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Hydrogenation of substituted nitroarenes by a polymer-bound palladium(II) Schiff base catalyst

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Abstract The catalytic activity of a polymer-bound palladium Schiff base catalyst was investigated toward the reduction of aryl nitro compounds under ambient temperature and pressure. The dependence of the rate of hydrogenation of *o*-nitroaniline and *o*-nitrotoluene on substrate concentration, catalyst concentration and temperature has been determined. Based on the results obtained a plausible mechanism for the hydrogenation reaction is proposed and a rate expression is deduced. The energy and entropy of activation have been evaluated from the kinetic data. The polymer-bound catalyst was found to be better than its homogeneous analog $PdCl_2$(NSBA) [NSBA = *N*-salicylidene benzylamine] for both stability and reusability. Recycling studies revealed that the catalyst could be used six times without metal leaching or significant loss in activity.

Introduction

The generation of large amounts of inorganic waste due to the use of stoichiometric reagents and multistep synthesis are major drawbacks of many conventional processes for fine chemicals and pharmaceuticals [1]. Environmentally clean synthesis using transition metal complexes as catalysis have therefore been the focus of much research in recent years [2]. Such complexes have been extensively used as catalysts for polymerization, hydrogenation, hydroformylation and isomerisation of alkenes and also for substitution reactions [3].

Homogeneous catalysts, in general, have the drawbacks of high susceptibility to reaction conditions and difficult separation from the product mixture. Low thermal and chemical stabilities can lead to their slow decomposition under stringent reaction conditions [4]. These problems can be addressed by immobilizing them on a suitable polymer matrix or on an inorganic support [5–8], which provides chemical and thermal stabilities; in addition, the catalyst can often be easily separated from the product mixture and reused. Steric crowding around the metal atom in the polymer matrix may also increase the substrate specificity and product selectivity. All these qualities can make such polymer-anchored catalysts more attractive than their homogeneous counterparts [9].

Investigations on the reduction of nitroaromatics using polymer-bound metal complexes are uncommon to date and have usually required high pressure [10]. Aromatic amines are important starting materials and intermediates for the manufacture of a variety of chemicals such as dye stuffs, pharmaceuticals, agricultural chemicals, surfactants and polymers [11]. The conventional method for hydrogenation involves the use of stoichiometric amounts of finely divided iron in the presence of acid [12].

Due to the importance of polymer-supported complexes, we have used various polymer supports for the hydrogenation of olefins, nitro compounds and Schiff bases [13–15]. In continuation of this work, we describe in this article an efficient and mild method for the reduction of aromatic nitro compounds using a palladium Schiff base complex anchored to polystyrene cross-linked with divinylbenzene (DVB) as catalyst.

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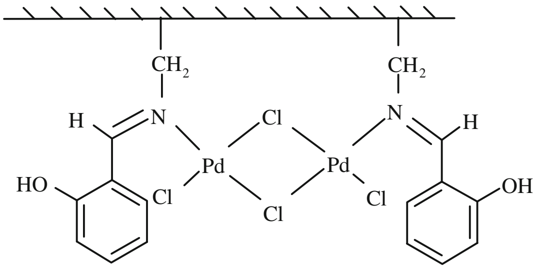


Fig. 1 Structure of polymer-bound palladium Schiff base complex

Experimental

Chloromethylated polystyrene divinyl benzene copolymer with 6.5% cross-linking (PSDVB) was obtained as a gift from Thermax India Ltd; Pune, India. Palladium chloride was obtained from Arora Matthey Ltd, India. Salicylaldehyde, *ortho-* and *meta*-nitro toluene were distilled under reduced pressure, while all the other nitroarenes were recrystallized before use. Super dry methanol was prepared according to the literature method [16]. The synthesis and characterization of the polymer-bound Schiff base (Fig. 1) catalyst has been reported elsewhere [13].

Catalyst activation

The supported palladium Schiff base complex (0.50 g) was suspended in ethanol (25 mL), and $NaBH_4$ (0.10 g, 2.64 mmol) was added during which the supported complex changed from beige color to gray [13]. After 60 min, the beads were filtered off, washed with ethanol, dried and used for hydrogenation reactions. The activated catalyst was effective for the reduction of various nitro aromatics at 30 °C and 1 Atm pressure.

