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Hydrogenation and hydrogenolysis of nitro-, nitroso-, azo-, azoxy- and other nitrogen-containing compounds on palladium

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Abstract

The formation of nitroso-, azo- and azoxy-aromatics depends of a relatively complex scheme involving consecutive reactions. However, all different products can be produced in good yields with palladium catalysts, using optimised kinetics, selective poisoning or alloying. These reactions show different dependencies of the reaction rate on Pd particle size and alloying. Solvents have different roles, in addition to the usual one consisting in the solubilisation of the reactants: they can change the solubility of hydrogen, compete with the reactants for adsorption at the metal surface or catalyse side reactions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The selective hydrogenation of nitro-compounds is commonly used to manufacture amines, which are important intermediates for dyes, urethanes, agro-chemicals and pharmaceuticals, often produced on a large industrial scale. Palladium is one of the best catalysts for the catalytic hydrogenation of nitroarenes, which has substituted the old Béchamp process [1] based on Fe and acids. Catalytic hydrogenation gives purer products at lower cost, and has thus, been investigated in detail [2,3]. The industrial aspects of these reactions have been analysed by Strätz [4] and recently by Baumeister et al. [5]. The present review will therefore, be focused on the fundamental aspects of these processes and recent potential applications. Moreover nitroso-, azo-, azoxy-, hydrazo-compounds are reaction intermediates in the hydrogenation of
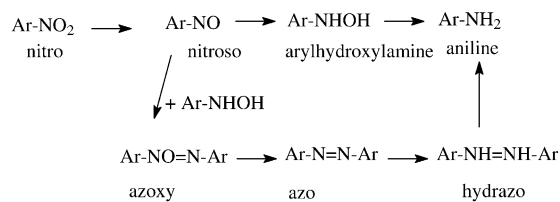
nitro-compounds (Scheme 1), and their reactivity on Pd-based catalysts will also be discussed.

2. Hydrogenation of nitrobenzene

Many authors point out that this reaction is strongly exothermic and very fast on most metals. The process is usually limited by diffusion. The reactor and process have then to be taken into account both the yield and the necessity to decrease the risk of explosion. Bulk chemicals such as aniline are produced by hydrogenation of nitrobenzene in the gas phase using a fixed or fluidised bed, or in the liquid phase with slurry reactors [4]. Since the reaction produces water, the preferred support of palladium is carbon due its hydrophobicity.

The reaction Scheme 1, established by Haber in 1898 [6] is widely accepted. The first step is an hydrogenolysis of N–O bond giving a nitrosobenzene, usually strongly adsorbed and not observed in the

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Ar-NO$_2$ $\longrightarrow$ Ar-NO $\longrightarrow$ Ar-NHOH $\longrightarrow$ Ar-NH$_2$
nitro   nitroso   arylhydroxylamine   aniline

$\downarrow$ + Ar-NHOH

Ar-NO=N-Ar $\longrightarrow$ Ar-N=N-Ar $\longrightarrow$ Ar-NH=NH-Ar
azoxy   azo   hydrazo

Scheme 1. Reaction network involved in nitrobenzene hydrogenation.

products. Indeed the only product of the hydrogenation of nitrobenzene at 50°C on Pd deposited on woven glass fibres was aniline. The reaction initially followed a zero order for nitrobenzene, therefore, an Eley Rideal mechanism was proposed in which nitrobenzene was adsorbed and hydrogen reacted from the gas phase [7]. The adsorption of the nitro-compound has also been proposed for Pd-containing polymers [8].

The same reaction general scheme is also observed for 1-(4-nitrobenzyl)-1,2,4-triazole in which an arylhydroxylamine intermediate is formed with a first order kinetics and an enthalpy of reaction $\Delta H_1 = -65$ kcal/mol. Arylhydroxylamine was further hydrogenated to the corresponding amine with a higher activation energy and an enthalpy $\Delta H_2 = -58$ kcal/mol [9]. A similar reaction scheme has also been reported for the hydrogenation of nitro-aliphatic compounds with also a zero order rate even at low concentration of substrate [10].

