Organic Process Research & Development **2001**, *5,* 263–266

Selective Hydrogenation. II. *m*-Dinitrobenzene To *m*-Nitroaniliine Using Palladium on Carbon As Catalyst

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Abstract:

In the present work *m*-dinitrobenzene (*m*-DNB) was hydrogenated to *m*-nitroaniline (*m*-NA) using palladium on carbon as catalyst. The reaction conditions were standardized to obtain *m*-NA with high selectivity. It was possible to obtain *m*-NA with 95% selectivity at 90% conversion and formation of *m*-phenylenediamine (*m*-PD) was restricted using suitable conditions. Kinetic studies of the reaction at different initial concentrations of substrate, catalyst loading, temperature, as well as pressure, were studied.

Introduction

m-Nitroaniline (*m*-NA) is used extensively as a dye-intermediate in azo and leuco dyes, as a corrosion inhibitor in the mechanical and electronic industry, in polymers for urethane synthesis, and also to a limited extent in pharmaceuticals.

Several chemical processes for the preparation of *m*-NA are known. The most common methods are based on the use of sulphides[1] and metal acid.[2]

As mentioned in the previous paper,[3] these methods of reduction are hazardous to the environment and require high cost for waste disposal, and work-up of the reaction mixture is cumbersome. Therefore, catalytic hydrogenation should be the method of choice for the preparation of *m*-NA from *m*-dinitrobenzene (*m*-DNB), provided high selectivities with respect to *m*-NA could be realized.

The catalytic hydrogenation of *m*-DNB leads to the formation of *m*-phenylenediamine (*m*-PD). However, for the selective hydrogenation of *m*-DNB to *m*-NA, modification of the catalyst system or addition of regulator or proper selection of reaction conditions is required.

Raney copper,[4] Raney nickel,[5] and Ni−Al[6] catalyst are used for the selective hydrogenation of substituted *m*-DNBs.

Various supports for the noble metal catalyst systems have been employed for the selective hydrogenation of *m*-DNB to *m*-NA.

Another approach is to introduce additives[7,8] in the reaction mixture for the selective hydrogenation of *m*-DNB to *m*-NA using noble metal catalysts. The use of noble metal catalysts may be more desirable for obtaining high selectivity. However, the crucial aspect appears to be not only the choice of catalyst system but also the manipulation of the reaction conditions and the selection of an appropriate solvent[9] for obtaining *m*-NA selectively.

In the current work *m*-DNB was hydrogenated to *m*-NA under suitable conditions using Pd/C as catalyst so that high selectivity at comparatively higher conversions could be obtained from viewpoint of process, research, and development.

Experimental Section

Materials. *m*-Dinitrobenzene, acetone, ethanol (procured from S.D. Fine Chemicals, Bombay, India), and 5% Pd/C (from Arora Mathews, Calcutta, India) were used for the above study.

Experimental Set-Up. The hydrogenation of *m*-DNB was carried out in the reaction set-up as described in the previous paper.[3]

Experimental Procedure. Predetermined quantity of *m*-DNB in the suitable solvent and the catalyst were placed in the autoclave which was repeatedly purged with hydrogen. Subsequently, the reaction was carried out as reported in the previous paper.[3]

Analysis. The reaction was monitored by analyzing the samples withdrawn at regular intervals by gas chromatography. The analysis conditions used were as follows: column: S.S., 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, 250 °C isothermal; injector temperature, 300 °C; detector temperature, 300 °C.

Results and Discussions

Effect of Speed of Agitation. The speed of agitation was studied in the range of 500−1500 rpm. It had negligible effect on overall conversion of *m*-DNB in the range of 1000−1500 rpm. With the mass-transfer effects being unimportant at speeds above 1000 rpm, all further experiments were carried out at 1080 rpm (Table 1). However, it may be emphasized that, depending on the size of the commercial reactor, the speed of agitator, and the number of impellers

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10.1021/op990039s CCC: $20.00

Table 1. **Effect of speed of agitation**[a]

no	rpm	% overall conversion
1	500	9.5
2	1080	31.2
3	1500	32.2

[a] *m*-DNB, 0.8929 gmol/L; solvent, acetone; catalyst, 5% Pd/C; catalyst loading, 1.0% g/L; temperature, 31 °C; pressure, 34 atm; reaction volume, 500 mL; reaction time, 90 min.; catalyst, 5% Pd/C; pressure, 34 atm; speed of agitation, 1080 rpm; reaction volume, 500 mL.

