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Hydrogenation of Alkenes and Alkynes Catalyzed by Polymer-Bound Palladium(II) Complexes

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A polymer-supported Pd(II) species has been prepared by means of an oxidative addition reaction between $Pd(PPh_3)_4$ and chloromethylated crosslinked polystyrene. This catalyst has been used for the hydrogenation of alkenes and alkynes under mild conditions. Quantitative studies on the rates of hydrogenation of selected substrates are reported with the mechanisms being discussed. Data on the high recycling efficiency of the catalyst as well as solvent effects on the reaction are presented. Comparisons of the catalyst with earlier reported Pd(II) species supported on polystyrene have been made.

INTRODUCTION

The technique of heterogenizing homogeneous catalysts by anchoring them on insoluble supports is well established (*1*). Such catalysts offer advantages in the recovery and recycling of the active species as well as enhanced specificity. However, leaching of the metal under the conditions of reaction is a serious drawback. If the mechanism of catalysis involves dissociation of the ligand binding the metal to the support, then leaching is inevitable. Multiple binding of the metal through more than one ligand to the support, while minimizing loss of metal, alters the nature of the intermediate species formed leading to significant differences in the product distribution compared to the homogeneous reaction (*1*). In this paper we report the use of an oxidative addition reaction for the loading of the catalyst on the support resulting in the metal being bound to the polymer by means of a sigma bond. This catalyst could be recycled several times with only minimal loss of activity.

Earlier work on polymer-supported Pd(II) species as hydrogenation catalysts are those due to Bruner and Bailar (*2*), Holy (*3*), Card and Neckers (*4*), and Terasawa *et al.* (*5*). The first three groups have employed insoluble polystyrene as support while Terasawa *et al.* have used linear polystyrene soluble in certain solvents. By using phosphinated crosslinked polystyrene and an exchange reaction with either Pd $(C_6H_5CN)_2Cl_2$ or $Pd(PPh_3)_2Cl_2$ Bruner and Bailar obtained a catalyst with good selectivity for the reduction of dienes to monoenes and greater reactivity toward conjugated dienes. It was shown that catalysis was due to Pd(II) and not Pd(0) by removing all the palladium from used catalyst by treatment with potassium cyanide in ethanol. No data on the recycling efficiency of the catalyst were given. Holy has anchored Pd(II) to the anthranilic acid derivative of chloromethylated polystyrene. At hydrogen pressures ranging from 50 to 500 psig and fairly high temperatures this catalyst was useful for the reduction of olefins, dienes, and alkynes. With alkynes as substrates, a highly stereoselective reduction to *cis*-olefins was demonstrated. However, the recycling efficiency was very poor with nearly 33% of the metal being lost after one cycle. Card and Neckers have used polystyryl bipyridine derivative as support material. Up to 7% of Pd could be loaded on these polymers by reaction with $Pd(OAc)_2$. The Pd(II) species could be reduced to Pd(0) by lithium aluminum hydride and the

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resulting catalyst was superior to the Pd(II) species. These authors suggest that the *in situ* reduction of Pd(II) by H_2 is essential for catalysis. Reduction of alkynes and conjugated dienes proceeded smoothly to the alkene and monoene stages, respectively, before any alkane could be detected. The extent of leaching of the catalyst was governed by the reaction conditions. Loss of metal under atmospheric hydrogenation conditions was negligible while at 30 psi of H_2 nearly 22% of the metal was lost. Olefin isomerization during the reduction was significant.

Extensively phosphinated soluble polystyrene was employed by Terasawa *et al.* to support $PdCl_2$ or $Pd(PPh_3)_2Cl_2$. Loading was very efficient with nearly 22% of the supported catalyst being made up of palladium. Pretreatment of the catalyst with H_2 resulted in the formation of a hydrido species active in the catalysis. The reduction of conjugated dienes and alkynes was faster than that of olefins and nonconjugated dienes. Extensive isomerization of the substrates was also reported. However, the rate laws derived by these authors do not correspond to the proposed mechanisms. X-Ray photoelectron spectra of the catalyst confirmed Pd(II) to be the active species. Of the several solvents in which reactions have been investigated it is not clear in how many the reaction was homogeneous. No details of recycling efficiency of the catalyst are given.

It is known that $Pd(PPh_3)_2Cl_2$ is a poor catalyst for homogeneous hydrogenation (*6*). But addition of 2 mol of stannous chloride to the system promotes catalysis due to the formation of species such as $Pd(PPh_3)_2(SnCl_3)Cl$ which can react with H_2 to yield the intermediate hydrido species (*6*). We felt that an analogous species can be obtained by causing the chloromethyl group of polystyrene to react with $Pd(PPh_3)_4$. Such a technique for loading catalysts onto brominated polystyrene has been reported earlier (*7*). However, such oxidative addition reactions proceed much better with benzyl halides with or without substituents on the aromatic ring (*8*). These reactions result in Pd(II) being bound to the support by means of the $\geqslant$C—Pd sigma bond.

