REACTION PATHWAYS AND THE ROLE OF SOLVENT IN THE HYDROGENATION OF CHLORONITROBENZENES

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Liquid phase hydrogenation of chloronitrobenzenes to corresponding chloroanilines over Pd on carbon (Pd/C) under mild reaction conditions was studied. On the basis of ^{1}H, ^{13}C NMR, GC-MS and HPLC analyses of reaction mixtures, the reaction pathways were evaluated. The reduction of substrates proceeds *via* the formation of chloronitrosobenzenes and *N*-(chlorophenyl)hydroxylamines and mainly results in the formation of the chloroanilines and aniline. Aniline is formed by hydrogenolysis of chlorine (dechlorination) in benzene ring. Other compounds (mono- and disubstituted azobenzenes and azoxybenzenes) were also detected by GS-MS and HPLC (<3 mole %). The used solvent influences the reaction mixture composition and catalyst activity.

Keywords: Reaction pathways; Chloronitrobenzenes; Catalyst activity; Selectivity; Deactivation; Catalyst surface hydrophobicity; Solvent effects; Heterogeneous catalysis; Reductions; Palladium.

Many efforts have been recently devoted to a more detailed description of the reaction pathways in the hydrogenation reactions of chloronitrobenzenes (CNB)[1–3]. Their true complexity shown by Scheme 1 is normally not visible but manifests itself when developing the process. Many variations in product composition could be obtained under different conditions. Choice of a proper catalytic and solvent system under suitable reaction conditions provides the possibilities to enhance the reaction pathways leading to the desired products, *i.e.* chloroanilines (CAN).

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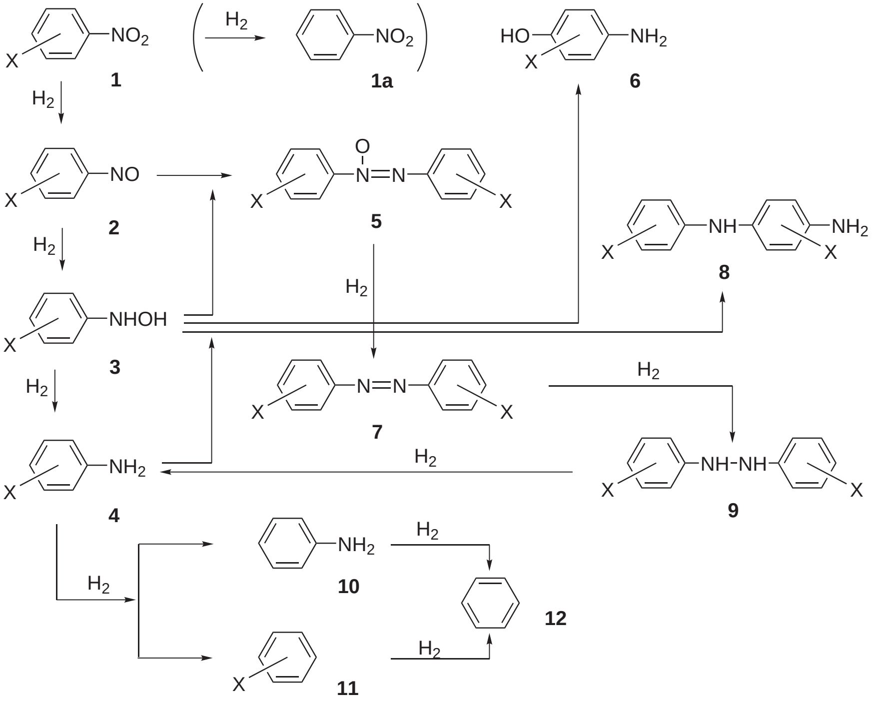
If CAN should be the main product of the hydrogenation reactions of corresponding CNB, platinum and nickel catalysts are the most widely used[2–4]. Metals with the most favourable selectivity patterns are ruthenium and iridium[5,6]. Simple palladium catalysts are reported as not very selective[7]. They are often modified with another metal or by the addition of some metal salts[4,6]. Selective poisoning of catalysts with compounds containing sulfur, nitrogen or phosphorus atoms has been also successful[1–3].