The sensitivity of the hydrogenation of nitrobenzene to the surface structure of palladium has not been reported, and is difficult to establish due to the fast kinetics. Several results however, show a sensitivity to alloy formation. The addition of 0.4% Pt to a solid containing 4% Pd increases the rate by 50%, and the further addition of Fe to the Pt–Pd bimetallic doubles it [4]. In the conditions of the reaction, Fe and Pt were proposed to be reduced to metals by a process catalysed by Pd, and alloys were then most probably formed at least on the surface. The catalytic activity of Pd for the hydrogenation of 2,4-dinitrotoluene (DNT) is reduced by the addition of Cu and Sn. Upon the addition of Fe a two-fold increase of activity is observed [11]. The formation of highly dispersed PdFe aggregates has been suggested where the Fe atoms next to Pd act as promotors activating the N=O bond. Actually, according to Bodnar et al. [12] Fe could be oxidised to Fe^{x+} due

to the strong oxidising reaction medium and the active site formed of Pd–Fe^{x+} pairs. Polymer protected colloidal Ni–Pd alloys have been recently reported to increase the rate by a factor of 4 [13].

In the case of 2-methyl-2-nitropropane [10] an effect of the preparation was observed suggesting that small particles could be more active. Increasing the pressure of hydrogen from 10 to 20 bar decreased the selectivity to arylhydroxylamine. A further increase to 50 bar decreased all rates, suggesting the possible formation of a palladium hydride phase of low activity. As we will see below poisons also show big effects and allow to selectively control the formation of the different intermediates. The modification of a commercial catalyst is the method usually preferred for this purpose.

A large number of solvents can be used, including alcohols, polyalcohols (glycerol, glycol), acetone, ethyl acetate, benzene, water and acidic solutions. Several large scale processes are also reported without any solvent [4,14]. According to Rylander [3] the choice of the solvent depends more on the overall chemistry than on the effect of the solvent on the rate of reduction, as expected for very fast reactions.

It has to be pointed out that the solubility of hydrogen depends on the solvent: volatile apolar solvents dissolve hydrogen better [15], and should then be more suited for reactions in which the rate is limited by the supply of hydrogen to the surface. Another important property is the possible adsorption at the Pd surface in competition with the reactant and products leading to changes in selectivity. However, for the hydrogenation of substituted nitrobenzenes the choice of the solvent may be restricted by the solubility of the substrates and then a limited range of solvents is available [5].

3. Hydrogenation of nitrosobenzene

This reaction has been investigated in detail by Smith et al. [16] who observed a small effect of the dispersion of Pd on the rate of hydrogenation of nitrosobenzene, with a higher activity for large particles. Some unidentified impurity of the substrate had a large effect on the rate (factor of 10), and aniline increased the conversion of nitrosobenzene. The reaction yielded phenylhydroxylamine, azobenzene, hydrazobenzene and aniline. The reactivities of some of these intermediate were determined.

Phenylhydroxylamine and nitrobenzene hydrogenated smoothly to aniline with comparable rates, but azoxybenzene and azobenzene yielded hydrazobenzene, which was unreactive in the conditions of reaction (temperature 24–26°C).

The reaction of nitrosobenzene and phenylhydroxylamine to form azoxybenzene was fast in homogeneous phase with methanol as solvent. Therefore, a high selectivity to aniline could be obtained only in diluted conditions where bimolecular condensation are unfavoured. The stability of substituted hydrazotoluene has been investigated by Kosak [17], who also observed a good stability of this compound against hydrogenation below 120°C, but fast hydrogenolysis at 175°C. This explains why industrial processes are run at relatively high temperature.

The hydrogenation of *N*-(1,4-dimethylpentyl)-4-nitrosobenzeneamine to the corresponding amine on Pd/C was first order relative to the nitroso-compound, with a lower rate at high hydrogen pressures [18]. This suggests a possible lower activity of Pd hydrides for this reaction also.