EXPERIMENTAL

Methods. Ultraviolet spectra were recorded using a Ziess DMR 21 spectrophotometer and infrared spectra obtained using a Perkin–Elmer instrument.

Materials. All reagents used were of AnalaR grade. Triphenylphosphine (Fluka, mp 80°C) and palladous chloride (Johnson Matthey) were used as such. Solvents were purified and distilled by standard methods. Substrates were purified by repeated crystallization or distillation under reduced pressure in an atmosphere of nitrogen. Cylinder hydrogen was purified by passing it through a tube containing copper gauze maintained at 400°C followed by passage through two wash bottles containing V^{2+}/Zn amalgam/1 *N* H_2SO_4 solution and one of water and dried by calcium chloride before admission to the reaction system.

$Pd(PPh_3)_4$ was synthesized using a reported procedure (*9*). Suspension polymerization of styrene and divinylbenzene in the ratio 98 : 2 yielded 2% crosslinked resin. This was chloromethylated under Gatterman conditions using trioxane depolymerized under acidic conditions as the source of formaldehyde, and anhydrous $ZnCl_2$ and HCl in nitrobenzene medium. The polymer was washed thoroughly and dried under vacuum. The chlorine content of the polymer varied from batch to batch in the range 2.6 to 3.6 meq per gram.

The polymer bound palladium complex was prepared as follows. $Pd(PPh_3)_4$ (4 g, 3.4 mmol) was added to 5 g of chloromethylated polymer swollen with 40 ml of deoxygenated toluene. The mixture was stirred at room temperature under nitrogen for 5–6 days. The supernatant solution turned brown during this time and the polymer became dark green in color. It was filtered and washed thoroughly with hot toluene, acetone, and methanol. Any adsorbed material was removed by extracting the polymer on the Soxhlet first with acetone and then with benzene for a total period of 6 h. An ether wash followed by drying under vacuum yielded the catalyst which could be stored in air for months without any apparent change. The palladium content of the catalyst was estimated by incinerating a known weight in a silica crucible and dissolving the residue in aqua regia followed by colorimetry (*10*). Estimation of the phosphorus content of the catalyst indicated that the ratio P/Pd was close to 2. Treatment of the catalyst with a saturated solution of KCN in ethanol results in the removal of all the palladium showing that the species is a Pd(II) complex. Catalysts used several times could also be stripped free of Pd by a cyanide treatment indicating that the catalysis is due to Pd(II) and not due to Pd(0).

Hydrogenation procedure. For qualitative studies, electrolytically generated hydrogen purified as described was passed through the reaction mixture contained in a double-walled reaction vessel which was maintained at 30°C. The catalyst (100 to 200 mg) was in suspension and the mixture was stirred magnetically for a period of 60–120 min. Then the catalyst was removed by filtration and the filtrate analyzed by spectrophotometry or bromometry depending on the substrate to determine the extent of reaction. For quantitative experiments the double-walled reaction vessel was equipped with a 20-ml pressure equalizing separating funnel attached by means of one of two standard tapered joints (₮ 14/20), the other being closed by a stopcock and used as gas vent during deaeration. The separating funnel could be connected to either the purified H_2 supply or the water-jacketed gas burette by means of a three-way stopcock. Required amount of the catalyst was taken in the reaction vessel and 10 ml of solvent added to the separating funnel. Solvent was deoxygenated by passing pure hydrogen for 15–20 min, the gas being vented through the reaction vessel. Deoxygenated solvent was run into the reaction vessel and the separating funnel was filled with 10 ml of the substrate solution of the required concentration. This was deoxygenated for 20 min while the catalyst and solvent mixture was stirred magnetically. Addition of the substrate was followed by opening the system to the gas burette while closing the exit stopcock. Hydrogen uptake commenced without any induction period in all cases and the volume absorbed at 1 atm pressure as a function of time was plotted to obtain rate data. Uniform rates of stirring were maintained to minimize diffusion effects and reproducibility was better than 4–5%. Reaction times were confined to a maximum of 40 min with the less reactive substrates and a minimum of 15 min with the more reactive ones. Data on the concentration of dissolved H_2 in the different media were obtained by employing the appropriate Henry's law constants (*11*). Variation of partial pressure of H_2 was carried out as follows. Purified H_2 and N_2 were mixed in a 10-liter aspirator bottle in the required ratio. This gas mixture at a total pressure of 1 atm was used to fill the gas burette as well as to degas the solvent and substrate solutions. Solvent composition was varied by adding the requisite amount of the second solvent along with the substrate. Similarly, when the effect of additives was studied, these were added along with the substrate and never added to the catalyst and solvent initially taken. At the end of a run the catalyst was separated by filtration and thoroughly washed with acetone and dried before recycling. The filtrate from the reaction was sometimes analyzed spectroscopically for the substrate remaining as well as the product. The Pd content of the catalyst was determined periodically to monitor loss of metal under the reaction conditions.

