Dihydrogen reduction of nitroaromatics, alkenes, alkynes using Pd(II) complexes both in normal and high pressure conditions

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Abstract

Pd(II) complexes of S-Triazines and anthranilic acid were found very efficient towards the catalytic hydrogenation of organic nitrocompounds, alkenes, alkynes, etc. No diminished catalytic activity was observed even after 6–8 repeated catalytic runs. Profound effect on the rate of reduction and nature of yield were observed in presence of extra ligand. Kinetics were studied. Mechanism has been proposed and rate equation has been derived.
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Keywords: Pd(II) complexes; Nitrocompounds; Alkenes; Alkynes; Catalytic hydrogenation

1. Introduction

Catalytic hydrogenation of organic nitrocompounds leads to very important and often valuable compounds such as amine, azo and azoxy, etc. These compounds are frequently used in dye industries [1]. Similarly selective hydrogenation of dienes and trienes to monoolefins has several useful applications in food industries more particularly in vegetable oil industries. Transition metal complexes have long been used as catalysts for the dihydrogen reduction of organic nitrocomounds [2–8], alkenes [9–12], alkynes [11–14], aldehydes [15], ketones [16], schiff bases [17] and nitriles [27]. Among the numerous homogeneous catalysts used for the dihydrogen reduction of various unsaturated organic compounds [2–4,10,13,18–23], only few are found stable enough to reduce nitro-compounds, ketones and nitriles [24–27] and in most of the cases the reduction mechanism could not be well established [4,28,29]. A good number of both orthometallated and non-orthmetallated Pd(II) complexes have been found to exhibit excellent catalytic activity towards the dihydrogen reduction of a wide variety of organic compounds. Catalyst decomposition and poor reproducibility at the time of its repeated use was the major disadvantages associated with these catalytic systems. The present paper reports the successful use of Pd(II) complexes of S-Triazines and anthranilic acid for the catalytic hydrogenation of a wide variety of organic substrates.

2. Experimental

2.1. Materials and equipments

AR grade chemicals and dry and ultra pure quality of N_2, Ar and H_2 were always used. Analytical grade solvents and liquid substrates were purified

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by distillation and dried on molecular sieves. Solid substrates were always recrystallized before use. Carbon, hydrogen and nitrogen were estimated by semi-microanalytical methods. Metal and halogen were estimated according to literature methods [30,31]. Electronic, vibrational and pmr spectra were recorded on Pye-Unicam PU-8600, Pye-Unicam SP3-300, Bruker AC-300F spectrophotometer, respectively. The product mixture were analysed by TLC on silica gel-coated plastic sheets (Merck silica gel F_{254}) and by GLC (5700 nucon gas chromatograph, using appropriate column). S-Triazines[1] OR-TH, DEt-ATH$_3$, DEt-ATH were prepared and purified as per literature methods [32,33]. Commercially available anthranilic acid were used after recrystallisation from benzene.

2.2. Catalyst preparations

2.2.1. Preparation of di-μ-chloro-bis(S-Triazino)palladium(II) [Pd$_2$(OR-T)$_2$Cl$_2$] *1a*

To the methanolic solution (25 ml) of palladium chloride (0.433 g), S-Triazine (0.113 g) in benzene (8 ml) was added drop wise with constant stirring at 30 °C. After complete addition of S-Triazine the mixture was stirred for 1 h more. The greenish yellow precipitate of the subject compound appeared slowly. The palladium S-Triazine complex was then filtered, washed several times with methanol and benzene. Finally, the compound was dried under vacuum. The other two palladium (S-Triazine) complexes, i.e. [Pd$_2$(DEt-ATH$_2$)$_2$Cl$_2$] **1b** and [Pd$_2$(DEt-AT)$_2$Cl$_2$] **1c**, were prepared following the same procedure.

Yield : **1a** = 80%; **1b** = 78%; **1c** = 75%

2.2.2. Preparation of bis(anthranilato)di-μ-chloropalladium(II) [Pd$_2$(An)$_2$Cl$_2$] *2 (where AnH is anthranilic acid)*

To the methanolic solution (25 ml) of PdCl$_2$ (0.086 g) anthranilic acid (0.133 g) in methanol (10 ml) was added drop wise with constant stirring for 20 min. The stirring was continued for 1 h more.

Greenish yellow subject compound was slowly precipitated out. Anthranilato complex was then filtered, washed several times with methanol and dried in vacuum desiccator.

Yield = 85%

2.3. Hydrogenation procedure

Normal pressure hydrogenations were carried out in a 100 ml reaction flask, in dry and deoxygenated DMF medium. In each case of catalytic run, the volume of the catalyst solution was always maintained to (15-*x*) ml. The temperature of the reacting solution was maintained constant by immersing the flask in a constant temperature oil bath and stirring the solution vigorously with the help of a magnetic stirrer. During the first 5–10 min, the original yellow colour of the catalyst solution changed either to green or greenish brown depending on the nature of the catalyst. Addition of *x* ml of substrate to the activated green or greenish brown solution slightly faded the colour of the solution and started hydrogen absorption immediately in all cases. The absorption of hydrogen stopped at the end of reduction. Small amount of reacting solutions (10^{-3} ml) was taken out from the reacting flask at regular intervals of time with the help of a syringe under hydrogen without altering the reaction pressure. The components present in this solution were estimated by gas chromatograph.

High pressure hydrogenations were carried out in a non-magnetic stainless steel high pressure autoclave. The products were identified by their boiling points/melting points and finally by GLC using appropriate columns. High pressure reductions were found only to increase the hydrogenation rate without altering the nature and yields of the products significantly, hence, the high pressure reduction were not studied in very detail.

3. Characterisation

Characterisations of the complexes were carried out on the basis of their physico-chemical properties, chemical analysis, UV-Vis, IR and NMR spectral analysis. The colour, melting point, molecular weight and

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[1] OR-TH, 2-*o*-hydroxyphenyl-4-amino-6-alkoxy-1,3,5-triazine; DEt-ATH$_3$, 2-*o*-hydroxyphenyl-4-amino-6-diethylamino-1,2-dihydro-1,3,5-triazine; and DEt-ATH, 2-*o*-hydroxyphenyl-4-amino-6-diethylamino-1,3,5-triazine.

