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Hydrogenation of Aromatic Nitro Compounds with A Pt/SiO_2-$AlPO_4$ Catalyst

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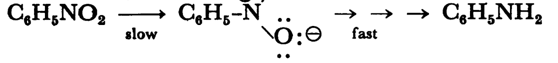
In this work we have carried out the reduction of aromatic nitro compounds bearing different substituents with gaseous hydrogen, over a Pt catalyst (3% by weight) supported on a SiO_2–$AlPO_4$ system. The catalyst was obtained by impregnation, the impregnating metal salt being reduced with α-phellandrene. The kinetic data found allow us to describe the reduction of nitrobenzene as a Langmuir-Hinslwood kinetic. The sequence of reaction rates for the different nitro compounds assayed conforms to the Hammett-Taft equation, which allows relating the electron density of the aromatic ring to the reduction rate of the nitro group. Finally, we propose mechanism for the process, characterized by the absence of intermediates with net charges.

The reduction of nitro compounds has been comprehensively studied by many authors with the aid of the metal–acid system,[1] using gaseous hydrogen,[2,3] or by hydrogen transfer[4–6] over Fe, Ni, or Pd catalysts supported on silica or alumina,[7,8] as well as in homogeneous phase.[9,10] In spite of being a well-known process, its remarkable industrial applications are responsible for the interest which it still arises among researchers. The solids most frequently used as supports are silica, alumina, carbon, and zeolites.

Aluminum orthophosphates, either pure or mixed with SiO_2 or Al_2O_3, are stable solids whose texture properties and acidity may be controlled in the synthetic procedure[11,12] and which have proved to be excellent as supports for Pd and Pt catalysts in some reduction processes.[13,14] These systems have also been used as supports for nickel (both by our team[15–17] and by Marcelin et al.[18,19]) and rhodium.[20,21] Recently, some authors have begun to prepare catalysts prereduced under reflux with olefinic[22] or hydroaromatic compounds or even other substances which decompose to simple products.[23]

The mechanism through which the reduction of nitro compounds takes place is quite well understood when the reduction is carried out with the metal–acid system; this process begins with the attack of a hydrogen atom:



$$C_6H_5NO_2 \xrightarrow[\text{slow}]{H\cdot} C_6H_5\text{-}\overset{\oplus\cdot\diagup O\text{-}H}{N}\,\underset{\ddot{}}{\overset{\cdot\cdot}{\diagdown O}}{:}\ominus \;\underset{\text{fast}}{\rightarrow \rightarrow} \rightarrow C_6H_5NH_2 \qquad (1)$$

However, when the reduction is performed with supported metals, the nature of the support may result in the formation of protons and hydride ions on the metal surface, these species becoming the actors of the reduction process.

On the other hand, in the hydrogenation of nitro compounds with supported palladium catalysts, Carturan et al.[24] found that the rate-determining step in the reduction of a nitro compound with a metal catalyst may be the hydrogenation of the metal surface oxidized by the sorbed nitro compound.

In this work we have carried out the reduction of aromatic nitro compounds with different substituents over Pt catalysts supported on SiO_2–$AlPO_4$. The results obtained seem to indicate that the reduction of the nitro group is not an isolated process of the molecular rest, and that the electron density of the neighboring aromatic ring influences the reduction rate.

Experimental

Support. We have used a support made of SiO_2–$AlPO_4$ (80:20% by weight) named F72, the synthesis and properties of which were described elsewhere.[11,12] Summarized, its texture properties are described as follows: S_{BET}=247 m^2g^{-1}; average pore radius=32 Å; cumulative pore volume= 0.59 mLg^{-1}.

Catalyst. We have used a Pt catalyst (3% by weight) deposited on support F72. It was prepared by impregnation from an aqueous solution of K_2PtCl_6.

The supported metal salt was reduced by keeping the solid under reflux with α-phellandrene at 453 K for 2 h. The resulting catalyst was washed several times with methanol and vacuum-dried prior to use.

The catalyst nomenclature includes the symbol of the metal deposited, the percent loading and the name of the support (F72 in this case).

Apparatus. The reduction of nitrobenzene with gaseous hydrogen was accomplished in a low pressure Gerhardt reactor fitted with a pressure gauge which measured the evolution of the hydrogen pressure in the reaction vessel. All reactions were carried out at 300 K, using methanol as solvent (V_{total}= 20 mL) and 3×10^{-3} g of metal. The reaction temperature was controlled by means of a thermostatic bath.

The reaction rate was calculated from the slope of the straight line obtained by plotting the consumption (in moles of hydrogen) as a function of time.

All reagents used were high-purity commercial chemicals.

Product Analysis. The reaction products were analyzed by gas chromatography, using high-purity standards in their characterization. Their presence was confirmed by mass spectrometry using GC-MS systems.