RESULTS AND DISCUSSION

The relative reactivities of the various substrates are indicated in Fig. 1 where percentage conversion is plotted versus time. It is clear that simple olefins are reduced more slowly than either conjugated olefins

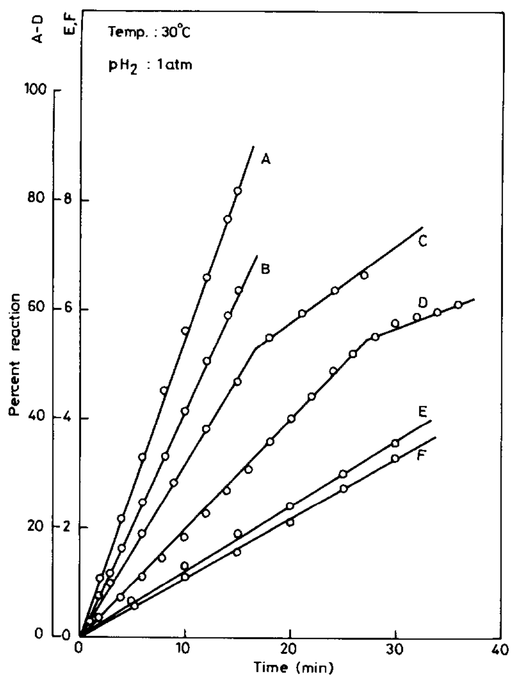
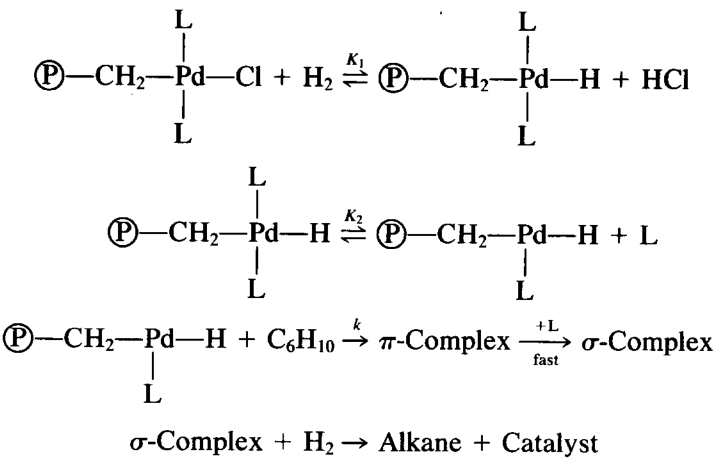


FIG. 1. Plots of percentage of reaction versus time for various substrates. Line A—[Styrene]$_0$ = 0.109 mol/dm^3 with 4.57 mmol/dm^3 catalyst in methanol. Line B—[Norbornadiene]$_0$ = 0.2458 mol/dm^3 with 3.65 mmol/dm^3 catalyst in methanol. Percentage calculated on the basis of conversion to norbornene. Line C—[2-Butyne-1,4-diol]$_0$ = 0.1 mol/dm^3 with 3.9 mmol/dm^3 catalyst in methanol/benzene (70/30). Line D—[2-Propyne-1-ol]$_0$ = 0.14 mol/dm^3 with 7.8 mmol/dm^3 catalyst in methanol/benzene (70/30). Line E—[Allyl alcohol]$_0$ = 2.2 mol/dm^3 with 3.9 mmol/dm^3 catalyst in methanol/benzene (70/30). Line F—[Cyclohexene]$_0$ = 2.95 mol/dm^3 with 5.9 mmol/dm^3 catalyst in methanol.

or alkynes, the exception being norbornadiene. With the alkynes as substrates there is a break in the plot when one equivalent of hydrogen has been absorbed with the uptake of hydrogen being linear for the rest of the reaction. Quantitative studies indicate that the mechanism of reduction depends very much on the substrate as detailed below.