4. Production and hydrogenation of arylhydroxylamine

The control of the formation of arylhydroxylamine in the hydrogenation of nitro-compounds is important: in some cases its formation is required, and in most cases is undesired due to the fact that arylhydroxylamines are carcinogenic and explosive [19]. The addition of bases such as morpholine or of phosphorous acid to the reaction medium favoured the production of arylhydroxylamine on Pt [17]. This was shown to be not an effect of pH but of the modification of the catalyst surface by a poison inhibiting selectively the hydrogenation of arylhydroxylamine.

The arylhydroxylamine accumulation is much lower on Pd. During the competitive hydrogenation of nitrobenzene and phenylhydroxylamine over Pt and Pd, nitrobenzene was reduced preferentially over Pt whereas phenylhydroxylamine disappeared preferentially over Pd [3]. The adsorption strength of phenylhydroxylamine is then higher on Pd, and the preferred catalysts for the manufacture of substituted hydroxylamines are therefore, based on Pt [20,21].

The higher accumulation of arylhydroxylamine in the products is mainly observed when the benzenic ring bears electron-withdrawing substituents: arylhydroxylamine yields of 35% at 67% conversion in the hydrogenation of 3,4-dichloronitrobenzene against 1.9% for *p*-chloronitrobenzene on Pt are then observed [17]. The accumulation of arylhydroxylamine in the products is also higher at low temperature [22]. Baumeister and co-workers [19,23,24] have recently proposed a strategy for elimination of this intermediate based on its disproportionation by metallic additives. In the case of the hydrogenation of benzenesulfonamide-*N*-cyclohexyl-*N*-methyl-2-nitro on Pd/C at 120°C the yield of the corresponding arylhydroxylamine dropped from 41% without any additive to <1% in presence of a V salt. The modifier slightly increased also the reaction rate and had to be deposited on the support to obtain the best efficiency. This suggests that the arylhydroxylamine had in that case some inhibitor effect.

In the case of DNT, the formation of 2-nitro,4-hydroxylaminotoluene reaches 80% at 50°C, and Pd/C is just slightly less active than Pt/C [25]. A significant structure effect is observed on the rate of hydrogenation of DNT when the Pd dispersion was changed from 0.38 to 0.01, with a much higher activity of the larger particles. This was accompanied by smaller changes of selectivity relative to the production of arylhydroxylamine, and the preferential formation of 4-amino-2-nitrotoluene on small particles. This particle size effect was attributed to steric factors in the adsorption of the reactant: it was assumed that the hydrogenation of DNT was easier on a flat surface on which the molecule could be π-bonded through the aromatic ring. In that case both nitro groups should have the same probability of hydrogenation, which corresponds to the experimental results. Pd catalysts of similar dispersion on different supports were compared: carbon was the best support for the formation of arylhydroxylamines whereas acidic supports such as silica and alumina gave lower yields. No formation of azo-compounds was observed.

5. Formation of azoxy-compounds

Azoxy-compounds are the product of the coupling of nitrosobenzene with arylhydroxylamine which

occur as a fast side homogeneous reaction [16]. These azoxy-compounds are unwanted contaminants of aniline or chloraniline but *p,p'*-di-*n*-alkyl azoxybenzenes containing 4–10 carbons in the alkyl groups have been found to be attractive liquid crystals having transition temperatures above their melting points [26,27].

Smith et al. [16] have determined the reactivity of azoxybenzene and compared it to the other intermediates observed in the hydrogenation of nitrobenzene on Pd/SiO$_2$: the TOF for the hydrogenation of nitrosobenzene to arylhydroxylamine at room temperature in methanol as solvent is 0.71 min^{-1}. The condensation of phenylhydroxylamine on nitrosobenzene is fast since the selectivity for arylhydroxylamine is low, and the determining step for the formation of azoxybenzene is the formation of phenylhydroxylamine. The TOF for azoxybenzene hydrogenolysis to hydrazobenzene is 0.27 min^{-1}. On that account azoxybenzene accumulates in the reactor, with an intermediate yield reaching 75%.