Catalytic hydrogenation

The activated catalyst (0.50 g) was added to methanol (30 mL) and the mixture was saturated in an atmosphere of hydrogen for 1 h. The system was evacuated and again saturated with hydrogen gas for 15 min. A known quantity of nitro compound was injected into the system followed by releasing the system to a gas burette filled with hydrogen. The reaction was monitored by the volume of hydrogen absorbed at different intervals of time. The products were identified by IR, melting point, TLC and HPLC.

Results and discussion

Chloromethylated polystyrene (crosslinked with 6.5% divinyl benzene) beads were chemically modified into aminomethylated beads. These beads were functionalized with salicylaldehyde to form the Schiff base as described previously [13]. The functionalized beads were then reacted with palladium chloride to form the supported palladium Schiff base complex.

Table 1 Initial rate of hydrogenation of *o*-nitroaniline with various solvents (30 mL), [catalyst] = 14.41×10^{-3} M and [substrate] = 0.033 M at 30 °C

Solvent	Initial rate × 10^{-5} (mol/dm^3/s)
Methanol	5.06
Ethanol	4.65
Acetone	1.70
Acetonitrile	2.66
THF	0.03
Benzene	0.29
Toluene	0.81

The interaction of the solvent with the polymer is a complicated process. The processes of diffusion, absorption and swelling of the polymer matrix take place simultaneously [17]. The nature of the solvent influences the flexibility of the polymers and the swollen polymer segments change the physical state. This contributes to the rate of catalytic reactions. In order to study the effect of variation in solvent on the hydrogenation of nitro compounds, the rate of hydrogenation of *o*-nitroaniline in various solvents was measured and the results are tabulated in Table 1. It can be seen that polar protic solvents are more favorable as a reaction medium than aprotic polar solvents and nonpolar solvents. Since the solubility of hydrogen and miscibility of substrates are optimal in methanol, further studies of the reduction of the nitro compounds were carried out in methanol.

Hydrogenation of various nitro compounds produced the corresponding anilines in good yields. Table 2 shows the initial rates, relative rates of hydrogenation of nitro compounds and their turnover numbers (TON). In general, the rate of reduction of nitro groups is enhanced by the presence of electron donating groups [17]. Our results indicate a similar trend. The rate of reduction follows the order: *o*-nitrotoluene > *m*-nitrotoluene > *p*-nitrotoluene > *o*-nitroaniline > *o*-nitrophenol > *p*-nitrophenol > *o*-nitrobenzoic acid > *m*-nitrophenol > *p*-nitrobenzoic acid > *p*-nitroaniline > *m*-nitroaniline > *m*-nitrobenzoic acid.

Among the *o*/*m*/*p* isomers, the *ortho* isomer is reduced much faster than the other isomers. Saha and Islam [4] reported the hydrogenation of nitro compounds with a polymer-supported Ru(II) complex. They observed that nitrobenzene and its *p*-substituted derivatives are reduced at a higher rate, followed by the *meta-* and *ortho*-substituted compounds. They attributed this to dominant steric factors.

Table 2 Rates, relative rates and turnover numbers for various nitro compounds with [catalyst] = 14.41 × 10^{-3} M and [substrate] = 0.033 M at 30 °C in 30 mL methanol

Substrate	Initial rate × 10^{-5} mol/dm^3/s	Relative rate	TON
o-Nitrotoluene	12.62	14.34	31.5
m-Nitrotoluene	11.74	13.34	29.3
p-Nitrotoluene	7.52	8.55	18.8
o-Nitrobenzoic acid	3.93	4.47	9.8
m-Nitrobenzoic acid	0.88	1.00	2.1
p-Nitrobenzoic acid	2.98	3.39	7.4
o-Nitrophenol	4.68	5.32	11.7
m-Nitrophenol	3.51	3.99	8.8
p-Nitrophenol	4.03	4.58	10.1
o-Nitroaniline	5.06	5.75	12.6
m-Nitroaniline	1.12	1.27	2.8
p-Nitroaniline	2.40	2.73	6.0

TON = Initial rate/[catalyst] × 60 × 60 M (g atom of Pd) h^{-1}

Our observation is that the reduction rate follows the order *ortho* > *para* > *meta* in most cases. This may be due to dominance of electronic factors over steric factors in our system.