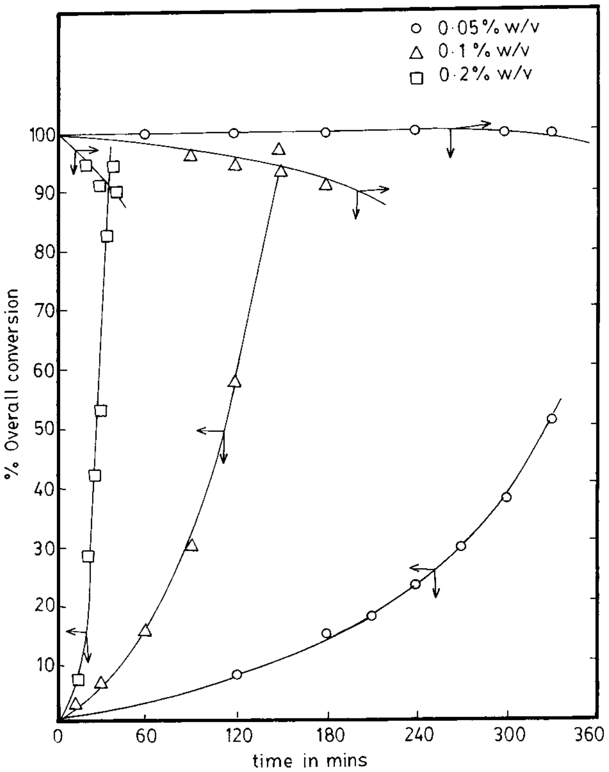

Figure 1. **Effect of catalyst loading on initial rates of reaction. *m*-DNB, 0.8929 gmol/L; solvent, acetone; catalyst, 5% Pd/C; pressure, 34 atm; speed of agitation, 1080 rpm; reaction volume, 500 mL.**

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 varied from 0.5 to 2.0% g/L (Figure 1). As the catalyst loading was increased, the reaction rates increased significantly. In view of the observations that the rate of reaction is independent of the speed of agitation (above 1000 rpm) and that it varies linearly with the catalyst loading (Figure 2), it appears that the overall reaction is controlled by reaction on the surface of the catalyst. For the conditions employed, the role of diffusion of hydrogen from the bulk liquid to the solid is estimated to be unimportant, and the data appears to represent the true kinetics of the process.

There was a significant decrease in selectivity at high catalyst loading mainly because of relatively high levels of overall conversion due to the high reaction rate.