Due to the relationship between the catalyst hydrophobicity or hydrophilicity and the used solvent, a special environment may be formed near the active catalyst sites favourable to the intended reaction. Generally, aprotic solvents (*e.g.* toluene, xylene, *N*-methylpyrrolidone) give better results with respect to low dechlorination. However, protic solvents (*e.g.* methanol, ethanol, propan-1-ol, propan-2-ol, diethyl ether; tetrahydrofuran, dioxane) usually allow higher reaction rates[1,3].



SCHEME 1
Reaction pathways of hydrogenation of chloronitrobenzenes

As a continuation of our previous study in the field of hydrogenation of aromatic nitrobenzenes[8–14] we report here on our investigation of the reaction path and the role of solvent in the hydrogenation reactions of CNB. We focused our attention on the influence of protic and aprotic anhydrous solvents under mild reaction conditions using palladium supported on carbon as a catalyst.

EXPERIMENTAL

Catalyst

An amount of 1 wt.% palladium supported on charcoal (Pd/C) was prepared by mixing a solution of 0.83 g of $PdCl_2$ (Safina Jesenice, Czech Republic; analytical grade, 40 wt.% solution) in 6.4 cm^3 of water with a solution of 0.33 g of Na_2CO_3. This mixture was refluxed at 80 °C under mild stirring for 2 h and then cooled to 25 °C. The obtained suspension was added to 150 cm^3 of water with 20 g of charcoal (Colorex, Hnusta-Likier, Slovak Republic; S_{BET} = 1210 m^2/g) and the mixture was stirred at 25 °C for 1 h. Then, 10 wt.% of aqueous solution of Na_2CO_3 was added gradually during 2 h to maintain pH 9–10. After stirring for 10 min, the mixture was filtered off and three times rinsed with 50 cm^3 of methanol. The moist Pd/C was dried at 120 °C to constant weight. Activation of the catalyst was carried out prior to use in methanol with hydrogen at 50 °C and 1 MPa for 1 h. For analytical purposes, some reduced catalysts were dried after reduction to constant weight.

Preparation of Phenylhydroxylamines

N-(4-Chlorophenyl)hydroxylamine (*N*-4-CHA), *N*-(3-chlorophenyl)hydroxylamine (*N*-3-CHA) and *N*-(2-chlorophenyl)hydroxylamine (*N*-2-CHA) were synthesised by the modified Blatt method[15]. A solution of 2.5 g of ammonium chloride in 40 ml of distilled water was mixed with a solution of 5 g of 4-CNB, 3-CNB or 2-CNB in 40 ml of methanol. The mixture was stirred vigorously with a mechanical stirrer and 6.2 g of zinc powder (85 wt.% purity) was added during 15–20 min. As the reduction proceeded, the temperature rose to 60–65 °C. After addition of all zinc powder, stirring continued for another 15 min. The end of reaction was indicated by a slight decrease in the reaction temperature. While still hot, the solution was filtered with suction in order to remove zinc oxide, which was washed with 50 ml of hot (60 °C) distilled water. The filtrate was cooled to 0 °C. The crude product crystallised out as long white needles. Then, the crude product was filtered by suction and dissolved in diethyl ether. The prepared solution was cooled down again and frozen water was filtered off. In order to remove traces of water, a negligible amount of anhydrous calcium chloride was added to the filtrate. After filtering off the inorganics, diethyl ether was evaporated and crude *N*-*x*-CHA containing a small amount of aniline (AN) was recrystallised from a mixture of benzene and hexane (1:5 by volume). After filtration of *N*-*x*-CHA, the white coloured crystals were dissolved in diethyl ether again. Then diethyl ether was evaporated from mixtures in an oven in nitrogen atmosphere at 40 °C and *N*-*x*-CHA crystals were dried to constant weight.

The purity of *N*-*x*-CHA was checked by melting points and NMR spectra. Such *N*-*x*-CHA were used as standards for HPLC and NMR investigation of the reaction mixtures.

Catalyst Characterisation

The reduced and dried catalyst was characterised by elemental analysis, X-ray powder diffraction, scan electron microprobe analysis (SEMA) and by adsorption–desorption of nitrogen[16]. The results are summarised in Table I.