The products obtained were the corresponding anilines; no by-products or reaction intermediates were detected in any case. *m*-Dinitrobenzene was reduced selectively to *m*-nitroaniline.

Determination of Metal Particle Size. The metal particle size was determined by X-ray diffraction. The X-ray diffractogram was recorded on a Philips 1130/00/60 apparatus, using the Co $K\alpha$ radiation, with λ=1.7889 Å. The half-peak width was measured graphically at an angle 2θ=46.52° corresponding to plane (1 1 1) of Pt, assuming a value of 0.89 for the Debye-Scherrer constant.

The metal surface, $S(\mathrm{m^2 g_{Pt}^{-1}})$ was obtained from the mean particle diameter, D (Å), using the relation: $S=6\times10^{-4}/\rho D$, where ρ is the density of platinum (g cm^{-3}).

The metal surface was determined by assuming the spherical particle model. The mean diameter of the metal cristallites was 55 Å and the metal surface 51 $\mathrm{m^2 g_{Pt}^{-1}}$ for the synthesized catalyst.

Results and Discussion

Influence of the Solvent. Table 1 shows the results obtained in the hydrogenation of nitrobenzene in various solvents. As can be observed, methanol provided the best results and was therefore chosen for all subsequents experiments.

Reaction Kinetic. We have carried out blank test at 300 K in order to confirm the absence of phenomena extraneous to the catalytic process. Neither the support nor any other part of the reactor was found to be active in the nitro compound reduction. Neither did we observe any diffusion phenomena when shaking the reaction mixture at 200 shakes min^{-1} nor intraparticular diffusion in the catalyst studied.

Table 1. Influence of the Solvent on the Reduction of Nitrobenzene with Gaseous Hydrogen Catalyst Pt 3 F72

Solvent	V_0/mol s^{-1} m$_{\mathrm{Pt}}^{-2}$ × 10^6	ε
Methanol	48.4	32.6
Tetrahydrofuran	15.7	
N,*N*-Dimethylformamide	14.4	38.0
Dioxane	11.1	2.2
Chloroform	3.6	4.8

* Hydrogen pressure: 5.06 bar; nitrobenzene concentration: 0.5 M; total volume: 20 mL; reaction temperature: 300 K. ε: dielectric constant at 298 K.

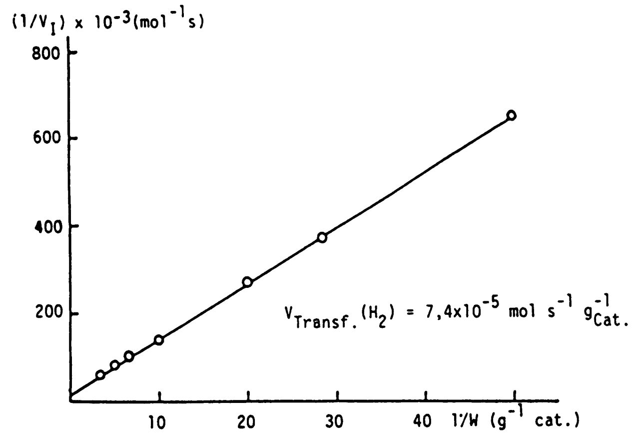


Fig. 1. Plot of $1/V_1$ vs. $1/W$ for the reduction of nitrobenzene with H_2 gaseous.

We have checked that the transfer hydrogen from the gas phase to the reaction medium is not the rate-limiting step of the process. Figure 1 shows the straight line obtained by plotting the reciprocal of the reaction rate (in mol of nitrobenzene s^{-1}) obtained at 300 K as a function of the reciprocal of the amount of catalyst used.

The rate of transfer of hydrogen from the gas phase to the catalyst, calculated from the intercept, is much higher than any of the reaction rates found in our experiments. Thus, we can state that the process is not governed by the diffusion of hydrogen to the catalyst surface through the liquid phase.

Hydrogen pressures in the range 3.1—6.2 bar and nitrobenzene concentrations between 0.1—1.0 M (1 M=1 mol dm^{-3}) were used in the determination of the kinetic parameters. The reaction kinetic was studied using methanol as solvent.

We have observed that, under the reaction conditions used, the reaction order with respect to nitrobenzene changes in the manner illustrated in Fig. 2. This order which has a value of 0.48 for nitrobenzene concentrations between 0.1—0.25 M, begins to decrease above this range until eventually becoming zero at a concentration of 0.4 M. The dependence of the reaction order on the concentration may be attributed to the sensitivity of adsorption equilibria to changes in the concentration of a liquid phase reactant.[25,26)

In the range wherein the order in nitrobenzene is zero, the reaction order with respect to hydrogen is 0.92. Under these conditions, the kinetic rate law found was:

$$V = K|P_{\mathrm{H_2}}|^{0.92}, \qquad (2)$$

where K is the pseudo rate constant.