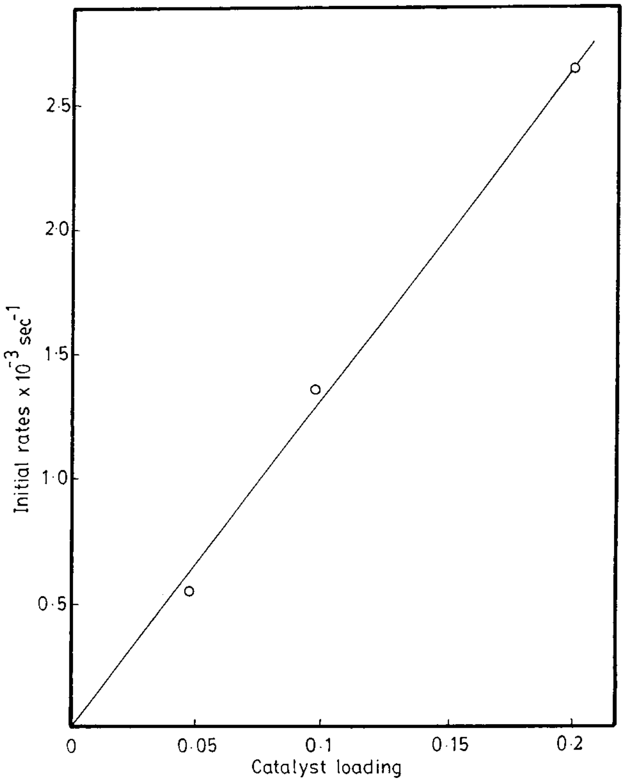

Figure 2. **Effect of catalyst concentration. *m*-DNB, 0.8929 gmol/L; solvent, acetone; catalyst, 5% Pd/C; pressure, 34 atm; speed of agitation, 1080 rpm; reaction volume, 500 mL.**

Preliminary Studies. Preliminary studies were carried out on the hydrogenation of *m*-DNB to *m*-NA using 5% Pd/C with ethanol as the solvent. The catalyst concentration was kept low (0.01% w/v), and temperature was varied from 30 to 90 °C, but no reaction took place. However, at 90 °C with a much higher catalyst loading (0.1% w/v), the reaction proceeded, but more of *m*-PD was obtained rather than desired *m*-NA. Lowering the temperature lowered the *m*-PD formation and enhanced the selectivity with respect to *m*-NA although the conversion obtained was much lower for the given period of reaction. At a catalyst loading of 0.1% w/v and the temperature of 31 °C the reaction was carried out using acetone as solvent. The selectivity was comparable, but the reaction rate was very high, since for the same period of reaction 90% overall conversion was obtained with acetone as compared to 25% overall conversion obtained with ethanol as a solvent (see Table 2). A detailed and systematic investigation is required before a proper explanation can be given about the effect of type of solvent on the reaction rate.

Effect of Temperature. As expected, with the rise in temperature, the reaction rate increased markedly. When the temperature was increased from 20° to 40 °C, the conversion of *m*-DNB increased from 7 to 93% in 1 h, and selectivity decreased marginally (Figure 4). Therefore, further reactions were carried out at 31 °C.

Effect of Partial Pressure of Hydrogen. The effect of hydrogen pressure was studied in the range of 10−34 atm. As seen in the Figure 3, there was marginal increase in the conversion to the product, but with a further increase in the pressure to 34 atm, the overall conversion of *m*-DNB was

Table 2. **Effect of solvent**[a]

catalyst concentration (%w/v)	solvent	temp. (°C)	%overall conversion of *m*-DNB	% selectivity wrt. *m*- NA	*m*-PD
0.01	ethanol	30	–	–	–
		50	–	–	–
		70	–	–	–
		90	–	–	–
0.1	ethanol	90	97.5	58.5	41.5
		31	25.0	84.1	15.9
0.1	acetone	31	90.0	86.0	14.0

[a] *m*-DNB = *m*-dinitrobenzene. *m*-NA = *m*-nitroaniline. *m*-PD = *m*-phenylenediamine. *m*-DNB, 0.2976 gmol/L; pressure, 34 atm; reaction volume, 500 mL; speed of agitation, 1080 rpm.