Among the *ortho* isomers, *o*-nitrotoulene is reduced at a much greater rate than *o*-nitroaniline and *o*-nitrophenol. The $–CH_3$ group is well known as an electron donating group, while the –OH and the $–NH_2$ groups are also electron donating by resonance [18]. The lower rates of hydrogenation for *o*-nitrophenol and *o*-nitroaniline may be due to partial blocking of coordination of the $–NO_2$ group on the available sites [4].

Kinetics of hydrogenation

The kinetics for the reduction of *o*-nitroaniline and *o*-nitrotoluene was studied in methanol medium. All reaction parameters except one were kept constant during any set of runs. The initial rate in each case was determined from a graph of hydrogen uptake versus time.

The concentration of *o*-nitroaniline or *o*-nitrotoluene was varied in the range 0.033–0.167 mol/dm^3 at a constant temperature of 30 °C and hydrogen pressure of 1 Atm using a fixed amount of palladium catalyst (14.41 × 10^{-3} M). The order of the reaction was calculated from the slope of the linear plot of log(initial rate) versus log(substrate) and was found to be fractional (Fig. 2). This indicates that an intermediate complex is formed during the reaction which could be strongly adsorbed on the catalyst surface [19, 20].

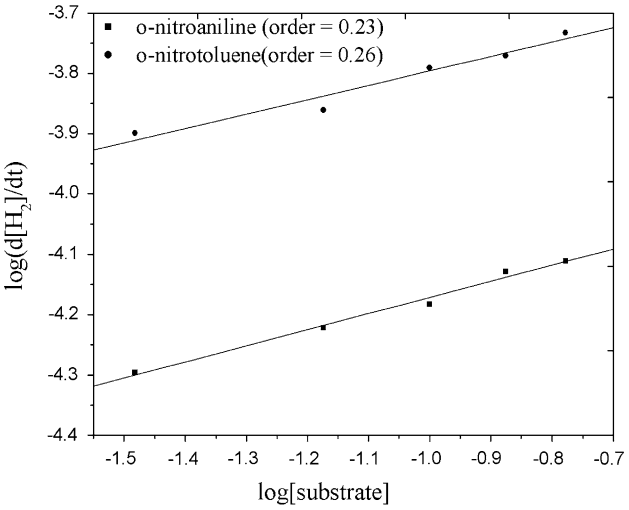


Fig. 2 Linear plot of log(initial rate) versus log(substrate)

The influence of the amount of catalyst on the rate of the reaction was studied over the range of 2.88 × 10^{-3} to 14.41 × 10^{-3} M at a constant substrate concentration of 0.033 mol/dm^3 at 30 °C keeping the pressure of H_2 at 1 Atm. The slope of the linear plot of log(initial rate) against log(catalyst) was first order for both the substrates (Fig. 3). Similar results for the hydrogenation of substituted nitrobenzenes with poly(vinyl pyridine) complexes of palladium(II) were observed by Saha and Bhattacharya [21].

From the experimental data, it is concluded that the rate of hydrogenation of nitroarenes is first order with respect to catalyst concentration and fractional order with respect to substrate concentration that leads to the experimental rate equation as follows:

$$\text{Rate} = k[\text{Catalyst}][\text{substrate}]^x$$

where $x = 0.23$ for *o*-nitroaniline and 0.26 for *o*-nitrotoluene.