Cyclohexene

Rates of reduction ($-d[H_2]/dt = -d$[Substrate]$/dt$) with this substrate were proportional to the catalyst concentration (Fig. 2) as well as the olefin concentration (Fig. 3). Large concentrations of the substrate, however, reduce the rates considerably as seen from the data in Table 1. With methanol as solvent the increasing concentrations of cyclohexene tend to make the medium less polar. Increasing the benzene content of the medium has a similar effect on the rates (Table 1). Variation of rates with the partial pressure of H_2 is given in Table 2. The data indicate the formation of intermediate hydride species in a reversible equilibrium. Plots of reciprocal rates versus reciprocal hydrogen concentration were linear with intercepts on the rate axis (Fig. 4). Addition of triphenylphosphine or triethylamine retards the rate of reduction while piperidine totally inhibits the reaction (Table 3). The following mechanism would account for the kinetics of reduction.



$$\text{Ⓟ—CH}_2\text{—}\underset{L}{\overset{L}{\text{Pd}}}\text{—Cl} + H_2 \overset{K_1}{\rightleftharpoons} \text{Ⓟ—CH}_2\text{—}\underset{L}{\overset{L}{\text{Pd}}}\text{—H} + HCl$$

$$\text{Ⓟ—CH}_2\text{—}\underset{L}{\overset{L}{\text{Pd}}}\text{—H} \overset{K_2}{\rightleftharpoons} \text{Ⓟ—CH}_2\text{—}\underset{L}{\text{Pd}}\text{—H} + L$$

$$\text{Ⓟ—CH}_2\text{—}\underset{L}{\text{Pd}}\text{—H} + C_6H_{10} \xrightarrow{k} \pi\text{-Complex} \xrightarrow[\text{fast}]{+L} \sigma\text{-Complex}$$

$$\sigma\text{-Complex} + H_2 \rightarrow \text{Alkane} + \text{Catalyst}$$

SCHEME 1

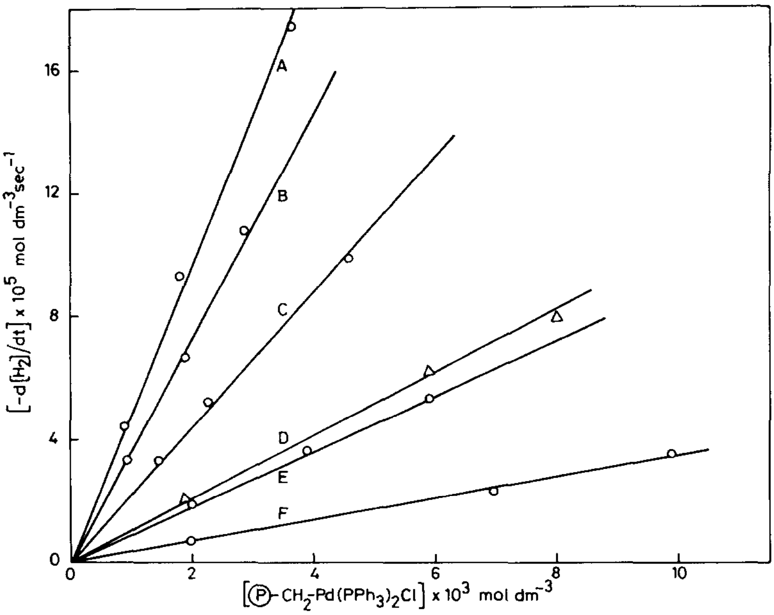


FIG. 2. Dependence of rate of hydrogenation on the catalyst concentration at 1 atm H_2 and 30°C. Line A—Norbornadiene = 0.24 mol/dm^3 in methanol. Line B—Allyl alcohol = 1.474 mol/dm^3 in methanol/benzene. Line C—Styrene = 0.109 mol/dm^3 in methanol. Line D—2-Propyne-1-ol = 0.1027 mol/dm^3 in methanol/benzene. Line E—2-Butyne-1,4-diol = 0.15 mol/dm^3 in methanol/benzene. Line F—Cyclohexene = 1.477 mol/dm^3 in methanol.

TABLE 1

Effect of Increasing the Benzene Content of the Medium on Rates of Reduction at 30°C and 1 atm H_2

Substrate (mol · dm^{-3})	Catalyst (× 10^3 mol · dm^{-3})	Solvent composition C_6H_6/CH_3OH (vol%)	Rate (× 10^5 mol · dm^{-3} sec^{-1})
Cyclohexene (1.477)	5.9	0/100	2.69
		10/90	1.58
		20/80	1.37
		30/70	1.04
Cyclohexene (4.916)	5.9	0/100	0.85
Styrene (0.109)	4.57	0/100	9.95
		33/67	9.02
		50/50	5.27
		60/40	3.69
Norbornadiene (0.2458)	3.9	0/100	17.40
		33/67	13.26
		50/50	11.90
		60/40	10.65
Allyl alcohol (1.474)	3.9	0/100	3.04
		30/70	3.83
2-Butyne-1,4-diol (0.20)	3.9	0/100	9.69
		30/70	12.60