Azoxybenzenes can therefore, be obtained from nitrobenzene at an industrial scale by catalytic hydrogenation of nitrobenzene [28]. The conditions of reaction involve the control of the amount of hydrogen in a prepared solution of an alkali metal alkoxide with the aid of a noble metal. With Pd/C at 40°C and 10 atm H$_2$, the yield of azoxybenzene was 75.4% after 75 min.

6. Hydrazo-compounds

Smith et al. [16] showed that hydrazobenzene is unreactive at room temperature on Pd/SiO$_2$, and can then be accumulated when formed. The selective hydrogenation of *o*-nitrotoluene (ONT) to *o*-hydrazotoluene (OHT) is a key step towards the obtention of *o*-tolidine, a diamine produced at a large scale (Scheme 2) which can be obtained by acid catalysed isomerisation of hydrazotoluene [29].

With Pd/C as catalyst, a selectivity to hydrazobenzenes up to 90% has been claimed in presence of 20% NaOH in a two-step process including a first reaction at 20–30°C followed by a second one at 90°C [29]. Basic additives favour the reaction of arylhydroxylamine and nitroso intermediates to the azoxy-compound which is the precursor of azotoluene and hydrazotoluene. Coe and Brockington [30] reported a key improvement of the process which consists in the addition of a quinone in conjunction with 1% NaOH to the reaction medium. The quinone blocks the hydrogenolysis of hydrazotoluene which
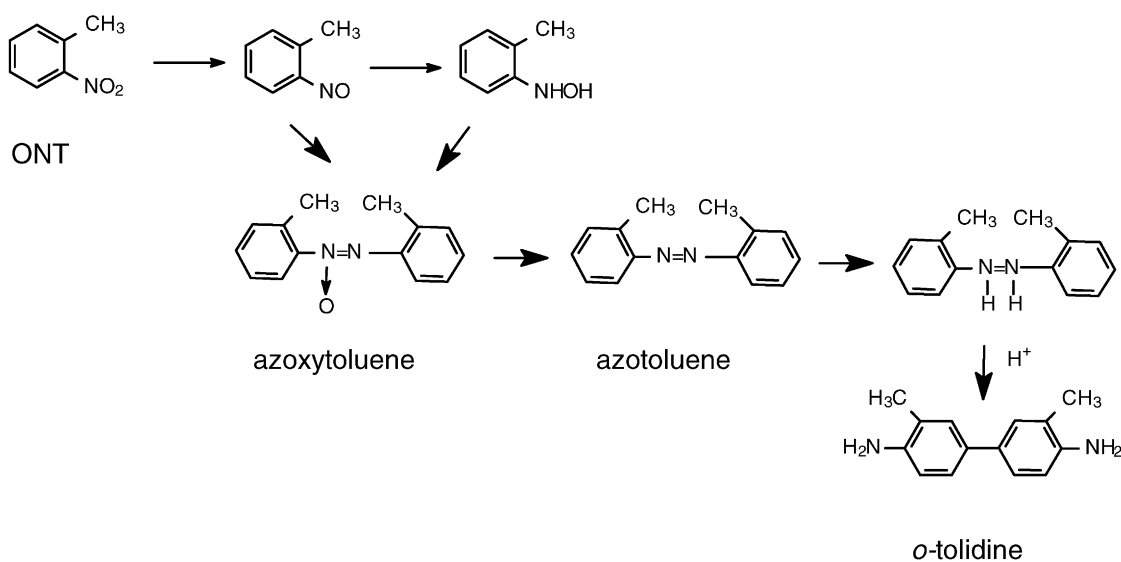
Scheme 2. Formation of *o*-tolidine.

otherwise starts immediately. A further increase of the yield can be reached by the addition of dimethyl-sulfoxide (DMSO) to the reaction medium at the expense of a longer reaction time.

This reaction was very sensitive to solvent effects: the OHT yield was, in water <5%, methanol 54%, ethanol 78%, mixture THF–ethanol–water 87% and THF–methanol–water 83% [28]. The effect of solvents is explained by the need to dissolve the reactants and additives. It can be pointed out that NaOH is required in the active phase for the condensation of arylhydroxylamine and nitrosotoluene, which explains the need of water.