Table 1
Analytical data of the complexes

Complexes	Colour	Melting point (°C)	Molecular weight	M%	Cl%	N%	C%	H%
[Pd$_2$(OEt-T)$_2$Cl$_2$] **1a**	Greenish yellow	225d[a]	451.78 (746.26)	28.44 (28.51)	9.46 (9.51)	15.01 (15.01)	35.39 (35.41)	2.90 (2.97)
[Pd$_2$(DEt-ATH$_2$)$_2$Cl$_2$] **1b**	Greenish yellow	230d	482.57 (804.43)	26.25 (26.45)	8.5 (8.83)	17.39 (17.41)	38.50 (38.82)	4.49 (4.51)
[Pd$_2$(DEt-AT)$_2$Cl$_2$] **1c**	Greenish yellow	240d	481.76 (800.40)	26.50 (26.58)	8.85 (8.87)	17.25 (17.49)	38.99 (39.02)	3.99 (4.03)
[Pd$_2$An$_2$Cl$_2$] **2**	Greenish yellow	220d	347.52 (532.03)	39.75 (39.99)	13.20 (13.34)	5.15 (5.26)	31.25 (31.60)	2.22 (2.27)

[a] Decomposition temperature; parenthesis indicate the calculated value.

Table 2
Electronic spectral data of ligands and complexes

Compounds	dd/CT transition (cm^{-1})	n–π*; π–π* (cm^{-1})
OEt-TH	–	29,840; 36,360; 40,750; 41,650
DEt-ATH$_3$	–	29,850; 36,360; 40,750; 46,580
DEt-ATH	–	29,850; 36,370; 40,855; 41,640
[Pd$_2$(OEt-T)$_2$Cl$_2$] **1a**	21,000 (25)	36,360; 40,700; 41,100
[Pd$_2$(DEt-ATH$_2$)$_2$Cl$_2$] **1b**	21,100 (21)	36,350; 40,050; 46,580
[Pd$_2$(DEt-AT)$_2$Cl$_2$] **1c**	21,150	36,360; 40,800; 41,640
[Pd$_2$An$_2$Cl$_2$] **2**	23,400	29,762

Electronic spectra of the ligands and the complexes were taken in DMF medium.

Table 3
IR spectral data of the complexes (cm^{-1})

Compounds	ν(NH/NH$_2$)	ν(OH phenol)	δ(NH$_2$)	ν_{as}(OCO)	ν(CO phenol)	ν_s(OCO)	ν(Pd–Cl)
OEt-TH	3460–3230	2870	1615	–	1525	–	–
DEt-ATH$_3$	3460–3230	2875	1615	–	1520	–	–
DEt-ATH	3395–3240	2865	1615	–	1525	–	–
1a	3385–3300	–	1615	–	1545	–	300–340
1b	3450–3210	–	1615	–	1535	–	310–360
1c	3385–3240	–	1615	–	1545	–	310–360
2	3160–3100	–	–	1580	–	1400	310–360

Only important peak positions are included.

analytical data of the complexes [Pd$_2$(OR-T)$_2$Cl$_2$], [Pd$_2$(DEt-ATH$_2$)$_2$Cl$_2$], [Pd$_2$(DEt-AT)$_2$Cl$_2$] and [Pd$_2$(An)$_2$Cl$_2$] suggest their formulation as presented in Table 1. Palladium complexes were soluble only in DMF and DMSO. The complexes were found stable in solid state and could be stored under nitrogen atmosphere for several months without any appreciable change. Molecular weight of palladium complexes were found lower than that required for their respective formula. This suggest partial or complete dissociation of the dinuclear palladium compounds to the corresponding mononuclear ones in solution in

accordance with the equation

$$Pd_2L_2Cl_2 + DMF \rightarrow 2PdL \cdot DMF \cdot Cl$$
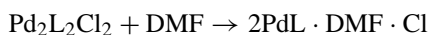
The Electronic, vibrational and pmr spectral data of the ligands and their metal complexes are presented in Tables 2–4.

4. Recycle of the catalyst

In the case of reduction of the nitroaromatics, the addition of the fresh substrate to the reaction mixture

Table 4
PMR spectral data of the complexes (δ)

1a	1b	1c	2	Assignment
6.6–7.3 (m, 8)	–	–	7.0–7.3 (m, 4); 7.5–7.7 (m, 4)	Ring protons
7.3–8.4 (m, 4)	7.9–8.9 (m, 4)	7.9–8.6 (m, 4)	6.5–6.9 (b, 4)	–NH$_2$
4.2 (q, 4)	3.4 (m, 4)	3.5 (m, 4)	–	–OCH$_2$/N–CH$_2$
–	5.9 (s, 1)	–	–	–CH-Triazine
1.3 (t, 6)	–	–	–	–CH$_3$–

PMR spectra were taken in DMSO-d$_6$.

at the end of reduction resumed hydrogen absorption with almost initial rate. In case of alkene reduction, the products and the unreacted substrate could be removed very easily by fractional distillation under reduced pressure of hydrogen or nitrogen. The catalytic activity of the residual solution was found same to that of original one. The catalytic activity of the solution remained unaltered even after 6–8 repeated catalytic runs.