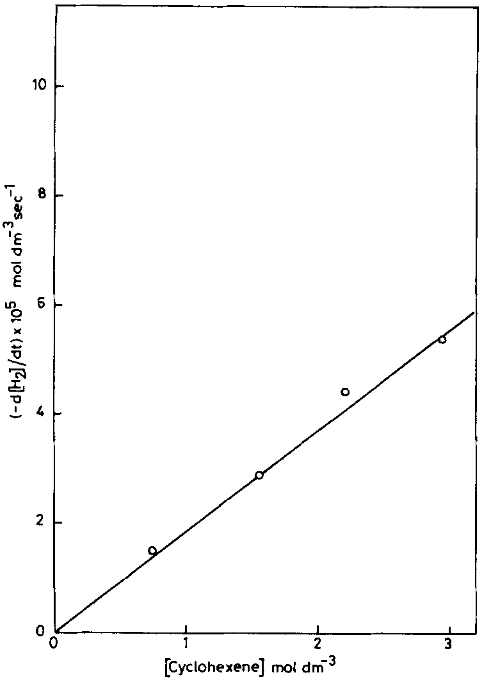


FIG. 3. Plot of rate versus cyclohexene concentration with 5.9 mmol/dm³ of catalyst at 30°C and 1 atm H_2 in methanol.

The reaction sequence leads to the following rate law with the first and second equilibria being combined such that $K = K_1 \times K_2$.

$$-d[\mathrm{H_2}]/dt = \frac{kK[\mathrm{Catalyst}]_{\mathrm{Total}}[\mathrm{H_2}][\mathrm{Olefin}]}{[\mathrm{PPh_3}][\mathrm{HCl}] + K[\mathrm{H_2}]}.$$

If the formation of the hydrido species is accompanied by the liberation of HCl one would expect the bases to accelerate the reaction but this is not observed. Perhaps the bases as well as PPh_3 merely function as catalyst poisons blocking the site necessary for reaction. An alternate mechanism involving a Pd(IV) species as intermediate can also lead to the same kinetics.

Again combining the first two equilibria such that $K' = K_3 \times K_4$, the sequence of reactions in Scheme 2 would lead to the rate law below.

$$-d[\mathrm{H_2}]/dt = \frac{kK'[\mathrm{Catalyst}]_{\mathrm{Total}}[\mathrm{H_2}][\mathrm{Olefin}]}{[PPh_3] + K'[\mathrm{H_2}]}.$$

The observed data cannot distinguish between these two mechanisms provided the rate-determining step in each case is the reaction of the olefin with the initially formed hydrido complex. In Scheme 1 the product is formed as a result of reaction between

TABLE 2

Variation of Rates with Partial Pressure of Hydrogen with Cyclohexene as Substrate in Methanol

Hydrogen partial pressure (atm)	Rate × 10^5 mol · dm^{-3} sec^{-1}	
	298 K	303 K
0.25	—	0.936
0.50	1.002	1.296
0.75	1.16	1.75
1.00	1.27	2.69

Note. [Cyclohexene] = 1.477 mol · dm^{-3}; [Catalyst] = 5.9 × 10^{-3} mol · dm^{-3}.

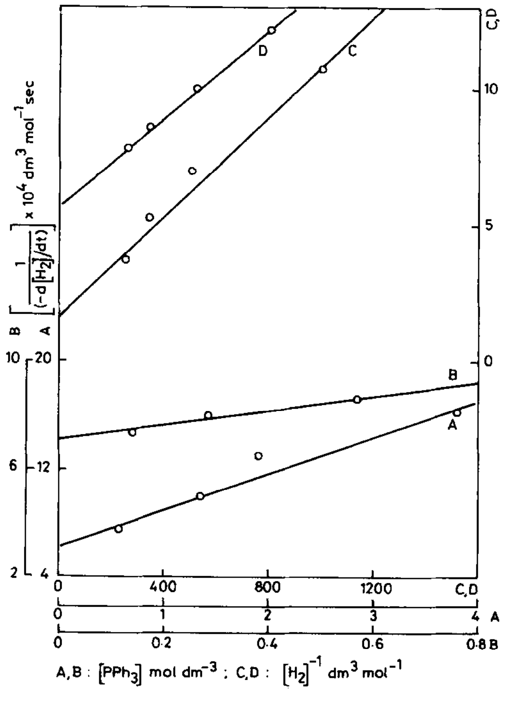
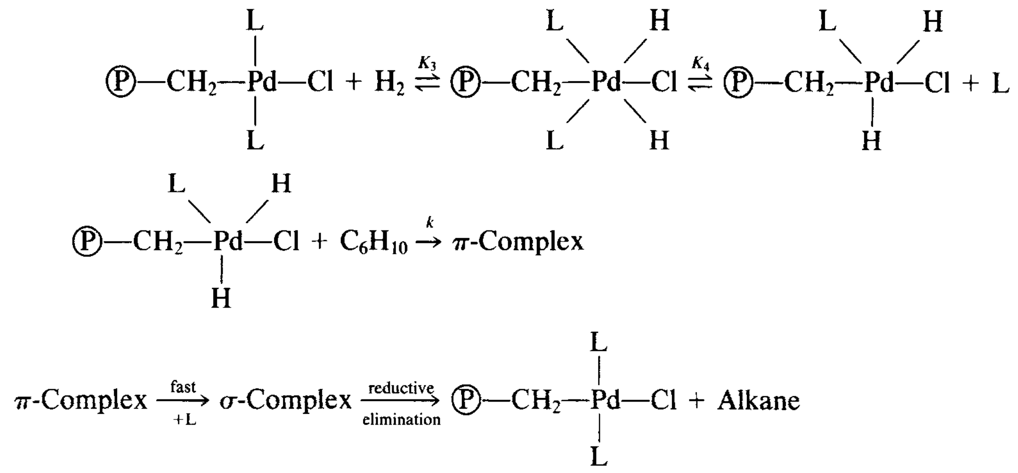