It is worth nothing that the reduction of ONT to OHT is probably structure sensitive on Pd: small metallic particles are more active than the large ones [30]. The selective inhibition of OHT hydrogenation by quinones also suggests that different sites are required for these two reactions.

7. Selective hydrogenation of nitro groups in presence of other functional groups on the benzenic ring

Several examples of chemoselective hydrogenation of an aromatic nitro group in presence of C–halogen, C=C, C≡C, C=O, CN and *N*- or *o*-benzyl bonds on Pd catalysts are discussed by Baumeister et al. [5].

7.1. C–halogen bonds

In this case the goal is to hydrogenate the nitro group with no hydrogenolysis of the C–Cl bond. Since Pd is the best catalyst for dehalogenation this is a difficult task. Only fluorinated nitrobenzenes can be selectively hydrogenated on Pd [31]. Craig et al. [32] claimed that chloronitrobenzenes (CNB) can be hydrogenated over Pd catalysts without Cl loss with triphenylphosphite as additive. Vollheim et al. [33] reported the hydrogenation of CNB on Pd/C with a 98% yield using a catalyst treated by a sulfoxide then by hydrazine.

On Pt catalysts [34] a particle size was observed corresponding to a change of the ratio λ_1/λ_2 of the adsorption coefficients of CNB and chloraniline (CAN), respectively. The highest selectivity (98%) was observed on large particles, on which the adsorption of CNB was stronger. These changes occurred for relatively large particles, in which the co-ordination of the surface atoms does not change much. The changes of the catalytic properties can therefore, be related to modifications of the collective properties of the Pt particles (electronic effect). Interestingly the addition of Zn to a well dispersed catalyst of low selectivity (82%) led to an increase of the selectivity up to 97% [35]. Zn possesses an electron-donor character and tends to induce a higher electronic density at the Pt sites, such as an increase of particle size. This model based on the collective properties of small metallic particles should be applicable at least in part to Pd and can rationalise the effect of basic additives on the catalytic properties.

A recent study of the hydrogenation of CNB on polymer protected Pd–Pt colloidal alloys shows a large increase of both reaction rate and selectivity to CAN upon the addition of several cations to the catalyst. Without any additive this selectivity reaches 77.5% for a composition Pt/Pd = 3/1, but the addition of Co^{2+} cations to the catalyst lead to a further increase to 92% [36]. A beneficial effect of alloying had been previously reported for the same reaction on polymer anchored PdRu and PdPt catalysts [37,38].

7.2. A second nitro group

The rates of the two reaction steps of dinitro to nitroaminotoluene and diaminotoluene are different so that an optimisation of the kinetics allows one to reach a yield of 67% in nitroaminotoluene on Pd/C [39]. The catalyst deactivates in this process [40] presumably by dissolution of palladium discussed by Bird and Thomson [41]. This phenomenon is rather general and has also been observed for the hydrogenation of nitrotoluene on polymer supported Pd [42]. This addition of cobalt on a prereduced Pd catalyst decreased Pd leaching and increased activity [43]. This behaviour was accounted for by the activation of nitro groups by oxidised Co species at the surface of Pd crystallites which induced then a protection of Pd against oxidation.

7.3. A C–C double bond as the side chain

The selective and quasi exclusive reduction of the nitro group to the amine is achieved in good yields on a Pd/CaCO3 catalyst poisoned with Pb (Lindlar catalyst) thanks to the addition of a carboxylic acid [44].

7.4. A CN group

The selective hydrogenation of the nitro group can be obtained using a Pd/C catalyst in the presence of concentrated HCl [45].

7.5. An epoxide function

The addition of ethylenediamine onto Pd/C drastically reduces the catalytic activity for the hydrogenolysis of epoxides. Therefore, a nitro group can be selectively hydrogenated with retention of the epoxide function using THF as solvent. The selectivity drops if THF is replaced by methanol [46]. The same type of catalysts poisoned by strong organic bases have been used to catalyse the selective hydrogenation of nitro groups in derivatives of benzyl ether [47].

