and only azoxybenzene is present as an intermediate product.

The decrease of aniline selectivity at high basicities of the solution (10^{-1} M and 1 M KOH) can be explained by the difficulty of hydrogenation of the dimeric products, and in particular of hydrazoben-

Table 2
Effect of KOH concentration on the selectivity of nitrobenzene hydrogenation products

Reaction media	95% C_2H_5OH	10^{-3} M KOH 95% C_2H_5OH	10^{-2} M KOH 95% C_2H_5OH	10^{-1} M KOH 95% C_2H_5OH	1 M KOH 95% C_2H_5OH
Initial selectivity in phenyl hydroxylamine (%)	36	0	0	0	0
Initial selectivity in nitrosobenzene (%)	0	67	3	2	0
Initial selectivity in aniline (%)	64	33	43	26	30
Maximum selectivity in aniline (%)	100	100	79	66	65
Initial selectivity in heavy products (%)	0	0	54	72	70

Table 3
Evolution of the hydrogenation rate of azoxybenzene and of hydrazobenzene as a function of the concentration of KOH

Reaction media	95% C_2H_5OH	10^{-3} M KOH 95% C_2H_5OH	10^{-2} M KOH 95% C_2H_5OH	10^{-1} M KOH 95% C_2H_5OH	1 M KOH 95% C_2H_5OH
Reduction rate of nitrobenzene (mol min^{-1} cm^{-2})	$6 \cdot 10^{-9}$	$6 \cdot 10^{-9}$	$2.3 \cdot 10^{-9}$	$1.8 \cdot 10^{-9}$	$0.9 \cdot 10^{-9}$
Reduction rate of azoxybenzene (mol min^{-1} cm^{-2})	$0.9 \cdot 10^{-9}$	$1 \cdot 10^{-9}$	$2.5 \cdot 10^{-9}$	$4 \cdot 10^{-9}$	$4 \cdot 10^{-9}$
Reduction rate of hydrazobenzene (mol min^{-1} cm^{-2})	$24 \cdot 10^{-11}$	$7.6 \cdot 10^{-11}$	$5 \cdot 10^{-11}$	0	0

zene (Fig. 3). Moreover, this compound should be strongly adsorbed on platinum (as does aniline in Ref. [8]) and inhibit the hydrogenation of nitrobenzene (Fig. 3).

Indeed, a study concerning the reduction of azoxybenzene and of hydrazobenzene in the presence of different concentrations of KOH confirms that the hydrazobenzene is slowly hydrogenated in basic solutions and in very basic solutions (10^{-1} M and 1 M KOH) its hydrogenation rate becomes equal to zero (Table 3).

3.3. Catalytic hydrogenation of allyl benzyl ether and benzyl crotyl ether

Before examining the competitive hydrogenation between the nitrobenzene and the benzylic ethers having a C=C group on the lateral chain (C_6H_5–CH_2–O–CH_2–CH=CH_2 and C_6H_5–CH_2–O–CH_2–CH=CH–CH_3) [16] a preliminary study concerning the simple hydrogenation of these two compounds was necessary. In particular, the effect of the pH of the ethanolic solution was studied in the same experimental conditions as the competitive hydrogenations (low reactant concentrations (10^{-3} M), hydrogen pressure $pH_2 \leq 1$ atm, temperature 299 K). The same 0.5% Pt/graphite catalysts were used for all these catalytic hydrogenation reactions.

It can be noted (Table 4) that the hydrogenation rates of nitrobenzene, allyl benzyl ether and benzyl crotyl ether decrease when the basicity of the solution increases, the most important decrease being obtained in the case of benzyl crotyl ether.

In an acid alcoholic solution the hydrogenation rate of nitrobenzene is lower than that of benzyl crotyl ether. However, in a neutral or basic alcoholic solution the hydrogenation of benzyl crotyl ether is strongly inhibited and becomes equal to zero when the concentration of KOH is high (Table 4).

