

# Selective Hydrogenation. I. *para*-Chloronitrobenzene to *para*-Chloroaniline Platinum on Carbon As Catalyst

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## Abstract:

*p*-Chloronitrobenzene (*p*-CNB) was selectively hydrogenated to *p*-chloroaniline (*p*-CA) using 5% Pt/C as catalyst. Using Pt/C as catalyst and with the proper choice of process conditions it was possible to obtain *p*-CA with 99% selectivity at a conversion level of 85%; implying that hydro-dehalogenation is minimized. The reaction was first order with respect to hydrogen and first order with respect to *p*-CNB. The energy of activation was 10.2 kcal/gmole.

## Introduction

*p*-Chloro aniline is an important intermediate which finds extensive applications in dyes, corrosion inhibitors, and polymers. It is also used as curing agent for epoxy resins, as cross-linking agent in some polymer preparation and in urethane manufacture. In pharmaceuticals, it is used for the synthesis of tranquilizers (diazepam) and in the preparation of herbicides such as anilophos and *N*-isopropylamine.

Synthesis of haloaromatic amines using catalytic hydrogenation starting with halonitroaromatic compounds offers several advantages over chemical reduction, including the low cost of hydrogen, the ease of product separation, and the advantage of nonpolluting process.

However, the hydrogenation of halo-substituted nitroaromatic compounds poses a serious problem due to the tendency towards hydro-dehalogenation which cannot be avoided unless modifications are made in the process.<sup>1</sup>

To avoid hydro-dehalogenation, one could either introduce suitable regulators to the reaction mixture such as acids, bases, sulphur, phosphorus<sup>2–4</sup> or modify the properties of the catalyst in a definite way like particle size and support<sup>5–10</sup> or use appropriate reaction conditions of temperature, pressure, and so forth.

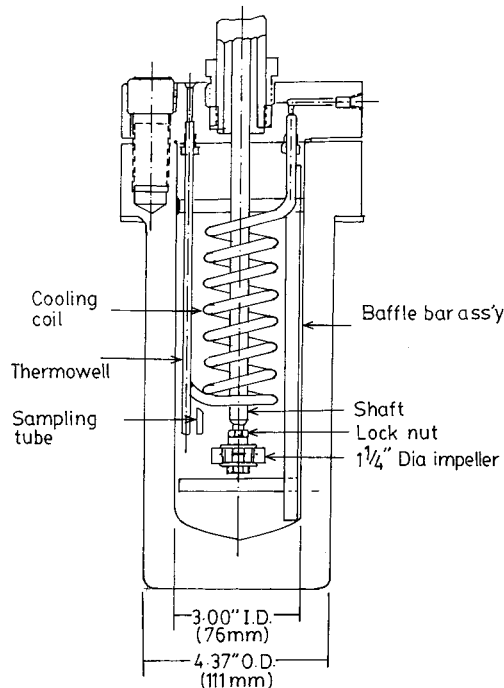


Figure 1. Autoclave.

The present work is an attempt to ascertain the suitable catalyst and process conditions for the hydrogenation of *p*-CNB to *p*-CA with a view to obtaining reasonably high activity and selectivity with respect to the desired product.

## Experimental Section

**Materials.** *p*-CNB (commercial grade), methanol, toluene (AR procured from S.D. Fine Chemicals, Bombay, India), 5% Pt/SiO<sub>2</sub>, 5%Pt/TiO<sub>2</sub>, and 2% Pt/C,<sup>11</sup> 5% Pt/C (from Aurora Mathews, Calcutta, India) were used for the above study.