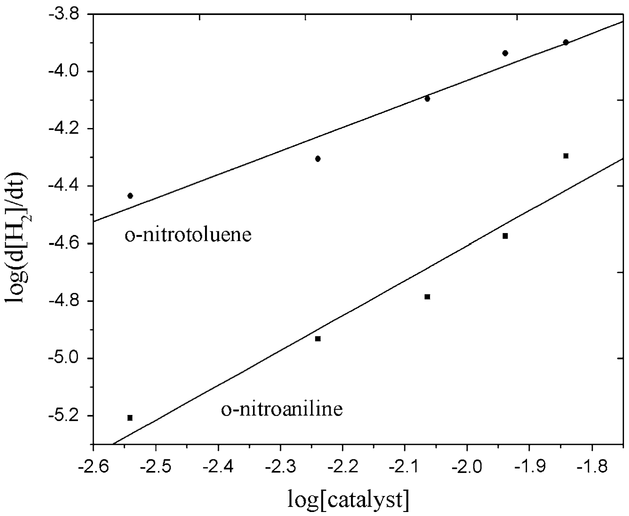
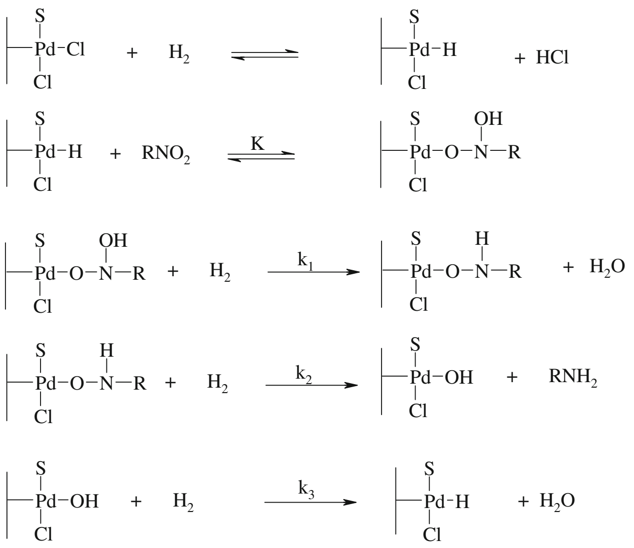


Fig. 3 Linear plot of log(initial rate) versus log(catalyst)



Scheme 1 Plausible mechanism for the hydrogenation of nitroarenes by polymer-bound Schiff base catalyst. *S* solvent

Based on the results obtained and evidence from the literature [22–24], a plausible mechanism can be proposed as in Scheme 1.

The rate equation derived from Scheme 1 is as follows;

$$\text{Rate} = \frac{k_1 k_2 k_3 K[\text{RNO}_2][\text{Cat}_{\text{tot}}][\text{H}_2]}{k_2 k_3\{1 + K[\text{RNO}_2]\} + k_1 k_3 K[\text{RNO}_2] + k_1 k_2 K[\text{RNO}_2]} \tag{1}$$

Since all reactions were carried out at a fixed hydrogen pressure of 1 atmosphere, Eq. 1 reduces to

$$\text{Rate} = \frac{k_1 k_2 k_3 K[\text{Cat}_{\text{tot}}][\text{RNO}_2]}{k_2 k_3\{1 + K[\text{RNO}_2]\} + k_1 k_3 K[\text{RNO}_2] + k_1 k_2 K[\text{RNO}_2]} \tag{2}$$

Taking the reciprocal of Eq. 2

$$\frac{1}{\text{Rate}} = \frac{1}{k_1 K[\text{RNO}_2]} + \left[\frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3}\right] \tag{3}$$

According to Eq. 3, if the order of the reaction is fractional with respect to substrate concentration, then a plot of 1/[Rate] versus 1/[RNO_2] should be a straight line with a positive intercept on the *y* axis (Fig. 4). This has been realized, supporting the proposed scheme.