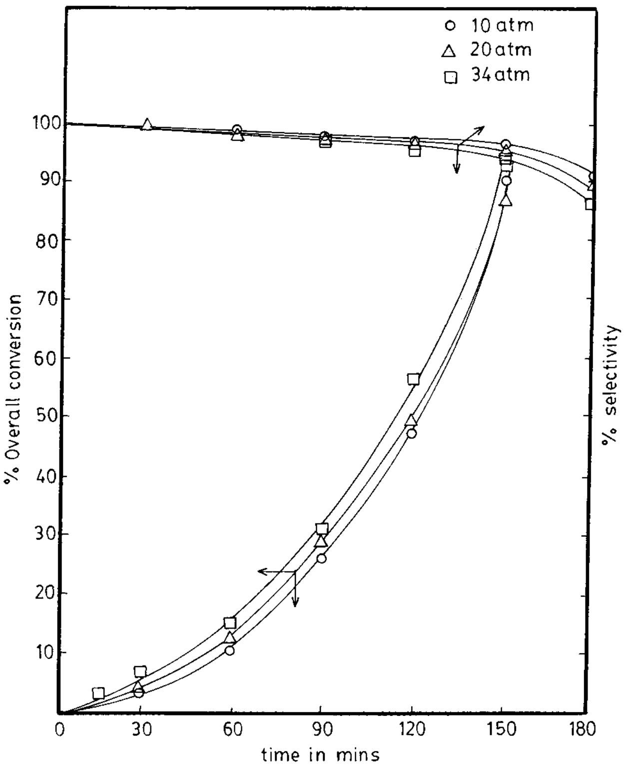

Figure 3. **Effect of pressure. *m*-DNB, 0.8929 gmol/L; catalyst, 5% Pd/C; catalyst loading, 0.1% w/v; speed of agitation, 1080 rpm; solvent, acetone; reaction volume, 500 mL.**

almost unaffected. Thus, in the pressure range of 10–34 atm, the reaction is almost independent of partial pressure of hydrogen.

Effect of Substrate Concentration and Period of Reaction. The effect of period of reaction for the hydrogenation of *m*-DNB in acetone as the medium using different catalyst loading, different pressures and different temperatures as well as different initial concentrations of *m*-DNB was studied. These are presented in Figures 1 and 3–5. In most of these cases, the selectivity obtained with respect to *m*-NA was above 90% indicating that all of these variables do not affect the selectivity in a marked way.

The kinetic data in most of the cases also indicated that with increase in the period of reaction, the rate of reaction increased substantially, presumably because the decrease in the concentration of *m*-DNB enhances the reaction rates. The same observation was made when the results with different initial concentrations of *m*-DNB were compared at various

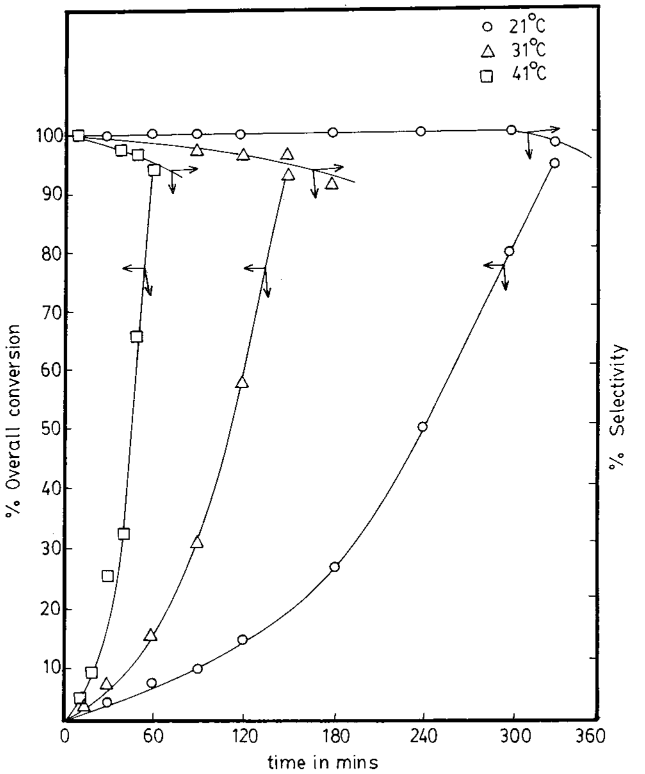

Figure 4. **Effect of temperature. *m*-DNB, 0.8929 gmol/L; catalyst, 5% Pd/C; catalyst loading, 0.1% w/v; pressure, 34 atm; speed of agitation, 1080 rpm; solvent, acetone; reaction volume, 500 mL.**