Catalytic Tests

The experiments were carried out in a stirred batch reactor equipped with a device for monitoring the hydrogen consumption. A typical reaction mixture consisted of about 500 mg of the catalyst and 6 ml of a solution of *x*-CNB in methanol (MeOH), diethyl ether (Et_2O), tetrahydrofuran (THF) or 1,4-dioxane (DOX). The hydrogenation was stopped after reaching the stoichiometric consumption of hydrogen ($n_{H_2}/n_{x\text{-CNB}}$, 3 mol of H_2 per 1 mol of *x*-CNB) or it was left proceeding further (when investigating the hydrogenolysis of chlorine).

Analysis

The reaction mixture was analysed by a gas chromatography. CP Sil-5 CB column (0.35 mm × 50 m) and a FID detector were used. An isothermal regime (200 °C) was used in analyses. The products were identified by GC-MS (GCMS-QP5000 Shimadzu). Phenylhydroxylamines were analysed using the HPLC method on a Shimadzu instrument equipped with a SPD-M10Vp photodiode array detector described in ref.[17]. *N*-4-CHA, *N*-3-CHA, *N*-2-CHA and some intermediate products were analysed by NMR. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 NMR spectrometer at ambient temperature in $CDCl_3$ solutions in 5 mm tubes at 299.9 and 75 MHz for ^1H and ^{13}C, respectively. A spectral width of 4 kHz was chosen for ^1H with 32 K data points using a 45° pulse and repetition time of 3 s. ^{13}C NMR spectra were measured with the 16 kHz spectral width and 32 K data points using a 45° pulse and WALTZ 16 decoupling sequence. Standard Varian pulse sequence and parameters were used for measurement of 1D APT spectra. The chemical shifts of compounds in recorded NMR spectra were compared with those from a handbook of NMR spectra, from ref.[18] and ^1H and ^{13}C ACD NMR predictions. Dechlorination was also estimated by a conventional acid-base titration. All the reaction mixtures were analysed for the presence of palladium, which was determined by atomic absorption spectroscopy (AAS)[9].

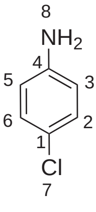
TABLE I
Characterisation of Pd/C catalyst

Property	Parameter
Surface $S_{BET,L}$, $m^2\ g^{-1}$	1180/1210[a]
Content of palladium, wt.%	1.02
Average size of Pd crystallites, nm	6
Type of support surface	hydrophobic

[a] Surface of the charcoal with reduced palladium/surface without palladium.

RESULTS AND DISCUSSION

In the course of catalytic hydrogenation of *x*-CNB there are four types of reaction pathways, which could proceed on active catalytic sites[1–3] (Scheme 1). The first one, the reduction of *x*-CNB in neutral and acid environment (**1**), proceeds *via* the formation of *x*-CNOB (**2**) and *N*-*x*-CHA (**3**) as the intermediates yielding *x*-CAN (**4**). In the second reaction pathway favoured by basic environment, intermediates may undergo condensation reactions to form dichlorinated 4-aminodiphenylamine (**8**), dichlorinated azoxy- (**5**) and azobenzenes (**7**). Azoxy and azo derivatives can be subsequently converted to dichlorinated hydrazobenzenes (**9**) and *x*-CAN. *x*-CAN itself may arise in such condensation reactions as well. The third type of reactions includes the hydrogenolysis of substituents in the benzene ring. Due to this unwanted reaction, the cleavage of substituents from intermediates and products can yield a variety of other products not involved in Scheme 1. The formation of nitrobenzene (**1a**), AN (**10**), chlorobenzene (**11**) and benzene (**12**) from corresponding *x*-CNB and *x*-CAN is shown in Scheme 1 as exam-



J	IP[a]		Value	Error
^5J	2	5	0.40	–
^4J	2	6	2.50	–
^3J	3	2	8.60	–
^4J	3	5	2.80	–
^5J	3	6	0.40	–
^3J	5	6	8.60	–

[a] Interaction of protons.

Proton	AP[b]	δ, ppm	Error
2	1	6.99	–
3	1	6.46	–
5	1	6.46	–
6	1	6.99	–
8	2	4.77	0.95

[b] Amount of protons.