8. Hydrogenolysis of N–N bonds in hydrazines

A method has been described for converting hydrazine and/or substituted hydrazines, particularly unsymmetric dimethyl hydrazine (UDMH), to ammonia or ammonia and the corresponding amines by hydrogenation over Pd on steam deactivated C [48]. Preferably, the hydrazines are dissolved in a solvent (toluene or water) and then hydrogenated at a temperature of about 150°C, followed by separation of the commercially valuable ammonia and amines. Alternatively, a gas phase reaction may be used.

Catalytic hydrogenolysis of the N=N bond of chiral hydrazines is possible on Pd/C at 110°C with a good selectivity (e.e. = 90–93%) for the formation of one enantiomer of the α-arylalkanamines [49].

9. Hydrogenation and hydrogenolysis by hydrogen transfer from methyl formate

The reduction by hydrogen transfer using not hydrogen gas but hydrogen donors is well known [50]. It works in mild conditions and does not require pressure, so can be attractive in some special cases. Recent examples concern the reduction of nitrobenzene with aqueous methyl formate using Pd(OAc)$_2$–phosphine complexes [51], the reduction of nitriles by formic acid on Pd catalysts [52], and

the reduction of 4,4′-dinitrostilbene-2,2′-disulphonic acid in water with formic acid or Na formate [53].

10. Heterogenised Pd(II) complexes

Recently Pd(II) heterogenised complexes have been applied to the hydrogenation of nitro-compounds. Silylamine anchored on MCM-41 and co-ordinated to Pd works well with nitrobenzene and *p*-nitrotoluene, but not with ONT [54]. Surprisingly these catalysts dehalogenate chloronitrobenzene and show a selectivity for the hydrogenation of dinitrobenzene to nitroaniline of 58%, comparable to the 67% reported for Pd/C [39], then suggesting the presence of small metallic particles of palladium. A Pd(II) complex obtained by co-ordination of Pd(OAc)$_2$ to a polymer grafted with bis(diphenylphospino)methane is an active catalyst at room temperature and atmospheric pressure for the hydrogenation of nitrobenzene; it can be recycled many times, so that leaching of Pd does not occur [55].

11. Catalytic reduction of nitrates

The hydrogenation of nitrates in aqueous solutions to obtain drinking water follows also the analogue of the Haber's reaction scheme with the formation of N$_2$O, hydroxylamine and N$_2$. Hydroxylamine is an intermediate compound which can obtained with good yields [56]. Ge promotes the activity of Pd/C and of Pt–Pd/C which are the best catalysts for the obtention of hydroxylamine. It has been proposed that the actual catalyst is an alloy in the steady state.

By contrast, the hydrogenation of nitrates to N$_2$ over Pd–Cu bimetallic catalyst offers a promising technique for their removal from contaminated drinking water. This reduction has been reported at $T = 298$ K and atmospheric pressure, using a bubble-column fixed-bed reactor in distilled water as reaction medium. The Pd–Cu/γ-Al$_2$O$_3$ catalyst showed long term stability. The reaction was so fast that the rate was determined by the mass transfer of hydrogen from the gas into the bulk liquid phase. At the given reaction conditions, only about 1–10% of the Pd–Cu/γ-Al$_2$O$_3$ bimetallic catalysts present in the reactor was therefore, efficiently used. Permanent hardness of water exhibits no inhibitive impact either on the extent of nitrate removal

or on reaction selectivity. On the other hand, the nitrate disappearance rate as well as nitrogen production yield decrease appreciably in the presence of hydrogencarbonates, which is attributed to competitive adsorption of these species at Pd–Cu active sites [57–60].

12. Conclusion

The hydrogenation of nitro-compounds on palladium catalysts is relatively well understood. Many processes exist to manufacture with good yields the different intermediates observed in the reaction scheme. A few experiments suggest that the hydrogenation of nitrobenzene and that of nitrosobenzene show opposite changes of rate when changing the dispersion of palladium. However, the fast rate and exothermicity of these reactions makes a detailed study rather difficult. The changes of solubility of hydrogen in alcohols containing small amounts of water can also complicate the interpretations of kinetic results.

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