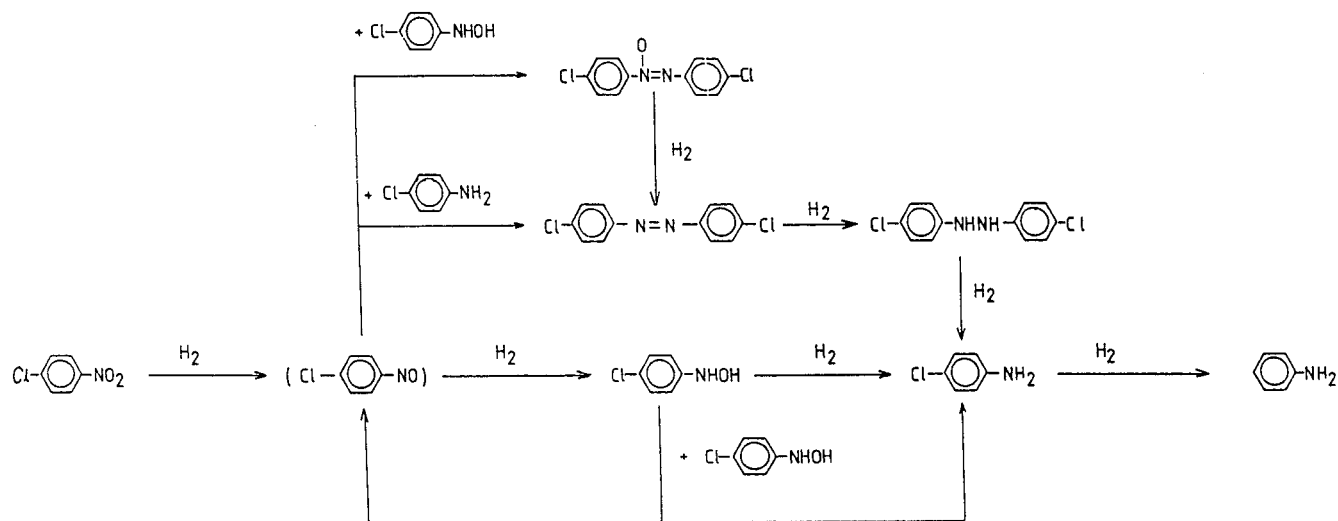
**Experimental Setup.** The hydrogenation reactions were carried out in a 7.6 cm i.d., 1 L stainless steel autoclave. It was provided with a glandless magnetically driven, six-bladed turbine agitator, a thermowell, two baffles, a cooling coil, gas inlet, and external electrical heating arrangement. The temperature in the autoclave was measured with a chromium–aluminum thermocouple which was maintained with  $\pm 1$  °C the desired value by controlling the heating rate and flow rate of cooling water (Figure 1).

**Experimental Procedure.** A predetermined quantity of *p*-CNB, solvent, and catalyst were taken, and the autoclave

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**Figure 2.** Formal reaction scheme.

was repeatedly purged with hydrogen. The reaction temperature was maintained within  $\pm 1$  °C of the desired temperature. The autoclave was pressurized with hydrogen to the desired pressure level and the agitation started. The time of reaction was reckoned from this point. A constant pressure was maintained throughout the reaction period. Samples of 1–2 mL taken at regular intervals were analyzed by gas chromatography.

**Analysis.** Samples were taken for the estimation of the overall conversion and selectivity to the desired product by gas chromatography (model: Chemito 8510). The GC column and conditions used were as follows: column, S.S. column, 3.2 mm i.d., 4 m length; stationary phase, 10% OV-17 on Chromosorb-W; carrier gas, nitrogen; flow rate, 30 mL/min; detector, F.I.D.; oven temperature, 150° C for 5 min, ramp, 10 °C/min to 300 °C for 5 min; injector temperature, 300 °C; detector temperature, 300 °C.

## Results and Discussions

**Product Distribution and Purification of Product.** A reaction scheme reported by Haber<sup>12</sup> and Kosak<sup>13</sup> for the hydrogenation of *p*-CNB to *p*-CA via the different intermediates along with the side-products is shown in Figure 2.

In this work, with the proper choice of catalyst and process parameters, it was possible to obtain *p*-CA with high selectivity, the only by-product being a high-boiling compound which is presumably due to the coupling of partially reduced intermediates.

The isolation of the product from the reaction mixture can be done by fractional distillation under vacuum. Since there is a difference of boiling points of *p*-CNB and *p*-CA (about 10 °C at absolute pressure of 40 mm Hg), it should be possible to recover the unreacted *p*-CNB and recycle it. The residue would be discarded as bottoms. Since the scale-up and design of fractional distillation can be done on the basis of physicochemical data, work in this direction was not carried out in the present investigation.