FIG. 1

Coding of carbons in 4-chloroaniline (4-CAN) and data used for the simulation of NMR spectra ples of such potential hydrogenolysis reactions. It is emphasised in the literature that under relatively mild reaction conditions (about 65 °C and atmospheric pressure or 30 °C and 0.1–0.5 MPa of hydrogen), hydrogenolysis of chlorine is preferred to that of nitrogen in NO_2 or NH_2 groups[6,7]. As the fourth type of reaction, the Bamberger's rearrangement of *N*-*x*-CHA in acid aqueous environment giving aminochlorophenol derivatives (**6**) is assumed[19].

Due to the fact that NMR results differed for various samples, we simulated ^{1}H NMR spectra for 4-chloroaniline. Figure 1 contains its carbon coding and the data used for this simulation. As shown in Fig. 2, the spectra dramatically depend on the resolution. With the NMR apparatus used, the resolution of 0.5 Hz is possible to obtain. ^{1}H NMR analysis (Table II) of the reaction mixture of 4-CNB in Et_2O (35% conversion) revealed only very lit-

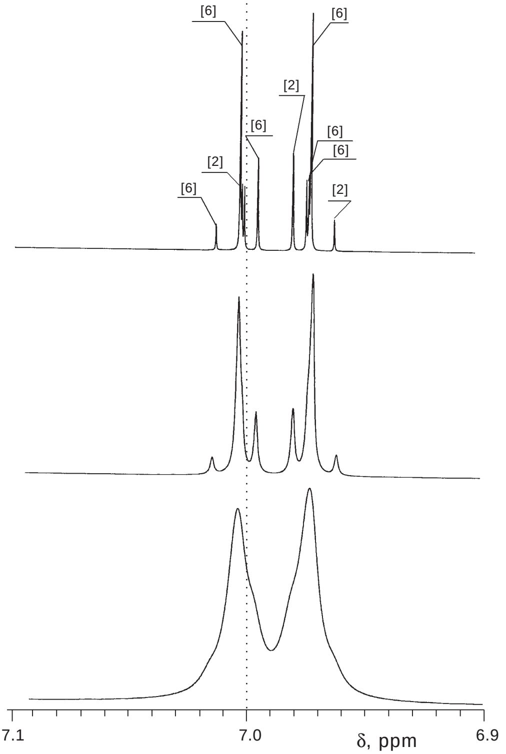
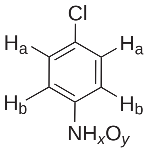


FIG. 2
Fragment of simulated ^{1}H NMR spectra (300 MHz) with characteristic multiplet of four-spin AA′BB′ system for hydrogens 2,6 of 4-CAN (Fig. 1) calculated with 0.1 (top), 0.5 (middle) and 2.5 (bottom) Hz resolution using ^{1}H NMR ACD predictor

tle intense signals of two doublets (Fig. 3; 7.6–7.8 ppm) related to 4-CNOB. At 65% conversion of 4-CNB (Fig. 4) it is possible to see only one doublet (in the same range of chemical shifts) related to an impurity. Practically no *x*-CNOBs were detected by HPLC (Fig. 5) at 33–36% conversion. The third intermediate in the reduction of the nitro group is *N*-*x*-CHA. This com-

TABLE II
^{1}H NMR (300 MHz) data for the reaction mixtures of 4-CNB hydrogenation (25 °C, 0.5 MPa, [Pd] = 7.8 mol/m^3, 1 wt.% Pd/C) in Et_2O. The samples were measured in oxygen-free $CDCl_3$ at room temperature



Compound	Compound or group	δ, ppm			J^a, Hz
		H_a	H_b	N–H	
1	4-CNB	7.44^b	8.10^b	–	8.70
2	4-CNOB	*	*	*	*
3	*N*-4-CHA	7.13^b	6.86^b	–	8.10
4	4-CAN	7.02^b	6.57^b	–	8.3
5	NH_2, NHOH^c	–	–	4.59, 4.78	4.783

^{a} Separation between adjacent peaks of two “doublets” in the AA′BB′ system. ^{b} Center of gravity of two “doublets” in the AA′BB′ system. ^{c} Amino and *N*-hydroxyamino protons overlap, hence only one peak appears in the recorded spectrum after the 35 and 65% conversion of 4-CNB (see Figs 3 and 4). * Compounds in negligible amounts.