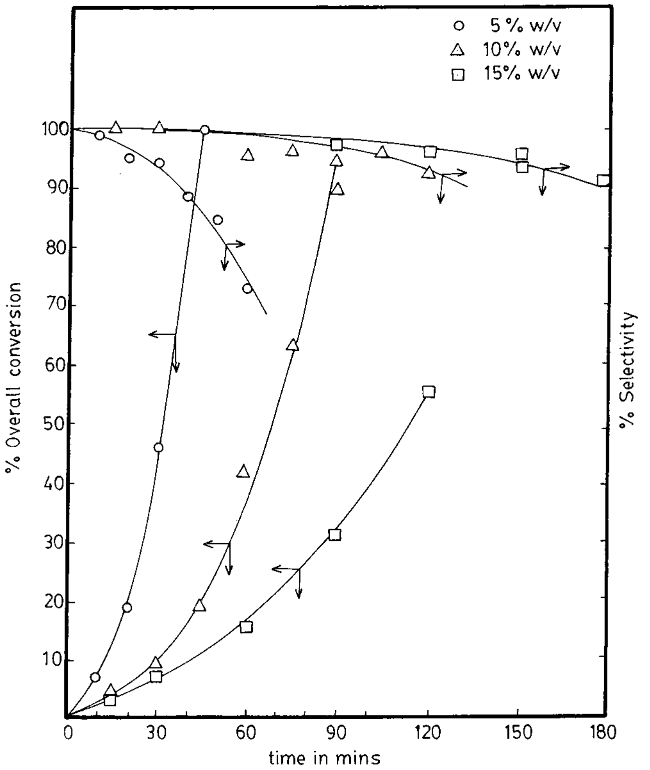

Figure 5. **Effect of substrate concentration. Catalyst, 5% Pd/C; catalyst, loading, 0.1% w/v; temperature, 31 °C; pressure, 34 atm; speed of agitation, 1080 rpm; solvent, acetone; reaction volume, 500 mL.**

Table 3. **Effect of catalyst reusability**[a]

no	catalyst	time (h)	% overall conversion of *m*-DNB	% selectivity wrt	
				m-NA	*m*-PD
1	fresh	2.5	93.7	96.4	3.6
2	used	5.0	13.5	100	–

[a] *m*-DNB, 0.8929 gmol/L; catalyst 5% Pd/C; catalyst loading 1.0% g/L; temperature, 31 °C; pressure, 34 atm; speed of agitation, 1080 rpm; reaction time, 4h.

levels of conversion (at different time intervals). This is contrary to usual expectations and could be explained if kinetic data are correlated by a suitable rate equation based on Langmuir–Hinshelwood mechanism because the present case is that of solid-catalyzed liquid-phase reaction. A detailed work in this direction was not carried out, and hence, a suitable rate expression is not proposed.

Reusability of the Catalyst. The catalyst was reused after decanting and washing with fresh solvent. Results in Table 3 show that the activity of catalyst decreased considerably, while there was a marginal enhancement in selectivity. The finding that the selectivity could be marginally better for reused catalyst is commercially not attractive. Since the conversion obtained is drastically reduced even when the reaction period is increased by a factor of 2 in the case of reused catalyst.

Isolation. No work was done regarding isolation of product. It should be possible to convert *m*-nitroaniline and *m*-phenylenediamine to the corresponding hydrochloride salts and separate these salts as aqueous solution so that unconverted *m*-dinitrobenzene is separated.

The salts maybe neutralized to obtain free amines, and these may be isolated and separated by fractional distillation under high vacuum The difference in the boiling points of *m*-nitroaniline and *m*-phenylenediamine is 20 °C at 10 mmHg.

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.

Conclusions

(1) *m*-DNB gave 90% overall conversion at 95% selectivity with respect to *m*-NA in 2.5 h.

(2) It higher catalyst loading, selectivity with respect to *m*-NA decreases, and therefore lower catalyst loading (0.1% w/v) was used.

(3) Pressure had no effect on the reaction rate, in the range of 10–34 atm.

Received for review May 4, 1999.

OP990039S