5. Results and discussion

On the basis of initial rate of reduction the complexes may be arranged in the following order in accordance to their catalytic activities (Table 5)

$[Pd_2(OEt-T)_2Cl_2] > [Pd_2(An)_2Cl_2]$

$> [Pd_2(DEt-AT)_2Cl_2] > [Pd_2(DEt-ATH_2)_2Cl_2]$
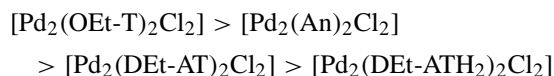
The $[Pd_2(OEt-T)_2Cl_2]$ appeared to be an efficient catalyst for the reduction of various substrates. The na-

ture of the products obtained for a particular substrate using different complexes, as catalyst were almost same, but the yield of different products was found to depend on the nature of the catalyst. The nature and yield of products, the turn over number, initial rate of hydrogen absorption and the optimum conditions for different substrates using $[Pd_2(OEt-T)_2Cl_2]$ are presented in Table 6. DMF medium was found best solvent for the catalytic hydrogenation. The nitroaromatics except the dinitrobenzene and nitrophenol were reduced finally to the corresponding anilines and the yields were found almost quantitative. Corresponding phenylhydroxylamine and azoxybenzene were detected at intermediate stages in case of nitrobenzene and its *p*-substituted derivatives. Corresponding phenylhydroxylamine was however detected as intermediate in case of other nitroaromatics also. These are however finally reduced to the corresponding anilines (Fig. 1). *m*-Dinitrobenzene was sequentially reduced first to monohydroxylamine and then to dihydroxylamine. Formation of dihydroxylamine started

Table 5
Relative activities of the palladium(II) complexes as homogeneous hydrogenation catalyst

Catalyst	Substrate (mol l^{-1})	Initial rate of H$_2$ absorption (ml min^{-1})	Initial turn over number (min^{-1})	Product with percent of yield
Nitrobenzene				
$[Pd_2(OEt-T)_2Cl_2]$	0.32	6.4	18	Aniline-98
$[Pd_2(An)_2Cl_2]$	0.32	5.9	17	Aniline-96
$[Pd_2(DEt-AT)_2Cl_2]$	0.32	5.2	15	Aniline-95
$[Pd_2(DEt-ATH_2)_2Cl_2]$	0.32	4.4	13	Aniline-92
Styrene				
$[Pd_2(OEt-T)_2Cl_2]$	0.29	10.4	87	Ethylbenzene-98
$[Pd_2(An)_2Cl_2]$	0.29	9.9	83	Ethylbenzene-96
$[Pd_2(DEt-AT)_2Cl_2]$	0.29	8.4	79	Ethylbenzene-95
$[Pd_2(DEt-ATH_2)_2Cl_2]$	0.29	7.2	60	Ethylbenzene-92

Medium, DMF; [Cat], 3.57×10^{-4} mol l^{-1}; total volume, 15 ml; P_{H_2}, 1 atm; temperature, 25 °C.

Table 6

Optimum conditions and yields of main products at 1 atm pressure of hydrogen and at 25 °C using [Pd$_2$(OEt-T)$_2$Cl$_2$]

Substrate	[Cat] × 10^4 (mol l^{-1})	Initial rate of H$_2$ absorption (ml min^{-1})	Initial turn over number (min^{-1})	Products with percent of yield
Styrene	3.57	10.4	87	Ethylbenzene-98
Acrylonitrile	3.66	9.4	77	Ethylcyanide-97
Pent-1-ene	3.66	7.4	60	Pentane-50; pent-2-ene-45
Hex-1-ene	3.66	6.1	50	Hexane-54; hex-2-ene-40
Hept-1-ene	3.66	5.2	43	Heptane-50; hept-2ene-42
w-Nitrostyrene	3.74	4.4	35	ω-Nitroethylbenzene-98
Cyclohexene	3.74	4.4	35	Cyclohexane-97
Maleic acid	3.79	1.5	12	Succinic acid-95
Fumaric acid	3.79	1.1	8	Succinic acid-96
Diphenylacetylene	3.57	7.23	30	Diphenylethane-98
Nitrobenzene	3.57	6.43	18	Aniline-98
p-Nitrotoluene	3.66	5.5	15	p-Toludine-96
m-Dinitrobenzene	3.74	4.4	12	m-Phenylenedihydroxyl-amine-92
p-Chloronitrobenzene	3.74	3.6	10	p-Chloroaniline-96
p-Nitroaniline	3.74	3.1	8	p-Phenylenediamine-95
m-Chloronitrobenzene	3.70	2.5	7	m-Chloroaniline-95
m-Nitroaniline	3.70	2.5	7	m-Phenylenediamine-96
o-Nitronaphthalene	3.79	2.2	6	o-Aminonaphthaline-95
o-Nitrotoluene	3.79	2.1	5	o-Toludine-95
o-Chloronitrobenzene	3.84	2.1	5	o-Chloroaniline-96
p-Nitrophenol	3.84	1.54	4	p-Hydroxyphenylhydroxyl-amine-95
Benzaldehyde	3.84	1.54	11	Benzylalcohol-96
Benzil	3.84	1.1	7	1,2-Diphenylethylglycol-97

Total volume, 15 ml; [Subs] = 0.32 mol l^{-1}; medium, DMF.

only after 90% conversion of *m*-dinitrobenzene to *m*-nitrophenylhydroxylamine (Fig. 2). Different nitroaromatics may be arranged in the following order in accordance to their initial rate of reductions.
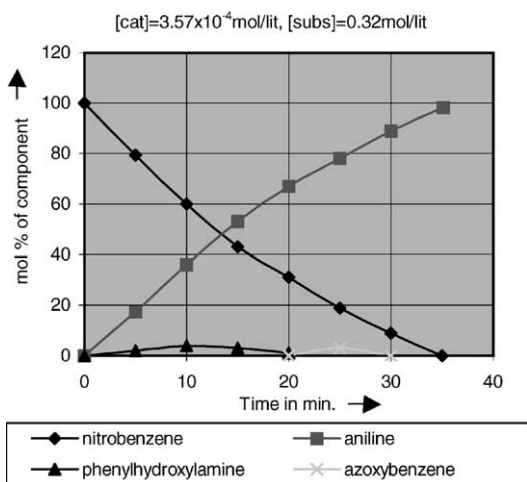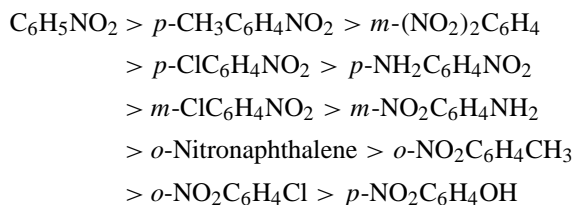
$$C_6H_5NO_2 > p\text{-}CH_3C_6H_4NO_2 > m\text{-}(NO_2)_2C_6H_4$$
$$> p\text{-}ClC_6H_4NO_2 > p\text{-}NH_2C_6H_4NO_2$$
$$> m\text{-}ClC_6H_4NO_2 > m\text{-}NO_2C_6H_4NH_2$$
$$> o\text{-Nitronaphthalene} > o\text{-}NO_2C_6H_4CH_3$$
$$> o\text{-}NO_2C_6H_4Cl > p\text{-}NO_2C_6H_4OH$$