Arrhenius plot

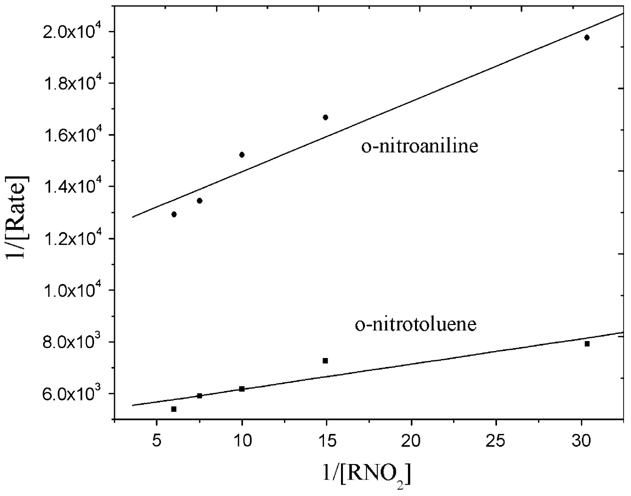


Fig. 4 Plot of 1/[rate] versus 1/[RNO_2]

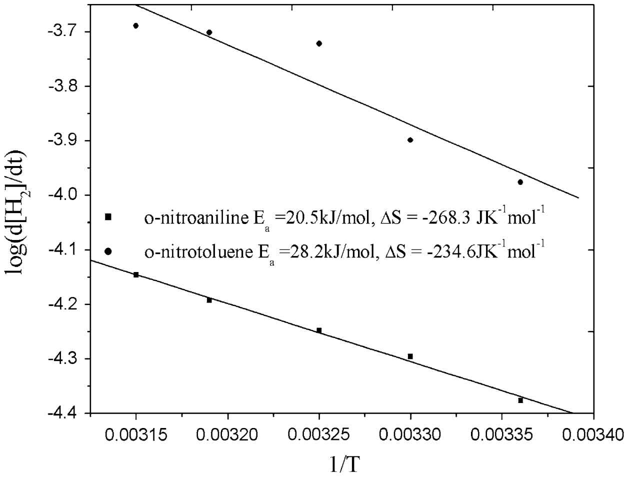


Fig. 5 Arrhenius plot: 1/*T* versus log(initial rate)

Hydrogenation of the nitro compounds was carried out using the polymer-supported palladium complex at various temperatures in the range of 25–45 °C. The activation energy was calculated from the slope of the straight line plot of log(initial rate) versus 1/*T* as 20.5 and 28.2 kJ/mol for *o*-nitroaniline and *o*-nitrotoluene respectively (Fig. 5). These low energies of activation indicate high activity of the catalyst [25]. The entropy of activation calculated from the kinetic data was −268.3 and −234.6 $\text{JK}^{-1}\ \text{mol}^{-1}$ for *o*-nitroaniline and *o*-nitrotoluene, respectively. The decrease in entropy suggests a considerable loss of freedom due to fixation of the catalyst molecule on the polymer support during the reaction.

Recycling efficiency of the catalyst

In order to find the recycling efficiency of the catalyst, a known quantity of *o*-nitroaniline was reduced and its initial rate was determined. The beads were then filtered off,

Table 3 Recycling efficiency of the catalyst over six cycles for the hydrogenation of *o*-nitroaniline at 30 °C in 30 mL methanol and hydrogen pressure of 1 Atm with a catalyst concentration of 14.41×10^{-3} M

No. of cycles	Initial rate $\times 10^{-5}$ mol/dm^3/s
1	7.58
2	7.47
3	7.25
4	6.58
5	6.02
6	5.38

washed, dried and reused. The catalyst was analyzed for its metal content after the first cycle by AAS. No leaching of the metal was observed. Also, aliquots of the reaction mixture were analyzed at regular intervals (every 10 min) for metal content by AAS. No metal was detected in solution, suggesting that there is no leaching and readsorption of metal during the reaction. The results show a marginal decrease in the initial rate after 3 cycles (Table 3). This decrease in the rate may be due to microstructural changes in the catalyst.

The homogeneous analog of the catalyst, namely $PdCl_2$(NSBA), was tested for the reduction of nitro compounds in methanol. As soon as the methanolic solution of the complex was saturated with hydrogen gas, metal precipitated out of solution, making it unsuitable for the reaction. On the other hand, the polymer-supported catalyst did not show any leaching even after six cycles and could be recycled over three times without significant change in the reaction rate.

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