FIG. 4. Plots of reciprocal rates versus $[PPh_3]$ or $[H_2]^{-1}$. Line A—Styrene = 0.109 mol/dm³, 4.57 mmol/dm³ catalyst, pH_2 = 1 atm in methanol at 30°C. Line B—Same conditions as A but at 25°C. Line C—Cyclohexene = 1.477 mol/dm³, 5.9 mmol/dm³ catalyst in methanol at 30°C. Line D—Same conditions as C but at 25°C.



SCHEME 2

the alkyl–Pd intermediate and H_2 while a reductive elimination yields the product in Scheme 2. Both these rate laws require that plots of $(-d[H_2]/dt)^{-1}$ versus $[H_2]^{-1}$ be linear. The intercepts of these plots yield data on the rate constant *k* for the reaction of the olefin with the hydrido complex. They are listed in Table 5. No attempt was made to evaluate the equilibrium constants. The rate constants reported are lower by two

TABLE 3

Effect of Added PPh_3 or Other Bases on the Rate of Reduction at 30°C and 1 atm H_2

Substrate (mol · dm^{-3})	Catalyst (× 10^3 mol · dm^{-3})	Additive (× 10^4 mol · dm^{-3})	Rate (× 10^5 mol · dm^{-3} sec^{-1})
Cyclohexene (1.477) in methanol	5.9	0.095(PPh_3)	0.963
		0.19 (PPh_3)	0.817
		0.38 (PPh_3)	0.396
		3.80 (PPh_3)	0.279
		7.14 (Et_3N)	1.06
		5.06 ($C_5H_{11}N$)	0.0
		None	2.69
Styrene (0.109) in methanol	4.57	5.7 (PPh_3)	1.32
		13.3 (PPh_3)	0.993
		19.0 (PPh_3)	0.717
		38.0 (PPh_3)	0.617
		None	9.95
Norbornadiene (0.2458) in methanol	3.9	9.5 (PPh_3)	17.63
		38.0 (PPh_3)	16.50
		None	17.40
Allyl alcohol (1.474) in methanol/benzene (70/30)	3.9	9.5 (PPh_3)	3.65
		38.0 (PPh_3)	3.55
		None	3.80
2-Propyne-1-ol (0.103) in methanol/benzene (70/30)	7.8	38.0 (PPh_3)	8.37
		None	8.07

TABLE 4

Variation of Rates with Substrate Concentration at 30°C and 1 atm H_2 in Methanol

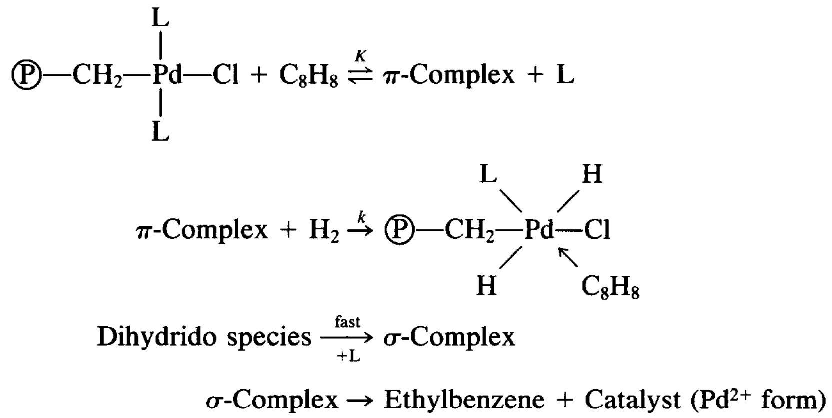
Styrene[a] (mol · dm^{-3})	Rate × 10^5 (mol · dm^{-3} sec^{-1})	Norbornadiene[b] (mol · dm^{-3})	Rate × 10^4 (mol · dm^{-3} sec^{-1})
0.057	8.06	0.02458	1.79
0.087	8.74	0.2458	1.74
0.109	9.95	0.737	1.75
0.24	12.38	0.983	1.75
0.48	13.40	1.474	1.80

[a] With 4.57 mmol · dm^{-3} of catalyst.
[b] With 3.65 mmol · dm^{-3} of catalyst.

orders of magnitude compared to the Rh(I)-catalyzed reduction of cyclohexene under homogeneous conditions. The activation energy is also larger (*12*). Comparison with earlier work (*5*) on the reduction of cyclohexene by a polymer-supported Pd(II) species as catalyst is not worthwhile because the mechanism suggested by these authors does not lead to the rate law derived by them and the rate-determining step for which they evaluate constants involves an alkyl–Pd species and H_2 as reactants.