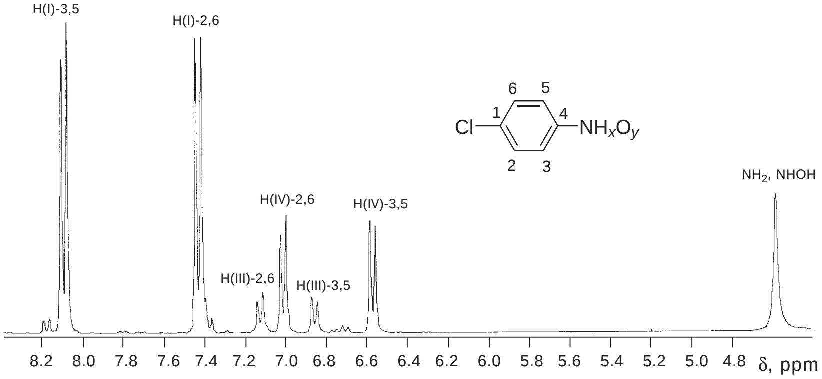


FIG. 3
Partial ^{1}H NMR spectra (300 MHz) of the reaction mixture from the 4-CNB hydrogenation (25 °C, 0.5 MPa, [Pd] = 7.8 mol/m^3, 1 wt.% Pd/C) in Et_2O recorded after 35% conversion of 4-CNB. Measured in oxygen-free $CDCl_3$ at room temperature

pound was detected by NMR and HPLC in all the samples. According to the proposed reaction pathway, a further reaction step is the hydrogenation of *N*-*x*-CHA to *x*-CAN.

Due to a very fast intermolecular exchange of protons between *N*-4-CHA and 4-CAN, the singlets of NH_2 and NHOH groups in ^{1}H NMR spectra overlap (Figs 3 and 4). The fact that the discussed signals comprised contribu-

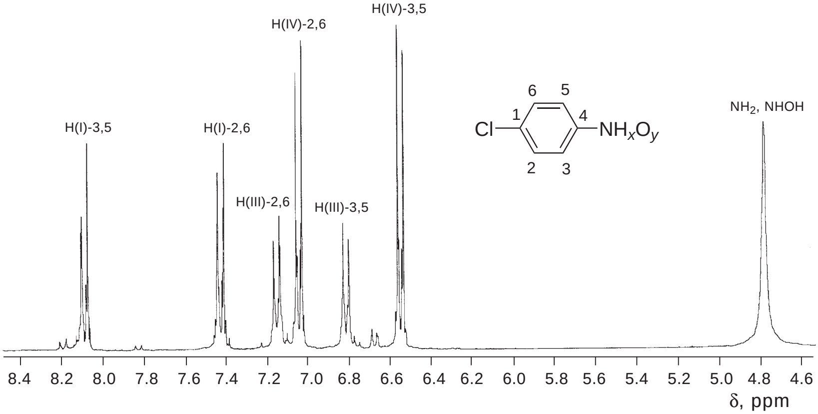


FIG. 4

Partial ^{1}H NMR spectra (300 MHz) of the reaction mixture from the 4-CNB hydrogenation (25 °C, 0.5 MPa, [Pd] = 7.8 mol/m^3, 1 wt.% Pd/C) in Et_2O recorded after 65% conversion of 4-CNB. Measured in oxygen-free $CDCl_3$ at room temperature