**Table 1.** Material balance<sup>a</sup>

	mol	%
<i>p</i> -chloronitrobenzene taken	0.316	100
<i>p</i> -chloronitrobenzene unreacted	0.0032	1
<i>p</i> -chloroaniline formed	0.299	94.6
high-boiling by-product	0.0138	4.4
<b>total</b>	<b>0.316</b>	<b>100</b>

<sup>a</sup> *p*-CNB, 0.316 gmol/L; solvent, methanol; reaction volume, 500 mL; catalyst, 5% Pt/C; catalyst loading, 0.01% w/v; temperature, 60 °C; period of reaction, 4 h; speed of agitation, 1080 rpm..

A typical run was carried out with a view to ascertaining the material balance. The reaction mixture was analyzed by gas chromatography. It was possible to account for 95.6% of *p*-CNB taken (Table 1).

As mentioned earlier, under some reaction conditions for which material balance is given, a significant amount of a high-boiling compound, presumably formed due to the coupling of partially reduced intermediates, is obtained. This has not been characterized. In the material balance, for typical reaction conditions 4.4% of the starting material is the high-boiling by-product (Table 1). Under suitable conditions, it is possible to avoid the by-product formation, and the selectivity is as high as 99%. Thus, for commercial development, identification was not an over-riding consideration. Moreover the by-product can be obtained as a bottom product in the distillation step and may be disposed of by incineration.

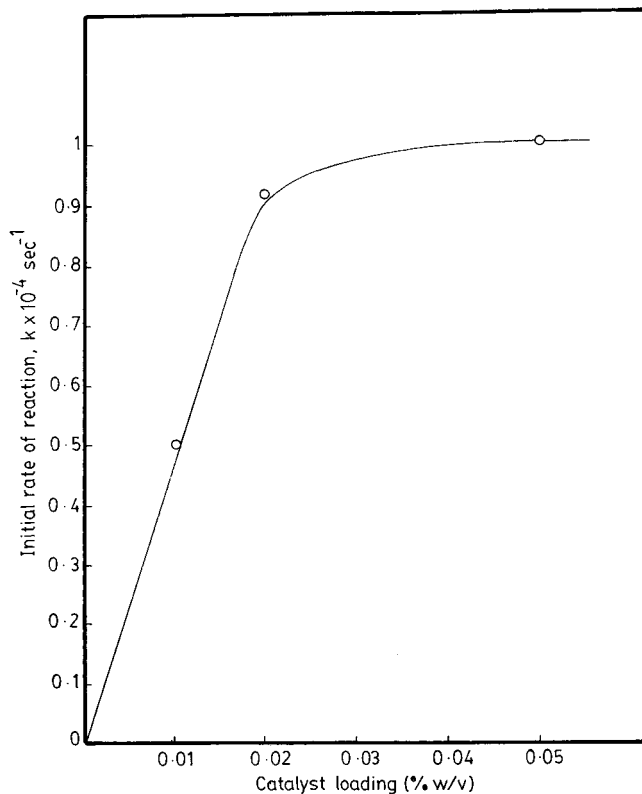
**Effect of Speed Of Agitation.** The effect of the speed of agitation was studied in the range 500–1500 rpm. Above 1000 rpm, there was no significant difference in the overall conversion of *p*-CNB which indicates the absence of external mass transfer at and above this level of agitation.

However, it may be emphasized that, depending on the size of the commercial reactor, the speed of agitator and the number of impellers used, and the catalyst loading, the mass transfer effects may play a significant role, and this needs to be assessed during scale-up.

**Effect of Catalyst Loading.** The catalyst loading expressed as weight percent of catalyst based on the total reaction volume was studied in the range of 0.01–0.05%

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**Figure 3.** Effect of catalyst loading on initial rate of reaction. *p*-CNB, 0.316 gmol/L; solvent, methanol; reaction volume, 500 mL; catalyst 5% Pt/C; pressure, 34 atm; temperature, 60 °C; speed of agitation, 1080 rpm.