Nitrobenzene and its *p*-substituted derivatives were found to reduce at the highest rate followed by *m*-substituted and then by *o*-substituted nitroaromatics. The reduction rate appeared to be primarily controlled by the steric factor. The least sterically hinders substrate were reduced at the fastest rate. In case of *p*-NH$_2$C$_6$H$_4$NO$_2$ and *p*-OHC$_6$H$_4$NO$_2$ the participation of lone pair electrons of –NH$_2$ and –OH group in the phenyl ring resonance make the –NO$_2$ group electron rich. This probably favoured stronger coordination of –NO$_2$ to metal and thus increase the stability of the corresponding metal nitroaromatic complex. This opposed the reduction of the coordinated nitroaromatics and hence the reduction rate became slower.
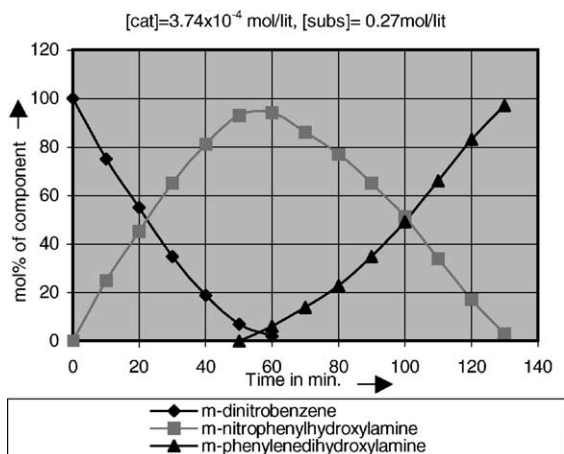

Fig. 1. Reduction of nitrobenzene with catalyst Pd$_2$(OEt-T)$_2$Cl$_2$ in DMF at 25 °C and 1 atm pressure.

Fig. 2. Sequential reduction of *m*-dinitrobenzene with catalyst Pd$_2$(OEt-T)$_2$Cl$_2$ in DMF at 25 °C.

The rate of reduction of alk-1-enes were found much faster than those of nitroaromatics. The reduction of alk-1-enes were always accomplished by isomerisation. Isomerised products were mainly corresponding alk-2-ene and to some extent alk-3-ene. Considering the rate of reduction, substrates containing C=C may be placed in the following order.

Styrene > acrylonitrile > pent-1-ene > hex-1-ene

> hept-1-ene > *w*-nitrostyrene

> cyclohexene > maleic acid > fumaric acid

From the result, it appeared that the double bond, which was a part of a delocalised system, was reduced more rapidly than the isolated one. Localised double bond with relatively higher electron density probably formed stronger metal substrate complex and hence was reduced more slowly than a delocalised one. Steric factor appeared to be important in influencing the reduction rate. Rate of reduction of alk-2-ene was very much slow as compared to the corresponding alk-1-ene. The course of reduction of styrene and hept-1-ene using [Pd$_2$(OEt-T)$_2$Cl$_2$], in DMF medium is shown in Figs. 3 and 4, respectively.

Stepwise reductions were also observed in case of diphenylacetylene and phenylacetylene. Diphenylacetylene was first reduced to *cis*-stilbene and then to 1,2-diphenylethane (Fig. 5).

It has already been mentioned that experimentally determined molecular weight of the compounds,
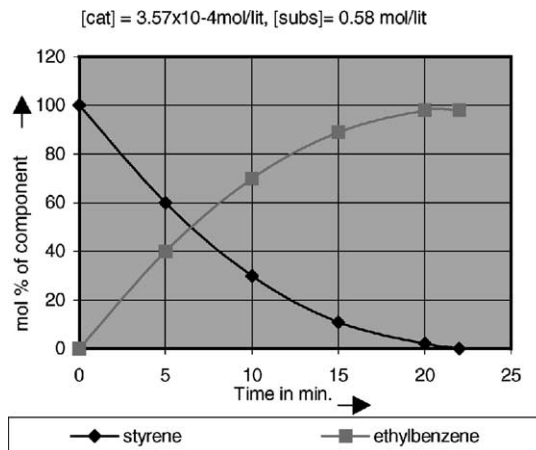
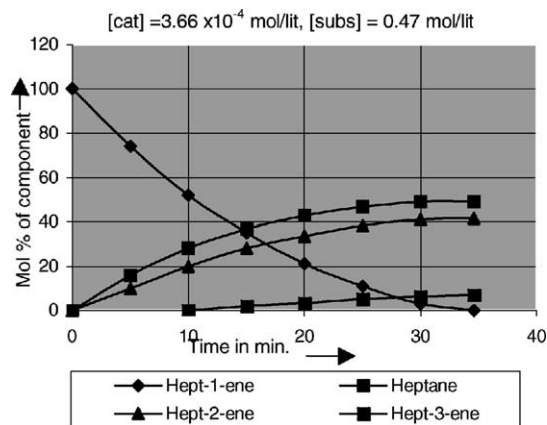Fig. 3. Reduction of styrene with catalyst Pd$_2$(OEt-T)$_2$Cl$_2$ in DMF at 25 °C and 1 atm pressure of hydrogen.