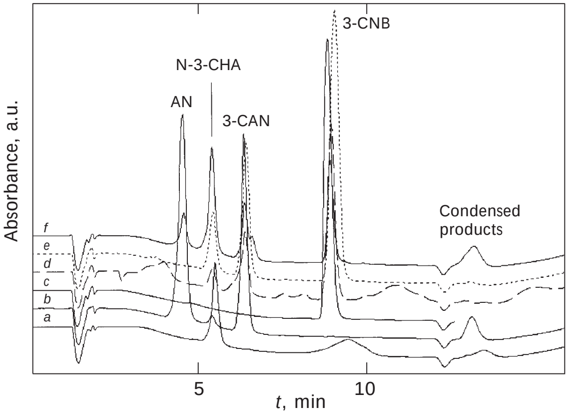


FIG. 5

HPLC patterns of the reaction mixtures of 3-CNB hydrogenation (25 °C, 0.5 MPa, [Pd] = 7.8 mol/m^3, 1 wt.% Pd/C) in various solvents at different conversions: *a* standard of *N*-3-CHA in MeOH, *b* total conversion of 3-CNB in MeOH, *c* pure 3-CNB in MeOH, *d* 3-CNB in THF at 33% conversion, *e* 3-CNB in Et_2O at 35% conversion, *f* 3-CNB in DOX at 36% conversion tions of both groups was also supported by comparison of their integrals and ^{13}C NMR (Table III).

NMR and HPLC analysis (Figs 3–5) proved that the reaction proceeds *via* the formation of nitroso and *N*-phenylhydroxylamine intermediates and yields mainly *x*-CAN and AN. Nevertheless, a negligible amount of condensed products (mono- and dichlorinated azo- and azoxybenzenes) was also detected by HPLC (Fig. 5) and GC-MS.

Precursors of these condensed products are also evident from ^{1}H NMR spectra (Figs 3 and 4; 8.2 and 7.4 ppm). 4,4′-Dichloroazoxybenzene is a compound detected by Montanari *et al.*[18], to which should be ascribed the signals. The total amount of condensed products in our experiments never exceeded 3 mole %. Hence, it is possible to conclude that mild reaction conditions, neutral environment and 1 wt.% Pd/C as the catalyst (Table I) are favourable to the formation of *x*-CAN obeying the first reaction pathway mentioned above.

Hydrogenation reactions of *x*-CNB are influenced by dechlorination which results in the formation of AN (Figs 5 and 6). The hydrogenolysis of chlorine can proceed in all reaction steps, but predominantly after reaching a stoichiometric consumption of hydrogen (Fig. 6). This finding allowed to simplify Scheme 1 and consider the two reactions: (i) hydrogenation of *x*-CNB to *x*-CAN and (ii) dechlorination of *x*-CNB to nitrobenzene (NB) and its hydrogenation to AN. Dechlorination is assumed to be the rate-determining step. Both reactions were taken as model reactions for the treatment of kinetic data and the power-law mathematical model was applied[12]. Originally, our kinetic model also considered the dechlorination of *x*-CAN as the third reaction. However, the zero value of the rate constant for this reaction with all the *x*-CNB isomers allowed to neglect this reaction and to state that hydrogenolysis of chlorine proceeds parallel with the re-

TABLE III
^{13}C NMR (75 MHz) chemical shifts (δ, ppm) for the reaction mixtures of 4-CNB hydrogenation (25 °C, 0.5 MPa, [Pd] = 7.8 mol/m^3, 1 wt.% Pd/C) in Et_2O. The samples were measured in oxygen-free $CDCl_3$ at room temperature

Compound	C_1	C_2	C_3	C_4	C_5	C_6
1	123.3	129.5	124.9	146.4	124.9	129.5
3	126.7	128.8	115.6	148.9	115.6	128.8
4	123.0	129.0	116.5	144.7	116.5	129.0

duction of the nitro group. A very strong chemisorption of all the tested substrates on the Pd surface was assumed from a very low reaction order. It was determined by mathematical treatment of kinetic data that the Pd/C catalyst is practically not deactivated during the hydrogenation (zero value of deactivation coefficient). This statement has been also supported by the zero content of palladium in the reaction mixtures[12]. In all the experiments presented here, more or less the same order of decrease of turnover frequencies (TOF) was found: 3-CNB > 4-CNB > 2-CNB (Table IV). This is in accordance with the influence of the electron-withdrawing effect of chloro substituents on the reactivity. If the Cl atom is in *meta* position, the positive electron effect of the chloro substituent may decrease the energy barrier of the nucleophilic attack of the hydride anion on the nitro group[1–3] and thus to accelerate the reaction rate.