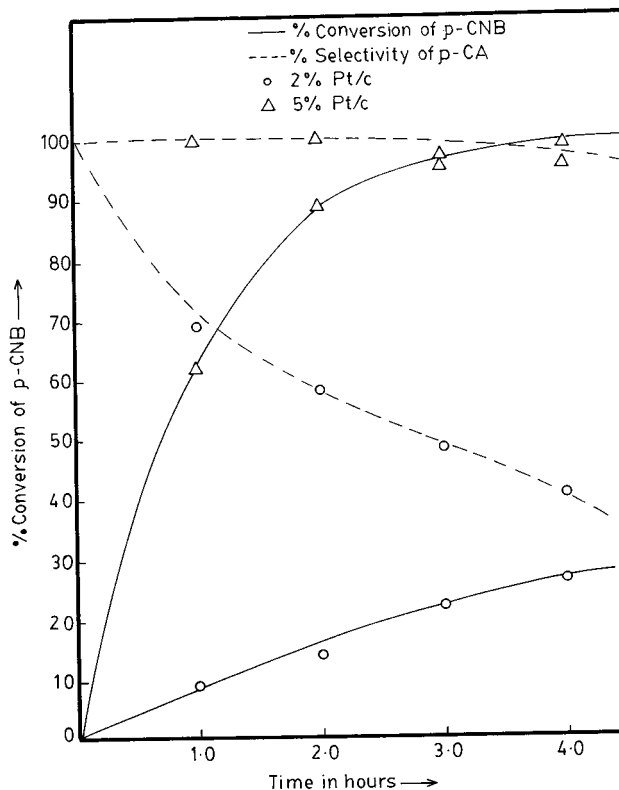
(w/v) (Figure 3). The reaction rate varied linearly with the increase in catalyst loading up to 0.02% (w/v) and then leveled off. Therefore, it appears that up to a catalyst loading of 0.02% (w/v) the reaction is mainly controlled by either the rate of mass transfer from the bulk liquid to the catalyst surface or the intrinsic kinetics of the reaction. Since, for the size of the catalyst used and the conditions employed, the diffusion of hydrogen from the bulk liquid to the solid is estimated to be unimportant, the data appears to represent the true kinetics of the process at a catalyst loading of 0.01% (w/v), temperature of 60 °C and 34 atm hydrogen pressure for 0.316 gmol/L of *p*-CNB.

**Effect of Metal Loading.** Pt/C (2% and 5%) was used to study the effect of metal loading (Figure 4). The 5% Pt/C showed higher conversions and selectivities as compared to 2% Pt/C for the same reaction time. Hence 5% Pt/C was chosen for all the subsequent runs.

**Effect of Type of Catalyst Support.** Pt, 5%, was taken on different supports such as carbon, silica, and titania. It is seen from Table 2 that carbon as a support gave the best results as compared to those from titania and silica.

**Reusability of the Catalyst.** It was seen that, when the catalyst was reused, there was significant decrease in the conversion of *p*-CNB (Table 3). Moreover, the selectivity with respect to *p*-CA decreased considerably. This suggests that the activity of the catalyst is not sustained for subsequent uses.

**Effect of Hydrogen Pressure.** The partial pressure of hydrogen was varied from 10 to 34 atm (Figure 5). As can



**Figure 4.** Effect of metal loading. *p*-CNB, 0.316 gmol/L; solvent, methanol; reaction volume 500 mL; catalyst loading, 0.01% w/v; temperature, 60 °C; period of reaction 4 h; speed of agitation, 1080 rpm.

**Table 2.** Effect of type of catalyst support on the conversion and selectivity<sup>a</sup>

no	catalyst	% overall conversion of <i>p</i> -CNB	% selectivity wrt <i>p</i> -CNB
1	5% Pt/C	99.1	95.7
2	5% Pt/SiO <sub>2</sub>	13.0	100
3	5% Pt/TiO <sub>2</sub>	8.0	100

<sup>a</sup> *p*-CNB, 0.316 gmol/L; solvent, methanol; reaction volume, 500 mL; catalyst loading, 0.01% w/v; hydrogen pressure, 34 atm; temperature, 60 °C; period of reaction, 4 h; speed of agitation, 1080 rpm.