Styrene

The next substrate chosen was styrene in order to study the effect of conjugation of the double bond with an aromatic ring. The rates were proportional to the catalyst concentration (Fig. 2) as well as the partial pressure of hydrogen (Fig. 5). Variation of the rates with substrate concentration (Table 4) indicated complex formation. Rates were also adversely affected by the addition of PPh_3 (Table 3). Plots of $(-d[H_2]/dt)^{-1}$ versus $[PPh_3]$ were linear with intercepts on the rate axis (Fig. 4). Increasing the benzene content of the medium caused a drop in rates as shown in Table 1. Thus the mechanism involves an initial complexation between catalyst and substrate with ligand displacement in a reversible manner. Reaction of this complex with H_2 in the rate-determining step would lead to an alkyl–Pd species which is most likely to be a Pd(IV) complex. Reductive elimination yields the alkane. These steps are outlined in the scheme below.



$$\text{Ⓟ—CH}_2\text{—}\overset{L}{\underset{L}{\text{Pd}}}\text{—Cl} + C_8H_8 \overset{K}{\rightleftharpoons} \pi\text{-Complex} + L$$

$$\pi\text{-Complex} + H_2 \xrightarrow{k} \text{Ⓟ—CH}_2\text{—}\overset{L\quad H}{\underset{H\quad C_8H_8}{\text{Pd}}}\text{—Cl}$$

$$\text{Dihydrido species} \xrightarrow[+L]{\text{fast}} \sigma\text{-Complex}$$

$$\sigma\text{-Complex} \rightarrow \text{Ethylbenzene} + \text{Catalyst } (\text{Pd}^{2+} \text{ form})$$

SCHEME 3

TABLE 5

Rate Parameters for the Reduction of Cyclohexene, Styrene, and Norbornadiene in Methanol

Substrate	Temp. (K)	k ($\text{dm}^3\ \text{mol}^{-1}\ \text{sec}^{-1}$)	E (kJ/mol)	K	ΔH (kJ/mol)	ΔS (J/K/mol)
Cyclohexene	298	2.013×10^{-3}	177.2	—	—	—
	303	6.56×10^{-3}		—		
Styrene	298	0.7984	15.75	0.0244	−24.66	−113.7
	303	0.8867		0.0203		
Norbornadiene	293	9.5	17.36	—	—	—
	303	12.0		—		

Note. For norbornadiene the values of k were calculated from the rate law $-d[H_2]/dt = k[\text{Catalyst}][H_2]$.

The rate law in this case would be

$$-d[H_2]/dt = \frac{kK[\text{Catalyst}]_{\text{Total}}[H_2][\text{Olefin}]}{[\text{PPh}_3] + K[\text{Olefin}]}.$$

Thus, from plots such as those in Fig. 4 we can estimate both the rate constant as well as the equilibrium constant. The collected data appear in Table 5. Both ΔH and ΔS are negative for the complex formation. From the fact that rates are strictly proportional to the H_2 partial pressure we can infer that the equilibrium constant for the formation of any hydrido species is very much lower than that reported for the formation of the olefin–catalyst complex. The kinetics of reduction of styrene catalyzed by a polymer-supported Pd(II) species reported earlier (*5*) are in sharp contrast to what we find. Terasawa *et al.* report that the reaction is zero order in the substrate but this result is not easily substantiated by their mechanism. Their scheme consists of a reversible reaction between the substrate and a hydrido–Pd species to yield an alkyl–Pd intermediate which reacts with H_2 in the rate-determining step to give the alkane. The rate law that can be derived from this scheme requires that the rates be proportional to the substrate concentration. The rate law derived by Terasawa *et al.* is, however, different and is not consistent with their mechanism.