Table 4
Comparative study of the hydrogenation rates of nitrobenzene, allyl benzyl ether and benzyl crotyl ether with a 0.5% Pt/graphite catalyst

Reaction media	Cat. activity for hydrogenation of nitrobenzene (mol min^{-1} cm^{-2})	Cat. activity for hydrogenation of benzyl crotyl ether (mol min^{-1} cm^{-2})	Cat. activity for hydrogenation of allyl benzyl ether (mol min^{-1} cm^{-2})
$5 \cdot 10^{-3}$ M H_2SO_4 95% C_2H_5OH	$10 \cdot 10^{-9}$	$15 \cdot 10^{-9}$	$37.5 \cdot 10^{-9}$
95% C_2H_5OH	$5 \cdot 10^{-9}$	$1.7 \cdot 10^{-9}$	$14.5 \cdot 10^{-9}$
10^{-3} M KOH 95% C_2H_5OH	$4 \cdot 10^{-9}$	$0.7 \cdot 10^{-9}$	$10 \cdot 10^{-9}$
10^{-2} M KOH 95% C_2H_5OH	$3 \cdot 10^{-9}$	$0.3 \cdot 10^{-9}$	$5 \cdot 10^{-9}$
10^{-1} M KOH 95% C_2H_5OH	$2 \cdot 10^{-9}$	0	$2 \cdot 10^{-9}$
1 M KOH 95% C_2H_5OH	$1.9 \cdot 10^{-9}$	0	$1.7 \cdot 10^{-9}$

In the case of allyl benzyl ether a weaker inhibition effect of increasing KOH concentrations can be remarked, since the hydrogenation rate of C=C remains higher than that of nitrobenzene even in quite basic solutions (10^{-2} M KOH) (Table 4).

The comparison of hydrogenation rates between the benzyl crotyl ether and the allyl benzyl ether indicates the occurrence of an important structure effect on the reactivity of C=C bonds.

3.4. Competitive hydrogenation between the nitrobenzene and the allyl benzyl ether

The reactions of competitive hydrogenation between the nitrobenzene (10^{-3} M) and the allyl benzyl ether (10^{-3} M) were carried out in the same experimental conditions as simple hydrogenations (299 K, $p(H_2) = 1$ atm, 0.5% Pt/graphite catalysts) in ethanolic solutions of different acidities.

The hydrogenation rates of nitrobenzene and allyl benzyl ether decrease with decreasing acidities (Table 5), as in the case of simple hydrogenations of these compounds (Table 4).

In acid, neutral and slightly basic solutions (in 10^{-3} M KOH) the hydrogenation rates of allyl benzyl ether are higher than those of nitrobenzene (as in the case of simple hydrogenations).

However, in more basic solutions (10^{-2} M, 10^{-1} M and 1 M KOH) the hydrogenation of the group $-NO_2$ is comparatively favoured, since the decrease of this rate with pH is lower than the decrease of the rate of hydrogenation of carbon double bond, C=C. This evolution can be explained by the adsorption of nitrobenzene, which, in a very basic solution, seems to be favoured in comparison to that of allyl benzyl ether, as it can be inferred from the values of the ratio of equilibrium adsorption constants, K_1/K_2 (Table 5). This parameter was calculated by dividing the selectivity, obtained in competitive hydrogenation, being equal to: $S = (K_1/K_2) \cdot (k_1/k_2)$, by the ratio of simple hydrogenation rates: $(v_1/v_2) = (k_1/k_2)$, k_1 and k_2 being the corresponding pure kinetic constants [22].

3.5. Competitive hydrogenation between the nitrobenzene and the benzyl crotyl ether

The competitive hydrogenations between the nitrobenzene (10^{-3} M) and the benzyl crotyl ether (10^{-3} M) were carried out in the same conditions as in the case of allyl benzyl ether.

As in the case of this last compound, the hydrogenation rates of nitrobenzene and of benzyl crotyl ether decrease with increasing pH (Table 6), but the ratios of rates v_1/v_2 are higher in the case of benzyl crotyl ether in consequence of the low reactivity of this compound. This difference of reactivity can be ascribed to the steric effect of methyl group and/or to the electron donor effect of this group [22,23]. This last electronic effect of methyl group should induce an increase of the