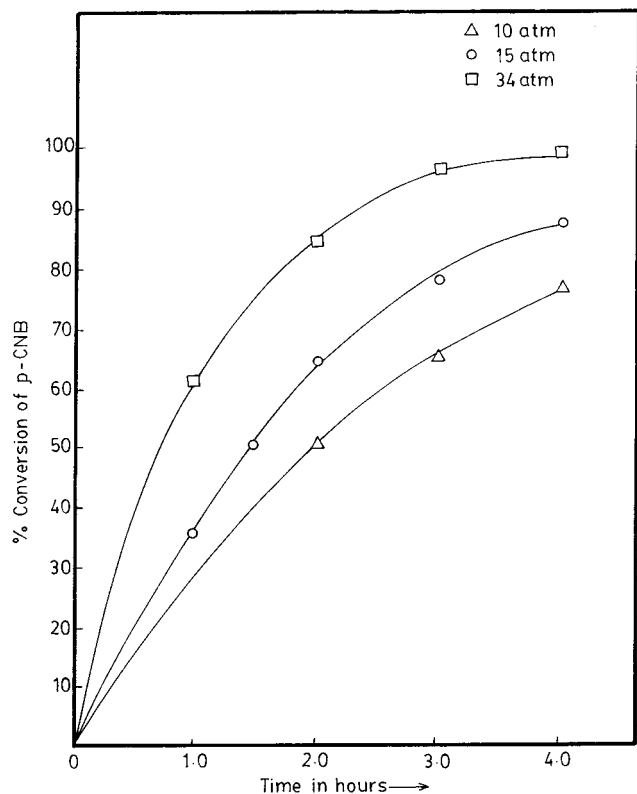
**Table 3.** Effect of repeated use of catalyst<sup>a</sup>

catalyst	% overall conversion of <i>p</i> -CNB	% selectivity wrt	
		<i>p</i> -CA	other product
fresh	85.0	99.0	1.0
repeated use	72.7	37.8	62.2

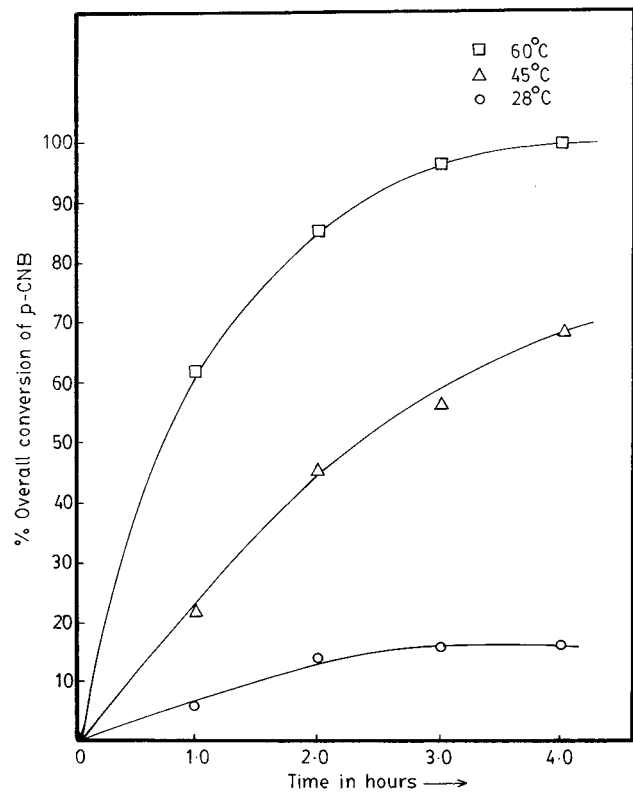
<sup>a</sup> *p*-CNB, 0.316 gmol/L; solvent, methanol; reaction volume, 500 mL; catalyst, 5% Pt/C; catalyst loading, 0.01% w/v; hydrogen pressure, 34 atm; temperature, 60 °C; period of reaction, 2 h; speed of agitation, 1080 rpm.

be seen from the Figure, the partial pressure of hydrogen had a significant effect on the rate of reaction.