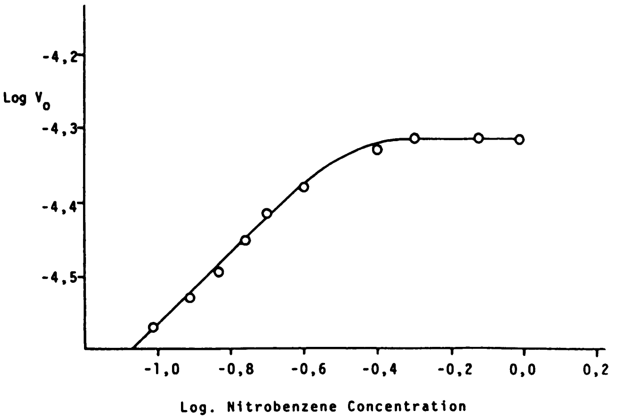


Fig. 2. Logarithmic plot of V_0 as a Function of the nitrobenzene concentration.

The results found are consistent with a Langmuir–Hinselwood type mechanism for which several expressions may be formulated.[27] Our experimental results comform the expression:

$$r_1 = K_0 \frac{KP_{H_2}}{1+KP_{H_2}}, \qquad (3)$$

with a correlation coefficient better than 0.99 and with a positive intercept for all temperatures studied. These results are in favor of a noncompetitive adsorption Langmuir–Hinselwood mechanism.

Hydrogenation of Various Nitro Compounds. Table 1 lists the rates of nitrobenzene reduction obtained by using different solvents. There is no correlation between the dielectric constant of the solvent and the reaction rate obtained, which indicates that no net charges (which would result in the formation of carbonium ions or carbanions) develop along the process. Similar results were obtained by using Pd catalysts supported on the same solid in the reaction of nitro compounds with dihydrogen.[28] However, the process is essentially different when the nitro compound reduction is carried out by hydrogen transfer.[29] In that case, the solvent polarity has a strong influence on the reduction rate of the nitro compound, and the determining step of the process may be assumed to involve the attack of a hydride ion or a proton, depending on the electron-withdrawing or electron-releasing nature of the substituent borne by the aromatic ring.[30,31]

Figure 3 illustrates how the results obtained in the reduction of various nitrocompounds in different solvents conform to the Hammett equation in the form: Log $V_I/V_{I0}=\sigma\rho$, where V_I and V_{I0} are the reduction rate of the substitued nitrobenzene and nitrobenzene respectively.

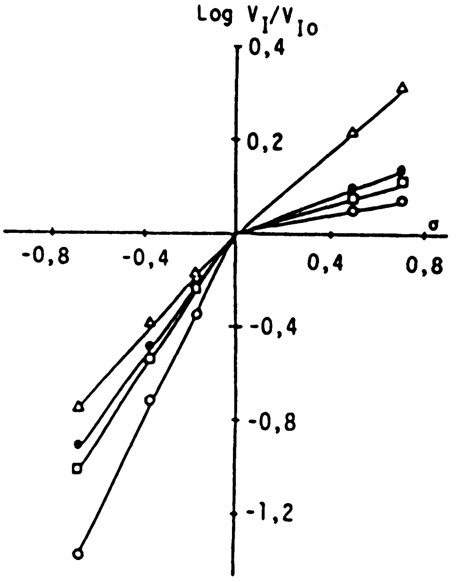


Fig. 3. Correlation between log(V_I/V_{I0}) and for various nitro compounds.

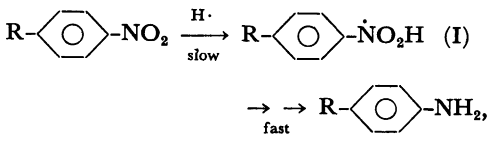
○ Methanol; □ DMF; ● THF; △ $CHCl_3$.

The straight line obtained show a different behavior of the nitro compounds according to whether the substituent is an electron-releasing of electron-withdrawing one. The substituents present only seem to participate through their electric effects. A worse fitting of the experimental results is observed by plotting the corresponding σ^+ or σ^- of the substituents, assuming the involvement of mesomeric effects which would stabilize charged intermediates. The electric effect of the substituent is transmitted through the aromatic ring, either increasing or decreasing the electron density on the nitro group to be reduced. The value of ρ (specific reaction constant), calculated from the slope of the straight lines shown in Fig. 3, provides information on the mechanism through which the process takes place. The value of ρ depends on the particular solvent used, as well as on the electron-releasing or electron-withdrawing nature of the substituents.