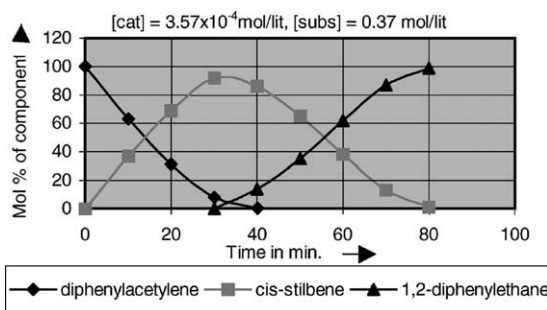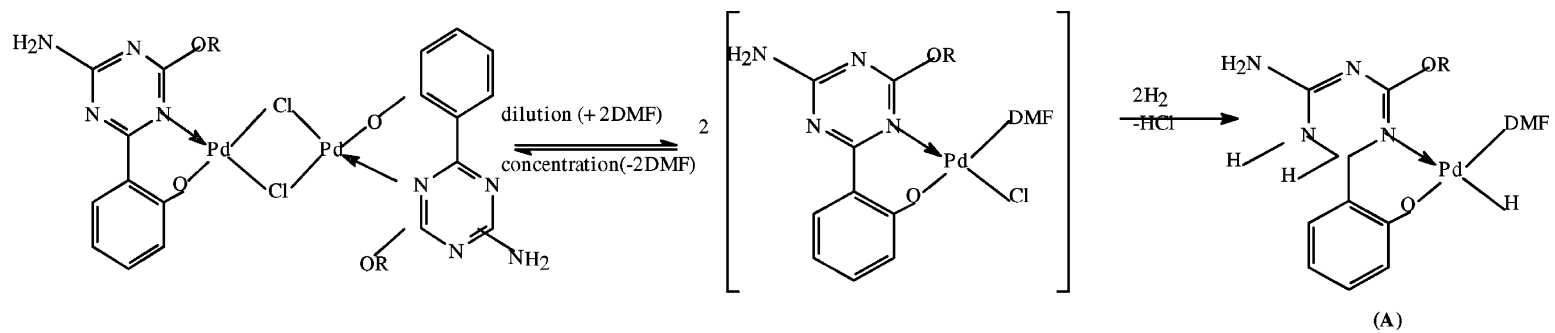Fig. 4. Reduction of hept-1-ene with catalyst Pd$_2$(OEt-T)$_2$Cl$_2$ in DMF at 25 °C and 1 atm pressure of hydrogen.

Fig. 5. Sequential reduction of diphenylacetylene with catalyst Pd$_2$(OEt-T)$_2$Cl$_2$ in DMF at 25 °C and 1 atm pressure of hydrogen.

Scheme 1.

$[Pd_2(OR-T)_2Cl_2]$, $[Pd_2(An)_2Cl_2]$, $[Pd_2(DEt-AT)_2Cl_2]$ and $[Pd_2(DEt-ATH_2)_2Cl_2]$ in DMF medium were found to be nearly half to that of the theoretical values. The DMF solution of the above complexes was changed to green/greenish brown within 5–10 min in contact with hydrogen. All attempts to isolate this green/greenish brown compounds were not succeeded. This green/greenish brown compound might be highly reactive palladium hydride species as reported elsewhere [34,35]. The colour of this greenish brown solution was change to its original one when the same was stirred with small amount of ammonium chloride. Removal of solvent from this ammonium chloride treated solution under reduced pressure led to the isolation of original $Pd_2L_2Cl_2$. In absence of ammonium chloride, the greenish brown solution decomposed to Pd(0) and the respective ligand. The above experimental observation led us to suggest the following scheme for the various transformations that the complexes underwent during stirring and hydrogenation (Scheme 1).

5.1. Effect of temperature

At 0 °C, the reduction rates of the substrates with any of the catalyst were extremely slow. The rate of reduction of different substrates was found to increase with increasing temperature up to 60 °C without any decomposition of the catalyst. The optimum temperature was found to lie between 25 and 30 °C for all types of substrates studied in the present investigation.

5.2. Effect of solvent

Among different organic solvents, DMF was found to be the best medium for these hydrogenation processes. The reduction rate was decreased both in stronger coordinating solvents like THF, DMSO and in non-coordinating solvents like C_6H_6, $C_6H_5CH_3$, etc. It appeared that some type of interaction between the complex and the solvent molecule required for the former to become catalytically active. Probably the dinuclear complex was converted to the mononuclear one containing solvent molecule in the coordinating sphere as

$$M_2L_2Cl_2 + 2S \rightarrow 2MLClS$$

where S is the solvent molecule. Moderately strong coordinating solvents might be sufficient for this pur-

pose. In presence of very strong coordinating solvents like pyridine, picoline, etc. the solvent coordination was strong and the solvent molecule from MLClS might not be replaced by the nitroaromatic or alkene molecule under the experimental conditions. Hence, no reduction was observed in strong coordinating solvent medium.

5.3. Effect of acid

Initial addition of acid (0.001–0.003 M HCl) to the catalyst solution prior to the introduction of H_2 resulted the delayed activation of catalyst. The rate of hydrogenation of nitroaromatics and alkenes in presence of acid however remained same to that of in pure DMF medium. Reduction of nitrobenzene in acid medium increased the amount of phenylhydroxylamine and decreased the amount of azoxybenzene at intermediate stages.

5.4. Effect of alkali

Addition of alkali (0.005 M NaOH) to the catalyst solution prior to the introduction of hydrogen accelerated the activation and formation of green colour without any appreciable change in the rate of hydrogen absorption. In presence of alkali, the formation of azoxybenzene near the end of nitrobenzene reduction increased.

5.5. Effect of extra ligand

The addition of extra ligand such as triphenylphosphine, pyridine, etc. has a profound effect on the rate of reduction. Reduction of all nitroaromatics stopped if the concentration of the extra ligand exceeded 0.5 M. Similarly, in presence of strong coordinating foreign ligands, the rate of both hydrogenation and isomerisation of alk-1-enes decreased considerably. The rate of hydrogenation was found to decrease more than that of isomerisation. Therefore, the yield of isomerisation products increased relative to that of alkanes.