**Effect of Temperature.** The effect of temperature was studied in the range of 30–60 °C (Figure 6 and Table 4). The conversion of *p*-CNB increased from 16 to 99% in the temperature range. The selectivity with respect to *p*-CA was also markedly higher at 60 °C. Although in this work the study was limited to 60 °C, higher temperatures may be more



**Figure 5.** Effect of pressure. *p*-CNB, 0.316 gmol/L; catalyst, 5% Pt/C; catalyst loading, 0.01% w/v; solvent, methanol; reaction volume, 500 mL; temperature, 60 °C; period of reaction, 4 h; speed of agitation, 1080 rpm.

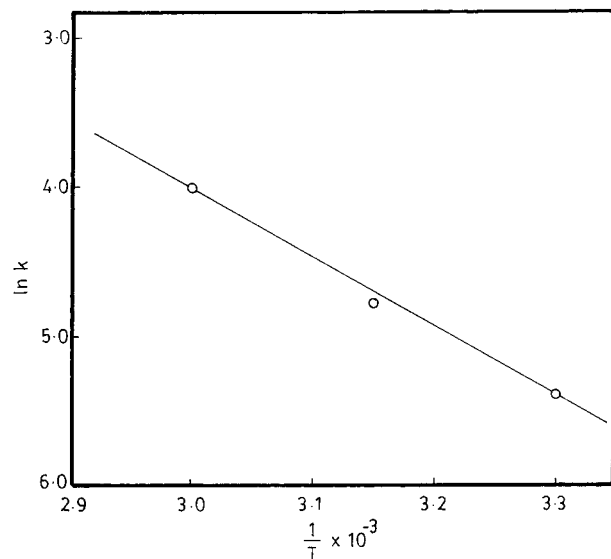


**Figure 6.** Effect of temperature. *p*-CNB, 0.316 gmol/L; catalyst, 5% Pt/C; catalyst loading, 0.01% w/v; solvent, methanol; reaction volume, 500 mL; hydrogen pressure, 34 atm; period of reaction, 4 h; speed of agitation, 1080 rpm.

**Table 4.** Effect of temperature<sup>a</sup>

temp °C	% overall conversion of <i>p</i> -CNB	% selectivity wrt		$k \times 10^{-5}$ (s <sup>-1</sup> )
		<i>p</i> -CA	other product	
28	16.4	38.6	61.4	6.7
45	68.3	48.7	51.2	7.8
60	99.1	95.7	4.3	30.8

<sup>a</sup> *p*-CNB, 0.316 gmol/L; catalyst, 5% Pt/C; catalyst loading, 0.01% w/v; solvent, methanol; reaction volume, 500 mL; hydrogen pressure, 34 atm; period of reaction, 4 h; speed of agitation, 1080 rpm.



**Figure 7.** Arrhenius plot-hydrogenation of *p*-chloronitrobenzene over 5% Pt/C.

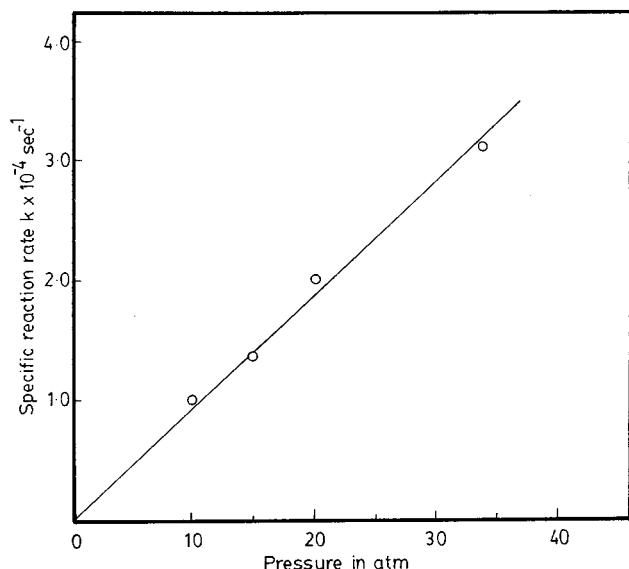
**Table 5.** Kinetic data at different hydrogen pressures<sup>a</sup>