As can be observed, the slope changes at the origin, which is indicative of a change either in the mechanism proper or in the sensitivity of the process to the electron-releasing or electron-withdrawing effect of the substituents. The small absolute values of ρ show the slow step of the process to involve a transfer of charge or electron density rather than an appreciable mass transfer.

The results obtained can be accounted for in two ways:

a) According to the following scheme:



(4)

in which the stability of intermediate I is affected by the electron-releasing or electron-withdrawing nature of group R. The mechanism involved in the reduction of nitro compounds is basically the same as that described for the reduction with metal-acid systems,[1] and differs from the one proposed for the reduction of aromatic nitro compounds by hydrogen transfer using Pd supported catalysts in that the rate-determining step of these is supposed to be the transfer of a hydride ion.[28] Other authors have proposed mechanism for the reduction of nitro compounds with metal hydrides[32] or by transfer[9] in which the process starts with the attack of a hydride ion. Recently, it has been observed that the attack of the hydride species can be regarded as the result of three successive stages; an electron, a proton and a new electron.[33] Our results do not seem to indicate the presence of species with net charges in the rate-determining step. The nature of substituent may facilitate or hinder the adsorption of the nitro compound, since it modifies the electron density on the aromatic ring. Taft et al.[34–36] have studied the variation of the electron density on the carbon atom to which the nitro group is linked as a function of the substituent borne by the ring in different aromatic nitro compounds. Such electron density varies in much the same way as the reaction rates found in this work and in several others.[28,32] For electron-withdrawing substituents, the slope of the straight line obtained is 0.1, whereas for electron-releasing groups, the slope is 2.0, the line corresponding to the reference compound (nitrobenzene) showing an inflection point. Therefore, the aromatic ring seems to inequivocally cooperate in the reduction of the nitro group. Electron withdrawing substituents favor the adsorption of the nitro compound and contribute to stabilize the intermediate generated, which bears unpaired electrons.

In view of the results obtained, the catalyst must have a metal surface with a high electron density which favors the adsorption of the nitro compound. By assuming the possible interaction between the aromatic ring and the metal surface, the ease of adsorption of the nitro compound will increase with decreasing electron density on the aromatic ring as a result of the electron withdrawing effect of the substituent. Table 2 shows the initial rates of hydrogenation of various nitro compounds. The electron configuration of platinum, $5d^9\ 6s^1$, suggests the possibility of an electron flux from the support to the metal, which would result in the filling of the vacant upper levels and hence in increased surface electron density.

b) On the other hand, the mechanism of the process may involve nitrenes according to the scheme proposed by Carturan et al.[24] for the hydrogenation of aliphatic and aromatic nitro compounds by use of supported palladium catalysts:

$$\mathrm{ArNO_2} + \text{metal} \xrightarrow[(1')]{} \text{oxidized metal surface} + \mathrm{ArN{:}}\ \text{(ads)}$$

$$\xrightarrow[(2')]{\mathrm{ArNO_2}} \mathrm{R{-}\overset{|}{N}{-}O{-}}\ \text{(dimeric or oligomeric intermediates)}$$

$$\xrightarrow{\mathrm{H_2}} \mathrm{R{-}NH_2} + \text{metal} + \mathrm{H_2O}\,. \tag{5}$$

By analogy with the mechanism proposed by these authors, we may think that the presence of electron releasing groups would slow down stage (1′) and hence inhibit the formation of the nitrene, thus giving rise to lower conversion than nitrobenzene. Conversely, the presence of electron withdrawing substituents would stabilize the intermediate nitrene and speed up stage (2′) with respect to nitrobenzene.

According to Carturan et al.,[24] the tentative formulation of dimeric or oligomeric R-N-O-intermediates is consistent with nitrene reactivity. On the other hand, the deoxygenation of nitro groups by metal catalysts via intermediate nitrenes is similar to the process described by Cadogan, who uses homogeneous phosphine catalysts.[37] The occurrence of nitrenes has also been proposed by Watanabe et al.[38] as intermediates in the reduction of nitroarenes to aminoarenes with carbon monoxide and water.

Table 2. Initial Rates of Hydrogenation of Various Nitro Compounds. Catalyst: Pt 3 F72

Nitro compound	σ	V_I/mol s^{-1} m$_\mathrm{Pt}^{-2}$ × 10^6
p-Aminonitrobenzene	−0.66	2.0
p-Nitrophenol	−0.37	9.0
p-Nitrotoluene	−0.17	21.6
Nitrobenzene	0.00	48.4
p-Nitroacetophenone	0.50	54.3
m-Dinitrobenzene	0.71	56.8

* Hydrogen pressure: 5.06 bar; nitro compound concentration: 0.5 M; Total volume: 20 mL; reaction temperature: 300 K; solvent: methanol.

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