6. Kinetic studies

Kinetic studies were made with $[Pd_2(OEt-T)_2Cl_2]$, $[Pd_2(An)_2Cl_2]$ and $[Pd_2(DEt-AT)_2Cl_2]$. The total

[styrene]=0.29mol/lit,[diphenylacetylene]=0.18mol/lit
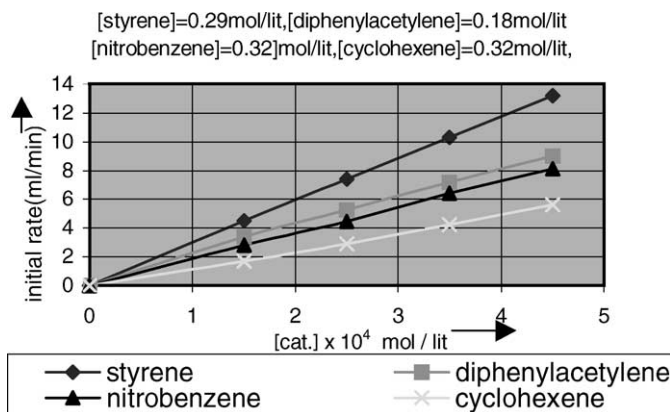[nitrobenzene]=0.32]mol/lit,[cyclohexene]=0.32mol/lit,

Fig. 6. Rate dependence on catalyst concentration, using catalyst $Pd_2(OEt-T)_2Cl_2$ in DMF at 25 °C and 1 atm pressure of hydrogen.

volume of the reacting solution was always kept to 15 ml. The initial rates were determined from graphical extrapolation of the rate curves to $t = 0$. Kinetic studies were made mainly with styrene, diphenylacetylene, nitrobenzene and cyclohexene. All the above three complexes follow the same rate law for a particular substrate.

6.1. Variation of catalyst concentration

Kinetic studies revealed that the initial rates of hydrogenation of styrene, diphenylacetylene, nitrobenzene and cyclohexene were first order dependent on catalyst concentration. The substrate concentration and hydrogen pressure were kept constant during the variation of the various catalysts concentration. The result with the catalyst $[Pd_2(OEt-T)_2Cl_2]$ are given in Fig. 6.

6.2. Variation of substrate concentration

Initial rate of reduction for all the substrates under investigation was found independent of the substrate concentration at constant catalyst concentration and hydrogen pressure. The results with $[Pd_2(OEt-T)_2Cl_2]$ are given in Fig. 7.

6.3. Variation of hydrogen pressure

The variation in initial rate of reduction on the pressure of H_2 has been found to depend on the nature of the substrate. In case of reductions of nitrobenzene and styrene, the initial rate of hydrogen absorption was found to be second order dependent on hydrogen pressure. However first order rate dependence on hydrogen pressure was observed for the reduction of cyclohexene and alk-1-ene. The results are summarised in Figs. 8–10.

The following mechanism may thus be suggested for the reduction of nitrobenzene and styrene (Scheme 2) and (Scheme 3), respectively.

According to Scheme 2

$$\text{Rate} = k_2[C][H_2]^2 \tag{1}$$

Let $[Cat]_T$ = total concentration of the catalyst, then

$$[Cat]_T = [A] + [B] + [C] + [D]$$
$$= [C] + [B] + [A] + [D] \tag{2}$$

$$[B] = \frac{k_2}{k_1}[C][H_2]^2 = K_5[C][H_2]^2$$

where

$$K_5 = \frac{k_2}{k_1}$$

$$[A] = \frac{(k_4 + k_1)[B]}{k_3[PhNO_2]} = \frac{(k_4 + k_1)K_5[C][H_2]^2}{k_3[PhNO_2]}$$
$$= K_3\frac{[C][H_2]^2}{[PhNO_2]}$$

where

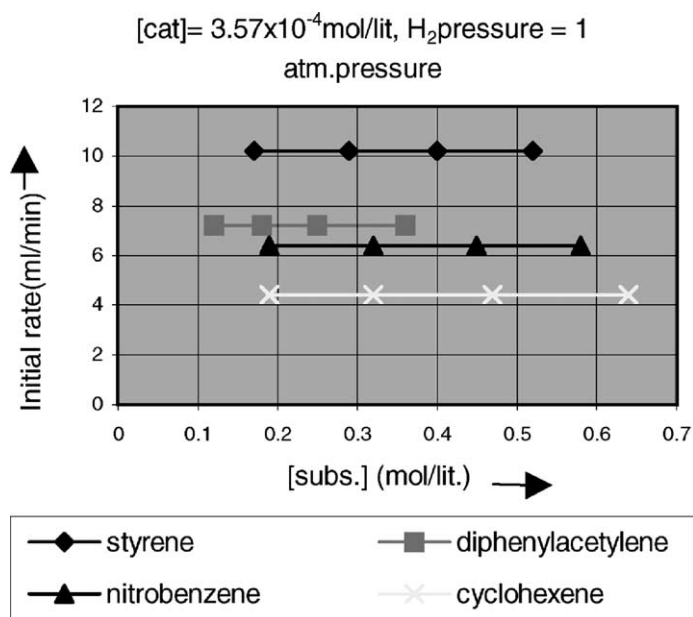$$K_3 = \frac{(k_4 + k_1)K_5}{k_3}$$

Fig. 7. Rate dependence on substrate concentration using catalyst $Pd_2(OEt\text{-}T)_2Cl_2$ in DMF at 25 °C and 1 atm pressure of hydrogen.

$$[D] = \frac{K_2[A][PhNHOH]}{[DMF]} = \frac{K_2 K_3 [C][H_2]^2 [PhNHOH]}{[DMF][PhNO_2]}$$

$$= \frac{K_4[C][H_2]^2[PhNHOH]}{[PhNO_2]}$$

where

$$K_4 = \frac{K_2 K_3}{[DMF]}$$

Fig. 8. Rate dependence on hydrogen pressure using catalyst $[Pd_2(OEt\text{-}T)_2Cl_2]$ in DMF at 25 °C.

Now, putting the value of [B], [A] and [D] in Eq. (2), we get

$$[Cat]_T = \frac{[C][[PhNO_2] + [H_2]^2\{K_5[PhNO_2] + K_3 + K_4[PhNHOH]\}]}{[PhNO_2]}$$

or

$$[C] = \frac{[Cat]_T[PhNO_2]}{[[PhNO_2] + [H_2]^2\{K_5[PhNO_2] + K_3 + K_4[PhNHOH]\}]}$$

Putting the value of [C] in Eq. (1), we get

$$Rate = \frac{k_2[Cat]_T[PhNO_2][H_2]^2}{[[PhNO_2] + [H_2]^2\{K_5[PhNO_2] + K_3 + K_4[PhNHOH]\}]}$$

As $[H_2]^2$ is of the order of 10^{-5} and $[PhNO_2]$ is of the order of 1 M. So, the equation reduces to

$$Rate = \frac{k_2[Cat]_T[PhNO_2][H_2]^2}{[PhNO_2]} = k_2[Cat]_T[H_2]^2$$

$$= K_1[Cat]_T[P_{H_2}]^2$$

This equation agrees well with the experimental results.