hydrogen pressure (atm)	reaction period (h)	% overall conversion <i>p</i> -CNB	rate of reaction $k \times 10^4$ sec	mean $k$ sec <sup>-1</sup>
10.0 <sup>b</sup>	1	31.6	1.055	1015 × 10 <sup>-4</sup>
	2	51.6	1.009	
	3	65.2	1.98	
	4	76.9	1.02	
15.3 <sup>c</sup>	1	36.3	1.25	1.395 × 10 <sup>-4</sup>
	2	64.5	1.439	
	3	79.0	1.444	
	4	87.6	2.00	
34.0 <sup>d</sup>	1	61.8	2.678	3.048 × 10 <sup>-4</sup>
	2	89.5	3.125	
	3	96.0	3.13	
	4	99.1	3.26	

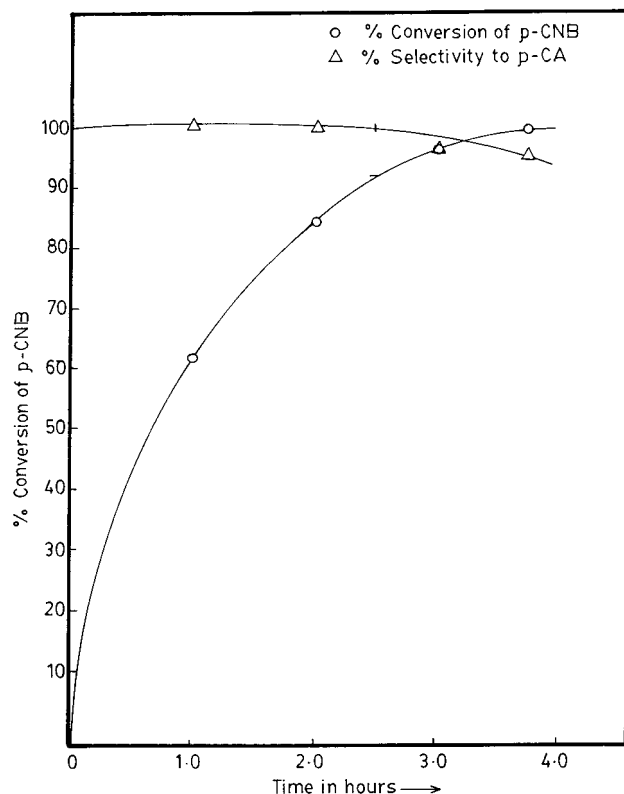
<sup>a</sup> *p*-CNB, 0.316 gmol/L; catalyst, 5% Pt/C; catalyst loading, 0.01% w/v; temperature, 60 °C; solvent, methanol; volume, 500 mL; speed of agitation, 1080 rpm. <sup>b</sup> Standard deviation at 10 atm. =  $2.7 \times 10^{-6}$  <sup>c</sup> Standard deviation at 15.3 atm. =  $8.4 \times 10^{-6}$  <sup>d</sup> Standard deviation at 34 atm. =  $2.2 \times 10^{-5}$

desirable. The apparent activation energy was found to be 10.2 kcal/mol from the Arrhenius plot (Figure 7).

**Kinetics.** The kinetic data at different pressures was studied (Table 5). When the rate of reaction versus partial pressure was plotted, it is seen that the reaction was first order with respect to hydrogen (Figure 8).