On the other hand, chloro substituents in *ortho* and *para* positions have an opposite effect, which results in a decrease in the reaction rate. Changes in the reactivity of *x*-CNB partly correspond to the Hammett constants of chloro substituents in 3-CNB and 4-CNB (0.37 and 0.24, respectively[20]). The influence of 2-CNB cannot be explained by the Hammett constants, because Cl and NO_2 groups in *ortho* position interact.

Significant differences in specific activity and selectivity of the catalyst when using diverse solvents (Table V) were observed in the hydrogenation of all *x*-CNB isomers. The TOF values (Table IV) increased in the order: DOX < THF << Et_2O < MeOH. If the reactions were carried out in MeOH or

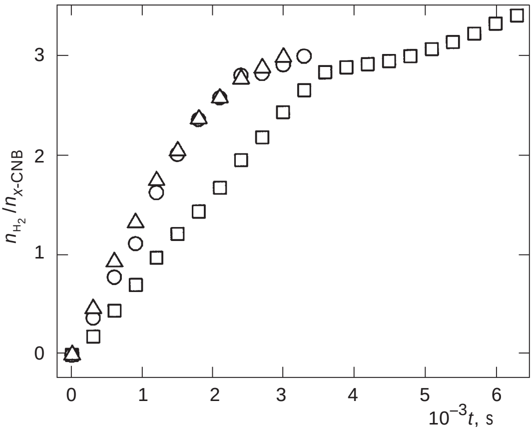


FIG. 6

Normalised H_2 consumption, $n_{H_2}/n_{x\text{-CNB}}$ (in mol/mol), *versus* time (in s) in the hydrogenation of 1.0 M 2-CNB (□), 1.0 M 3-CNB (○) and 0.5 M 4-CNB (△) to *x*-CAN in methanol (25 °C, 0.5 MPa, [Pd] = 7.8 mol/m^3, 1 wt.% Pd/C)

TABLE IV
Hydrogenation[a] of *x*-CNB catalyst (starting concentration of substrate was 1 mol/dm^3; 25 °C, 0.5 MPa, [Pd] = 7.8 mol/m^3, 1 wt.% Pd/C) in different solvents

Solvent	Substrate	$t_{R_{1/2}}$, s	$S_{x\text{-CAN}}$, %	TOF[b] mol H_2/mol$_{Pd \cdot s}$	$n_{H_2}/n_{x\text{-CNB}}$ mol/mol
MeOH	2-CNB	1848	61.3	0.10	3.4
	3-CNB	1146	85.2	0.17	3
	4-CNB[d]	1056[d]	86.8[d]	0.10[d]	3
Et_2OH	2-CNB	2118	97.9	0.09	3
	3-CNB	1386	96.7	0.15	3.1
	4-CNB	1644	97.5	0.12	3
THF	2-CNB	10200	99.2	0.02	2.3
	3-CNB	3000	94.2	0.07	2.9
	4-CNB	6420	96.7	0.03	3
DOX	2-CNB[d]	9630	96.7[d]	0.01[d]	2.5
	3-CNB	6720[d]	90.1	0.02	3
	4-CNB[d]	6420[d]	96.7[d]	0.02[d]	3

[a] $t_{R_{1/2}}$, half-time of reaction of the 50% of stoichiometric hydrogen consumption; $S_{x\text{-CAN}}$, selectivity to *x*-CAN. [b] TOF (turnover frequency) calculated with *t* for the 50% stoichiometric consumption of hydrogen (1.5 mol of H_2 per 1 mol of *x*-CNB). [c] $n_{H_2}/n_{x\text{-CNB}}$ normalised consumption of hydrogen (the final ratio of hydrogen consumption to the starting amount of *x*-CNB). [d] Starting concentration of substrate was 0.5 mol/l.