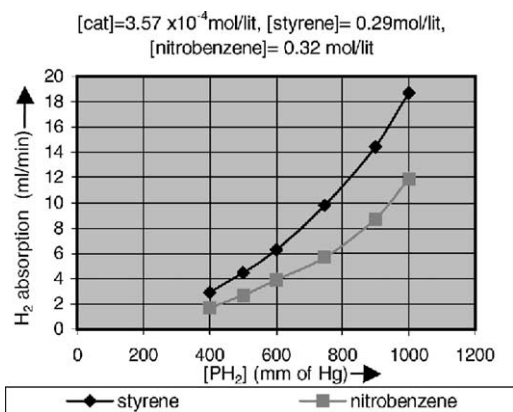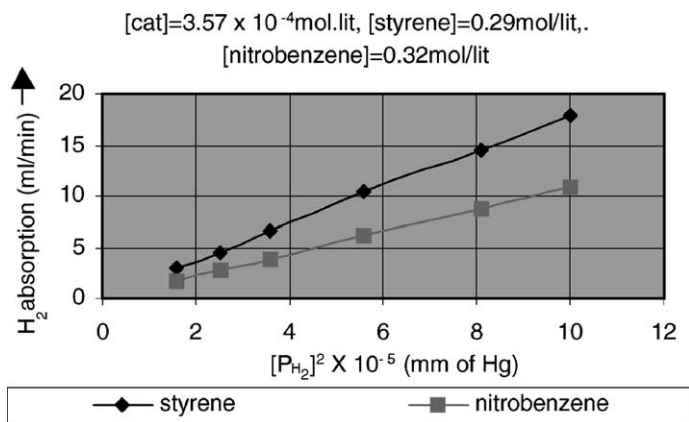Fig. 9. Rate dependence on hydrogen pressure using catalyst $[Pd_2(OEt-T)_2Cl_2]$ in DMF at 25 °C.

According to Scheme 3

$$\text{Rate} = k_2[C][H_2]^2 \tag{3}$$

Let $[Cat]_T$ = total concentration of the catalyst, then

$$[Cat]_T = [A] + [B] + [C] = [C] + [B] + [A] \tag{4}$$

$$[B] = \frac{k_2}{k_1}[C][H_2]^2 = K_2[C][H_2]^2$$

where

$$\frac{k_2}{k_1} = K_2$$

$$[A] = \frac{(k_4 + k_1)[B]}{k_3[S]^2} = \frac{[B]}{K_1[S]^2}$$

Fig. 10. Rate dependence on hydrogen pressure using catalyst $[Pd_2(OEt-T)_2Cl_2]$ in DMF at 25 °C.

where

$$K_1 = \frac{k_3}{k_4} + k_1 = \frac{K_2[C][H_2]^2}{K_1[S]^2} = \frac{K_3[C][H_2]^2}{[S]^2}$$

where

$$K_3 = \frac{K_2}{K_1}$$

Now, putting the value of [B] and [A] in Eq. (4), we get

$$[Cat]_T = [C] + K_2[C][H_2]^2 + \frac{K_3[C][H_2]^2}{[S]^2}$$

$$= \frac{[C][[S]^2 + [H_2]^2\{K_2[S]^2 + K_3\}]}{[S]^2}$$

$$[C] = \frac{[Cat]_T[S]^2}{[[S]^2 + [H_2]^2\{K_2[S]^2 + K_3\}]}$$

Now, putting the value of [C] in Eq. (1), we get

$$\text{Rate} = \frac{k_2[Cat]_T[S]^2[H_2]^2}{[[S]^2 + [H_2]^2\{K_2[S]^2 + K_3\}]}$$