Table 5
Competitive hydrogenation between the nitrobenzene and the allyl benzyl ether

| Reaction media	Cat. activity for hydrogenation of nitrobenzene v_1 (mol min^{-1} cm^{-2})	Cat. activity for hydrogenation of allyl benzyl ether v_2 (mol min^{-1} cm^{-2})	$S = v_1/v_2$	K_1/K_2
$5 \cdot 10^{-3}$ M H_2SO_4 95% C_2H_5OH	$6 \cdot 10^{-9}$	$16 \cdot 10^{-9}$	0.4	0.6
95% C_2H_5OH	$5.5 \cdot 10^{-9}$	$10 \cdot 10^{-9}$	0.5	1.5
10^{-3} M KOH 95% C_2H_5OH	$3.5 \cdot 10^{-9}$	$5 \cdot 10^{-9}$	0.7	1.75
10^{-2} M KOH 95% C_2H_5OH	$3.2 \cdot 10^{-9}$	$1.5 \cdot 10^{-9}$	2	1.2
10^{-1} M KOH 95% C_2H_5OH	$2.7 \cdot 10^{-9}$	$1.2 \cdot 10^{-9}$	2.3	2.3
1 M KOH 95% C_2H_5OH	$1.4 \cdot 10^{-9}$	$0.3 \cdot 10^{-9}$	4.7	4.7

Table 6
Competitive hydrogenation between the nitrobenzene and the benzyl crotyl ether

Reaction media	Cat. activity for nitrobenzene v_1 (mol min^{-1} cm^{-2})	Cat. activity for benzyl crotyl ether v_2 (mol min^{-1} cm^{-2})	$S = v_1 / v_2$	K_1 / K_2
$5 \cdot 10^{-3}$ M H$_2$SO$_4$ 95% C$_2$H$_5$OH	$2.2 \cdot 10^{-9}$	$2.6 \cdot 10^{-9}$	0.85	3
95% C$_2$H$_5$OH	$1.85 \cdot 10^{-9}$	$0.9 \cdot 10^{-9}$	2	0.7
10^{-3} M KOH 95% C$_2$H$_5$OH	$2.7 \cdot 10^{-9}$	$0.6 \cdot 10^{-9}$	4.5	0.6
10^{-2} M KOH 95% C$_2$H$_5$OH	$0.9 \cdot 10^{-9}$	$0.2 \cdot 10^{-9}$	5.6	0.52
10^{-1} M KOH 95% C$_2$H$_5$OH	$0.9 \cdot 10^{-9}$	0	–	–
1 M KOH 95% C$_2$H$_5$OH	$0.3 \cdot 10^{-9}$	0	–	–

electronic density on the carbon double bond, C=C, resulting to a decrease of the ratio of equilibrium adsorption constants, K_1/K_2. Consequently, the benzyl crotyl ether should be more strongly adsorbed than the nitrobenzene, in all the studied solutions of different pH (neutral and basic), in the exception of the acid solution (Table 6). Taking into account $S = (K_1/K_2) \cdot (k_1/k_2)$ [22], it can be concluded that the evolution of the selectivity in function of pH should result rather from the evolution of the ratio of kinetic constants, k_1/k_2, than from the evolution of adsorption equilibrium constants, K_1/K_2.

4. Discussion

The hydrogenation of nitrobenzene is complex involving several parallel and consecutive reactions and different semi-hydrogenated intermediates. Haber [7] proposed a general reaction scheme which is largely known in the literature (Scheme 1).
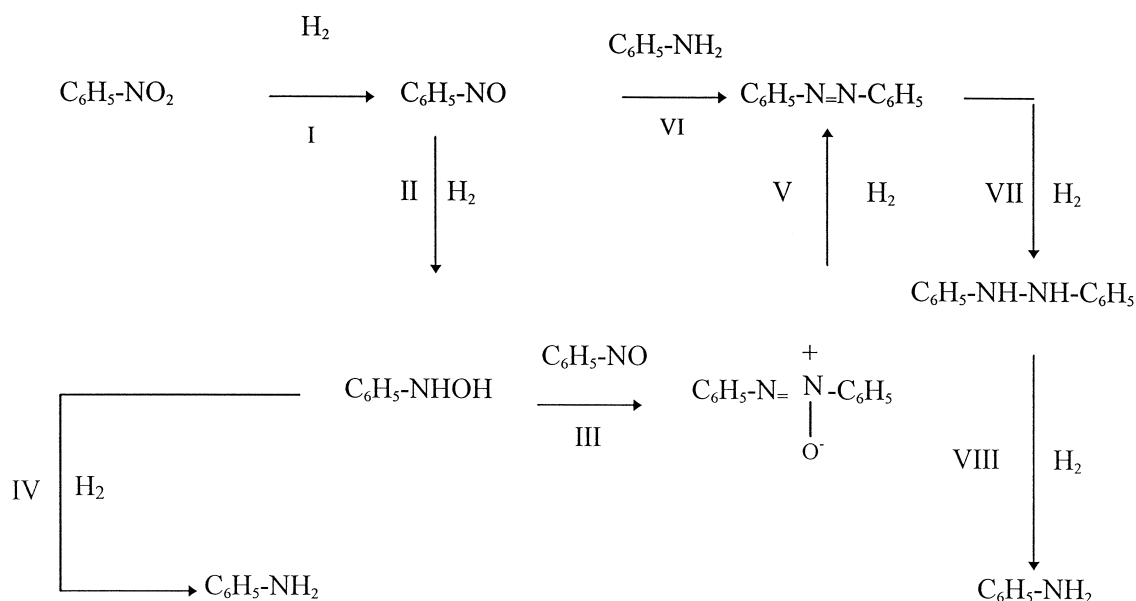
Scheme 1.