TABLE V
Characteristics[a] of solvents used

Solvent	ρ_{20}, kg m^{-3}	η_{20}, cP	ε	μ, Cm	x_{H_2} 10^5, kg/kg
MeOH	791.3	0.59	32.7	1.70	4.5
Et_2OH	713.3	0.24	7.58	1.15	8.3
THF	888.0	0.55	4.33	1.63	4.1
DOX	1033.6	1.37	2.25	0	2.1

[a] ρ_{20} density, η_{20} dynamic viscosity, ε permittivity, μ dipole moment and $x_{H_2,0.5}$ solubility of hydrogen in various solvents (20 °C, 0.5 MPa)

Et_2O, the highest reaction rates and TOFs were found. Very low reaction rates and TOFs were found in experiments in THF and DOX as solvents (Table IV). The most selective medium for the formation of *x*-CAN was Et_2O, THF and DOX. The lowest selectivities to *x*-CAN were obtained in MeOH. The influence of reaction solvent on product selectivity is expressed by the order: Et_2O > THF > DOX > MeOH. The effects of the used solvents can be partly explained by the differences in physical and chemical properties (Table V). Very low TOF in THF and DOX can be ascribed to their higher density and viscosity. Due to these characteristics and rather poor dissolution of hydrogen (mainly in DOX), concentration of hydrogen in the neighbourhood of catalytic sites is low and, consequently, the reaction rate is low. Comparable and rather higher values of TOF were achieved in Et_2O and MeOH. For such effects of Et_2O and MeOH, the main reasons could lie in a low density and viscosity of the solvents, which facilitate the liquid transport. Higher solubility of hydrogen (see Table V) and the favourable diffusion properties make the hydrogenation in Et_2O or MeOH faster than in case of THF and DOX.

Et_2O was found to be the most selective solvent (Table V). Sufficient and still very high selectivities to the desired products (*x*-CAN) were obtained in THF and DOX. The selectivities to *x*-CAN are very low in MeOH. As we mentioned above, the reaction mechanism of conversion of the nitro group and hydrogenolysis of chlorine may be parallel or consecutive. If the reactions are parallel, the substrate molecules must be oriented with both reactive groups (NO_2 and Cl) to the catalyst surface. In solvents where the diffusion barriers are minimised, the influence of permittivity (ε) of solvents and their polarity (dipole moment, μ) may also play an important role. The permittivity of MeOH is the highest of all the investigated solvents, which suggests a very poor chance to establish the natural polarisation between molecules of substrate and the active catalyst sites through NO_2 favourably. More probably, the induced polarisation of substrate molecules takes place and interaction *via* both the reactive groups occurs. This interaction results in decreasing *x*-CAN selectivity while the production of AN is increased. In contrast, ε of Et_2O is relatively low and natural polarisation orients the NO_2 group of the substrate molecules towards the catalyst surface. This orientation makes NO_2 be converted preferably and the selectivity to *x*-CAN can be high. Et_2O is practically immiscible with water (small μ). Thus, Et_2O together with the hydrophobic character of Pd/C catalyst enhances removal of the reaction water from the catalyst surface and the chemisorbed molecules can be protected to dechlorination by the nonpolar environment of Et_2O. In a polar medium of MeOH, the reaction water is miscible with the solvent and so remains in the neighbourhood of Pd particles on the catalyst surface. This causes a stronger dechlorination of chemisorbed molecules. THF and DOX showed satisfactory selectivity to *x*-CAN but the hydrogenations of substrates in these solvents proceed very slowly due to above effects of lower solubility of hydrogen and diffusion limitations. These solvents have very low permittivity and thus they can provide a high selectivity to the desired product. Since DOX has a zero dipole moment and is immiscible with water, it ensures a better selectivity to *x*-CAN in comparison with MeOH, similarly to Et_2O (Table IV).

CONCLUSIONS

Hydrogenation of chloronitrobenzenes (*x*-CNB) under mild reaction conditions over Pd/C catalyst proceeds *via* the formation of nitroso- and *N*-phenylhydroxylamine intermediates and yields corresponding chloroanilines (*x*-CAN). However, a small amount of aniline was formed and traces of condensed products (mono- and dichlorinated azoxy- and azobenzenes) were also detected by HPLC and GC-MS. The treatment of kinetic data revealed the reaction mechanism to be more parallel than consecutive. Practically no deactivation of the Pd/C catalyst was found. The strong influence of solvents on the specific catalyst activity (expressed by TOF) and selectivity was observed. Diethyl ether was the best solvent for hydrogenation of all *x*-CNB from the point of view of the highest TOF and product selectivity.

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