As $[S]^2 \approx 1$ and $[H_2]^2 \approx 10^{-5}$

$$\text{Rate} = \frac{k_2[Cat]_T[S]^2[H_2]^2}{[S]^2} = k_2[Cat]_T[H_2]^2$$

$$= K[Cat]_T[P_{H_2}]^2$$
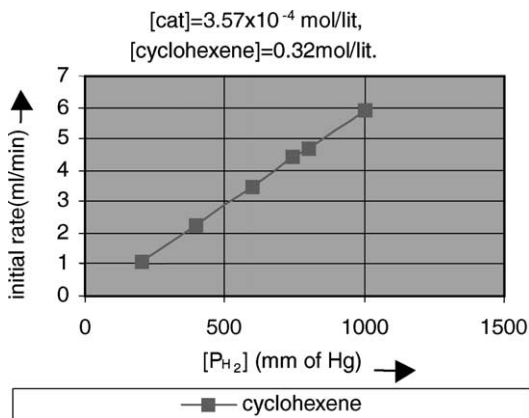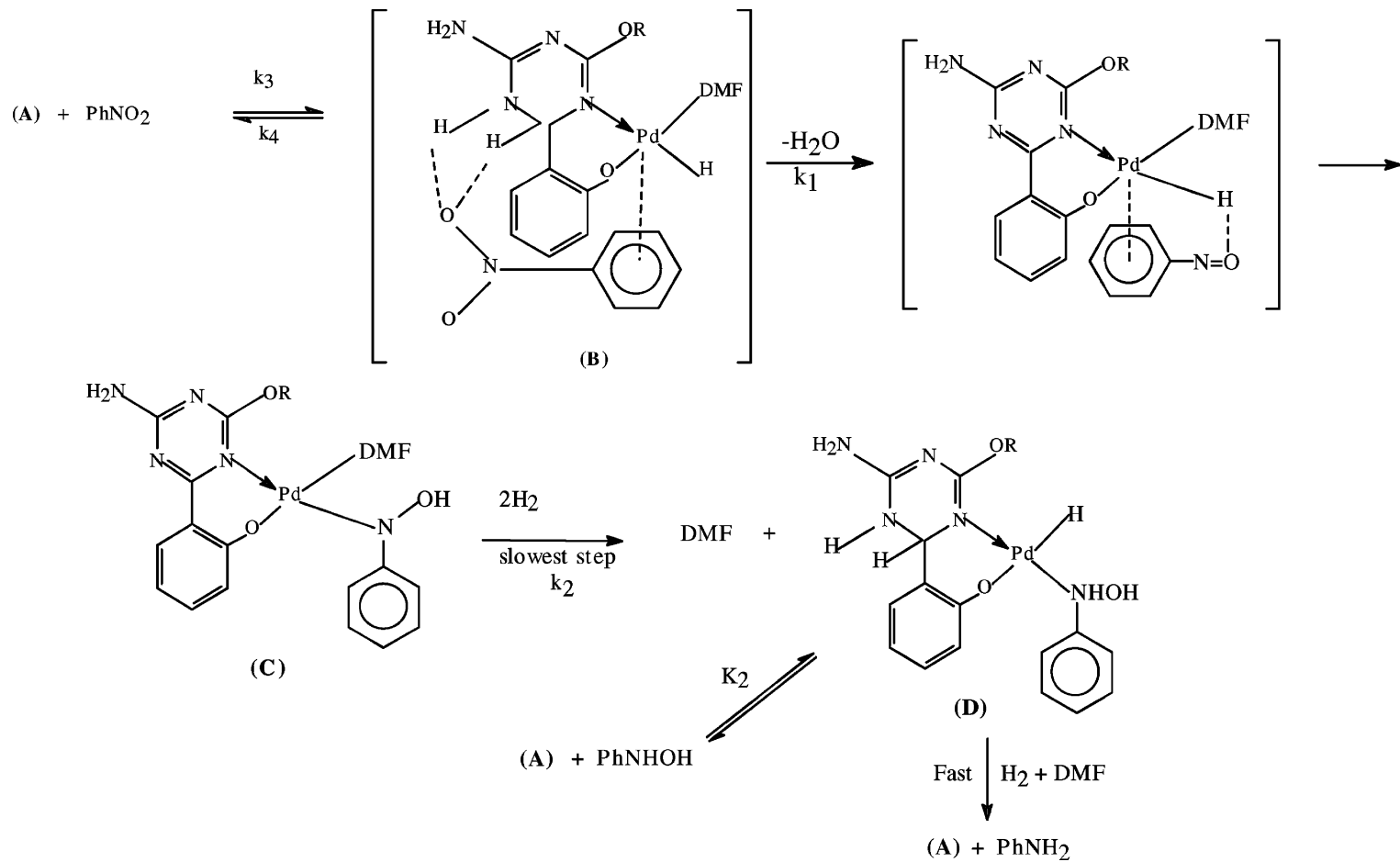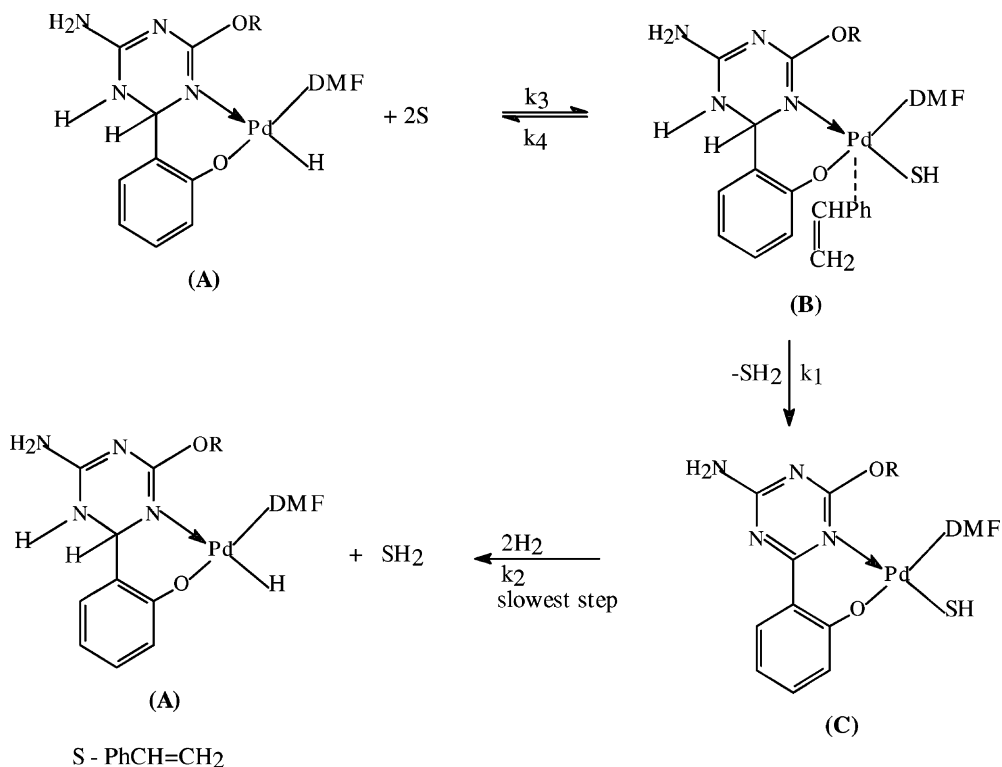
This equation agrees well with the experimental results.

Scheme 2.

Scheme 3.

7. Conclusion

Pd(II) complexes of S-Triazines and anthranilic acid could be used as active catalysts for the dihydrogen reduction of a number of organic compounds. Among $[Pd_2(OEt-T)_2Cl_2]$, $[Pd_2(An)_2Cl_2]$, $[Pd_2(DEt-AT)_2Cl_2]$ and $[Pd_2(DEt-ATH_2)_2Cl_2]$, the first one was found most efficient. The rate of reduction of substrates was found to depend both on steric and electronic factors. DMF was found best solvent for these catalytic systems.

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