Indeed, according to this scheme, the reduction of nitrobenzene in aniline can occur following three principal pathways:

1. Following the pathway I, II and IV aniline is produced via three consecutive hydrogenations leading to nitrosobenzene and phenylhydroxylamine as reaction intermediates.
2. Formation of azobenzene by condensation of nitrosobenzene and aniline, followed by reduction to hydrazobenzene and then to aniline (pathway VI, VII, and VIII).
3. Condensation of the two intermediates: nitrosobenzene and phenylhydroxylamine, leading to azoxybenzene (pathway II and III). This last intermediate can also be obtained by condensation of nitrobenzene and of aniline [1].
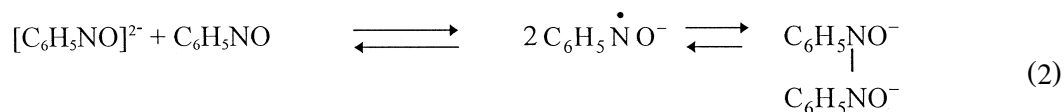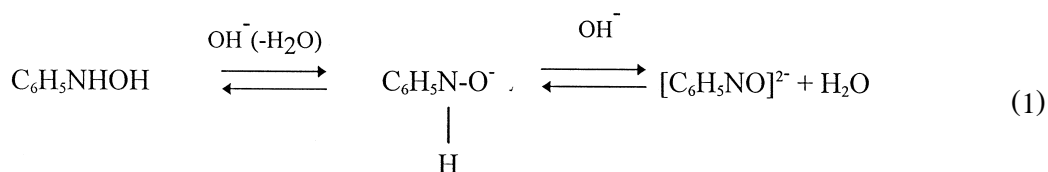
The azoxybenzene is further reduced to azobenzene and then to hydrazobenzene leading to aniline (pathway V, VII, and VIII).

The presence of a base favours the formation of dimers [9,24]

Although this reaction scheme concerns mainly the hydrogenation of nitrobenzene in presence of Raney nickel catalysts it is still generally accepted and a more recent extensive kinetic study [1] didn't result to a more appropriate mechanistic scheme.

The results obtained in this work and in a previous study [8] carried in an acid solution confirm the above reaction scheme and show clearly the importance of acidity (or basicity) of the solution.

The absence of phenylhydroxylamine among the products in basic solution confirms the results obtained by Russel et al. [24] during the reaction between the nitrosobenzene and the phenylhydroxylamine in presence of an excess of potassium tertiobutanolate:

$$C_6H_5NHOH \xrightleftharpoons{\ OH^-\,(-H_2O)\ } \underset{\overset{|}{H}}{C_6H_5N\text{-}O^-} \xrightleftharpoons{\ OH^-\ } [C_6H_5NO]^{2-} + H_2O \qquad (1)$$

$$[C_6H_5NO]^{2-} + C_6H_5NO \rightleftharpoons 2\,C_6H_5\overset{\bullet}{N}O^- \rightleftharpoons \underset{C_6H_5NO^-}{\overset{|}{C_6H_5NO^-}} \qquad (2)$$

The decrease of selectivity in nitrosobenzene obtained when the concentration of KOH increases can be explained by the reaction Scheme 1 and by taking into account the high reactivity of this compound. Indeed Debus and Jungers [9] proposed the following classification of reactivities: $C_6H_5NO \gg C_6H_5NO_{2} > C_6H_5NHOH \gg C_6H_5NH_2$.