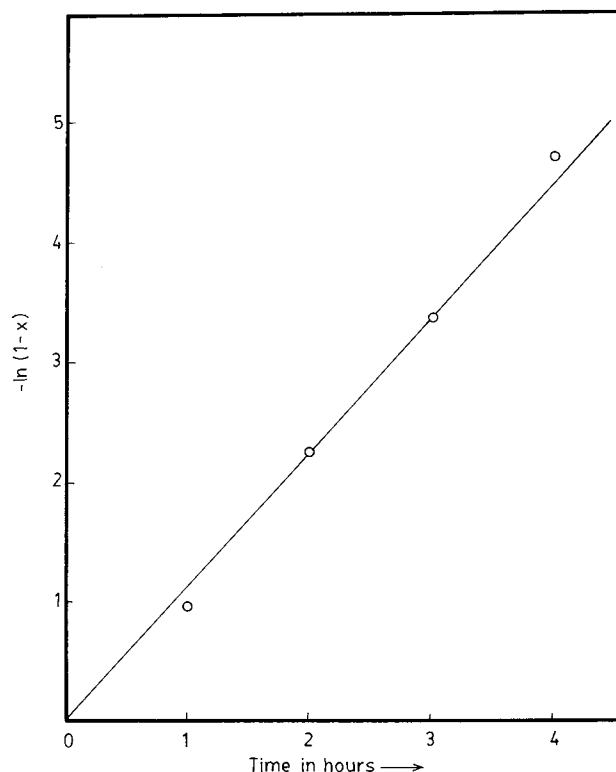


**Figure 8.** Effect of hydrogen pressure on rate constant. *p*-CNB, 0.316 gmol/L; catalyst, 5% Pt/C; catalyst loading, 0.01% w/v; temperature, 60 °C; solvent, methanol; volume, 500 mL.



**Figure 9.** Effect of reaction period. *p*-CNB, 0.316 gmol/L; solvent, methanol; reaction volume, 500 mL; catalyst, 5% Pt/C; catalyst loading, 0.01% w/v; temperature, 60 °C; pressure, 34 atm; period of reaction, 4 h; speed of agitation, 1080 rpm.

The effect of the reaction time for the hydrogenation of *p*-CNB (0.316 gmol/L) was studied at a hydrogen pressure of 34 atm, 60 °C with 0.01% w/v of 5% Pt/C (Figure 9). For the same conditions a plot of  $-\ln(1-x)$  versus time (Figure 10) shows that the hydrogenation of *p*-CNB is first order with respect to *p*-CNB. It is observed that with the increase in the reaction time, the selectivity with respect to *p*-CA decreased markedly. Therefore, the period of reaction



**Figure 10.** First-order plot with respect to *p*-chloronitrobenzene. *p*-CNB, 0.316 gmol/L; solvent, methanol; reaction volume, 500 mL; catalyst, 5% Pt/C; catalyst loading, 0.01% w/v; temperature, 60 °C; pressure, 34 atm; period of reaction, 4 h; speed of agitation, 1080 rpm.

may be restricted to 3 h and the conversion to 85%. When the catalyst was reused, the selectivity was markedly low, it may be inferred that the deactivation of catalyst with reaction time is mainly responsible for the steep decrease in the selectivity with respect to *p*-CA. The observation that 2% Pt/C gave very poor selectivity as compared to 5% Pt/C also could be expected in the light of faster deactivation of the catalyst with less metal loading which presumably deactivates faster.

**Scale-Up Aspects.** Under the conditions recommended for the process, the kinetic data represent the intrinsic kinetics of the process. Hence, the scale-up should pose no problem. While designing the industrial equipment, it should be ascertained that the mass-transfer effects do not play any significant role so that the selectivity would not change. This could be done by proper scale-up and design of the agitator system.

It may be mentioned that on industrial scale, when the diameter of the impeller is large, the speed of the agitation would be correspondingly low. The scale-up is based on equal power consumption per unit volume of the reactor.

The choice of the batch versus continuous process would be governed by the capacity of the proposed plant. In both the cases, the intrinsic kinetic data reported in the paper are relevant.

## Conclusions

(1) High selectivity of almost 99% with respect to *p*-CA could be obtained at a conversion of 85% *p*-CNB.

(2) Hydro-dehalogenation of *p*-CNB was minimized using 0.316 gmol/l of *p*-CNB at 60 °C, 0.01% w/v of 5% Pt/C at 34 atm hydrogen pressure with methanol as solvent.

(3) A catalyst loading as low as 0.01% w/v was sufficient to carry out the reaction.

(4) Aniline, which may be formed due to hydro-dehalogenation, was absent in the reaction mixture.

(5) The main reaction was accompanied with the formation of a by-product which could be due to the coupling of

partially reduced intermediates. This could, however, almost be eliminated by proper choice of reaction conditions.

(6) The hydrogenation of *p*-CNB is first order with respect to *p*-CNB and first order with respect to hydrogen.

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