Moreover, the production of aniline through the formation of dimers (pathways (2) and (3)) can involve homogeneous reactions [9,24–26]. Indeed, Russel and al. [24], in the presence of a strong base, detected the formation of nitrosobenzene radical anions from nitrosobenzene and they argued that this radical anion is an intermediate in the condensation reaction yielding azoxybenzene.

However, as the intermediate dimers can be strongly adsorbed on the catalyst, catalytic condensation reactions cannot be excluded and this question still remains open.

The obtained results show clearly that the best yields in aniline are obtained in neutral or slightly basic solutions (Table 2), because of the low reactivity of dimer intermediates (Table 3) formed in strongly basic solutions.

On the other hand, it has been found in a previous work [8], that in an aqueous acid solution the maximum selectivity in aniline was equal to 60–70%, because of the further hydrogenation of this compound on the aromatic nucleus into cyclohexylamine.

Consequently, the use of a neutral aqueous or alcoholic solution (in absence or in presence of small base concentration) should be the best choice, in the case of nitrobenzene hydrogenation, in order to obtain a high yield in aniline.

The results concerning the competitive hydrogenation between the nitrobenzene and the two benzylic ethers (the allyl benzyl ether and the benzyl crotyl ether) point out that the selectivity depends on the pH of the solution and on the structure of the olefin. Indeed, in an acid solution the double bond C=C is more easily hydrogenated than the group $-NO_2$, but in an alkaline solution the group nitro is more reactive.

The decrease of hydrogenation rate of olefin with increasing pH is reported in the literature [27] and also found in our laboratory [28], but the explanation of this result is not yet clear. It can be assumed that the competition of adsorption of reactants with OH^- adsorbed or present in the double layer is not favourable for this reaction. Moreover, the weakly found hydrogen species, which are active for this reaction [29], are probably less abundant in alkaline solutions.

Otherwise, this study confirms previous results obtained in our laboratory concerning the substitution effect in the hydrogenation of C=C [22]: indeed, a strong decrease of the reactivity of the crotyl group $(-CH_2CH=CHCH_3)$ in comparison to the reactivity of the allyl group $(-CH_2CH=CH_2)$ is obtained and can be explained by the steric effect of the group $-CH_3$, and/or by the inductive electron donor effect of this group. Similar trends were observed also in the case of hydrogenation of maleic, methylmaleic and dimethylmaleic acids studied [30].

5. Conclusion

The results obtained confirm the important role of the pH of the solution in the catalytic hydrogenation of nitrobenzene.

Different mechanisms are involved in acid [8] and in alkaline media leading to different reaction intermediates and selectivities.

In alkaline ethanolic solutions (with 10^{-2} to 1 M KOH) the formation of dimers (as azobenzene and hydrazobenzene), which are strongly adsorbed on the catalyst, causes a decrease of selectivity in aniline.

On the other hand, it has been found previously [8] that, in an acid solution, the obtained aniline can be further hydrogenated (on the benzenic nucleus) thus lowering the yield in aniline. Hence, the best selectivity in aniline (equal to 100%), is obtained in a neutral aqueous or alcoholic solution.

In competitive hydrogenations of nitrobenzene with a benzylic ether bearing an unsaturated lateral chain (allyl benzyl ether: $C_6H_5-CH_2-O-CH_2-CH-CH_2$ and benzyl crotyl ether: $C_6H_5-CH_2-O-CH_2-CH=CH-CH_3$) the evolution of the reactivity of the aromatic NO_2 group is different to that of carbon double bond, C=C: in an acid alcoholic solution the hydrogenation rate of C=C is higher than that of the group NO_2, but in an alkaline alcoholic solution the group NO_2 is the most reactive. The best selectivities, in this case, are obtained in a 1 M KOH ethanolic solution.

It should be emphasized that the group crotyl is less reactive than the group allyl in all pH of the solution and its hydrogenation rate becomes equal to zero in strongly alkaline solutions. Hence, the selectivity in competitive hydrogenation of the couple nitrobenzene-benzyl crotyl ether is better than

that of the couple nitrobenzene-allyl benzyl ether. This result can be ascribed to a steric effect and/or an electronic effect of the methyl group.

References

[1] J. Wisniak, M. Klein, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984) 44.
[2] P. Rylander, Catalytic Hydrogenation over Platinum Metals, Academic Press, New York, 1967, p. 168.
[3] I.D. Entwistle, A.E. Jackson, R.A.W. Johnstone, R.P. Telford, J. Chem. Soc. Perkin Trans. I (1977) 443.
[4] M.A. Aramandia, V. Borau, C. Jimenez, J.M. Marinas, J.A. Pajares, J. Catal. 78 (1982) 188.
[5] K. Weissermel, H.J. Arpe, Chimie Organique Industrielle, translated from german by Ph. Dubois, Masson (Ed.), 1981, p. 347.
[6] H.D. Burge, D.J. Collins, B.H. Davis, Ind. Eng. Chem. Prod. Res. 19 (1980) 389.
[7] F.Z. Haber, Elektrochem. 22 (1898) 506.
[8] E. Lamy-Pitara, B. N'Zemba, J. Barbier, F. Barbot, L. Miginiac, J. Mol. Catal., A: Chemical 106 (1996) 235.
[9] H. Debus, J.C. Jungers, Bull. Soc. Chim. Fr. (1959) 785.
[10] D.V. Sokol'skii, O.S. Popov, Dokl. Akad. Nauk SSSR 38 (1952) 873.
[11] H.C. Yao, P.H.A. Emmett, J. Am. Chem. Soc. 84 (1962) 1086.
[12] G.S. Samuelsen, V.L. Garic, G.B.L. Smith, J. Am. Chem. Soc. 72 (1950) 3872.
[13] L. Cerveny, V. Ruzicka, Catal. Rev.-Sci. Eng. 24 (4) (1982) 503–566.
[14] L. Cerveny, V. Ruzicka, Collect. Czech. Chem. Commun. 41 (1976) 1984.
[15] K.A. Zhubanov, N.F. Schumateva, K.K. Kuzembaev, Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk. Kaz. SSR. 5 (1973) 57.
[16] E. Lamy-Pitara, B. N'Zemba, J. Barbier, F. Barbot, L. Miginiac, J. Mol. Catal. A: Chem., in press.
[17] J. Barbier, M.E. Gonzalez, C.R. Acad. Sci. Paris 287 (Serie C) (1978) 313.
[18] E. Lamy-Pitara, L. El Ouazzani-Benhima, J. Barbier, J. Electroanal. Chem. 335 (1992) 363.
[19] R.C. Cookson, S.R. Wallis, J. Chem. Soc. B. (1966) 1245.
[20] R. Woods, in: A.J. Bard (Ed.), Electroanal. Chem., Vol. 9, Marcel Dekker, New York, 1976, p. 1.
[21] D. Duprez, J. Chim. Phys. 80 (6) (1983) 487.
[22] R. Maurel, J. Tellier, Bull. Soc. Chim. France (1968) 4191–4194, 4650–4653.
[23] G. Descotes, J. Sabadie, H. Tawil, Bull. Soc. Chim. 9 (1972) 3487.
[24] G.A. Russell, E.J. Geels, F.J. Smentowski, K.Y. Chang, J. Reynolds, G. Kaupp, J. Am. Chem. Soc. 89 (1967) 3821.
[25] S. Oae, T. Fukumoto, M. Yamagami, Bull. Chem. Soc. Japan 36 (1963) 78.
[26] J. March, Advanced Organic Chemistry, 4th edn., 1992, p. 1232.
[27] D.V. Sokol'skii, Hydrogenation in Solutions, Academy of Sciences of the Kazakh SSR, translated from russian, Israël program for Scient. translations, Jerusalem, 1964, p. 419.
[28] J. Barbier, thesis, University of Poitiers, 1975.
[29] E. Lamy-Pitara, I. Belegridi, L. El Ouazzani-Benhima, J. Barbier, Catal. Lett. 19 (1993) 87.
[30] E. Lamy-Pitara, L. Lghouzouani, C. Sieiro, J. Barbier, J. Chim. Phys. 87 (1990) 1981.