Norbornadiene

This was the most reactive substrate investigated as seen from Fig. 1. Variation of rates with catalyst concentration and partial pressure of hydrogen are given in Figs. 2 and 5, respectively. Rates were independent of substrate concentration as shown in Table 4. Addition of benzene caused a drop in rates (Table 1) but even large concentrations of PPh_3 did not affect the rates significantly (Table 3). A mechanism similar to the one suggested for styrene with a very high value for the equilibrium constant ($K[\text{Olefin}] \gg [\text{PPh}_3]$) would explain the kinetic features. Another possibility is a fast reaction between the olefin and a hydrido–Pd species formed in the rate-determining step. From the slopes of rate versus catalyst or H_2 we can estimate a second-order rate constant listed in Table 5. The value of this constant is much too large to be associated with the reaction of H_2 with the catalyst. It is more likely to be associated with the reaction of H_2 with the olefin–substrate complex. Such complexes are postulated in many reactions involving norbornadiene. Although product analysis as a function of time has not been carried out there seems to be no stepwise reaction with the monoene accumulating before any alkane is formed. With limited amounts of substrate

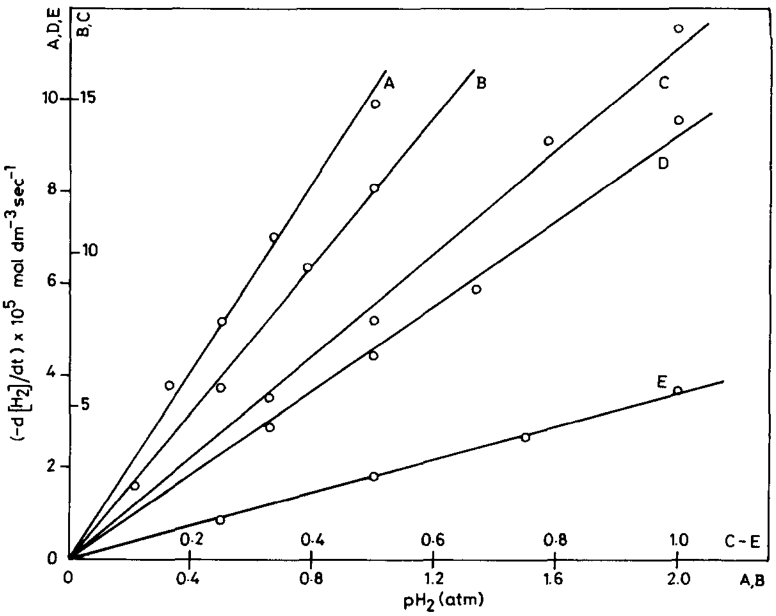


FIG. 5. Variation of rates of hydrogenation with partial pressure of H_2 at 30°C. Line A—Styrene = 0.109 mol/dm^3; catalyst = 4.57 mmol/dm^3 in methanol. Line B—2-Propyne-1-ol = 0.1027 mol/dm^3; catalyst = 7.8 mmol/dm^3 in methanol/benzene. Line C—Norbornadiene = 0.24 mol/dm^3; catalyst = 3.65 mmol/dm^3 in methanol. Line D—2-Butyne-1,4-diol = 0.05 mol/dm^3; catalyst = 3.9 mmol/dm^3 in methanol/benzene. Line E—Allyl alcohol = 1.474 mol/dm^3; catalyst = 3.9 mmol/dm^3 in methanol/benzene.

the uptake of H_2 was linear for up to 95% of the reaction.

Allyl alcohol, 2-Butyne-1,4-diol, and 2-Propyne-1-ol

These three substrates are grouped together because of the similarity of the mechanisms of reduction. All three were investigated in the mixed solvent 30% benzene–70% methanol since the rates were enhanced by addition of benzene (Table 1). Data on the extent of reaction as a function of time appear in Fig. 1. The alkynes are reduced in a stepwise manner with a distinct break in the H_2 uptake curves when one equivalent of H_2 had been absorbed. Similar selective reductions of alkynes has been reported by Card and Neckers (*4*) using Pd^0 supported on a polystyrene bipyridyl matrix. Terasawa *et al.* (*5*) also demonstrate such selectivity with their polymer-supported Pd(II) catalyst.

With all three substrates, rates were proportional to the catalyst concentration (Fig. 2) as well as the partial pressure of H_2 (Fig. 5). Variation of rates with substrate concentration indicated complex formation and plots of $(-d[H_2]/dt)^{-1}$ versus $[\text{Substrate}]^{-1}$ were linear as shown in Fig. 6. Addition of PPh_3 was without any effect on the rates as can be seen from Table 3. Thus the common mechanism for these substrates involves initial complex formation between catalyst and alkene or alkyne without ligand displacement. Reaction of the complex with H_2 constitutes the rate-limiting step which is followed by several rapid steps leading to products. Except for the loss of PPh_3 in the initial equilibrium the mechanism is similar to that postulated for styrene and the rate law has the form

$$-d[H_2]/dt = \frac{kK[\text{Catalyst}]_{\text{Total}}[H_2][\text{Substrate}]}{1 + K[\text{Substrate}]}.$$

Thus from the plots in Fig. 6 we can esti-

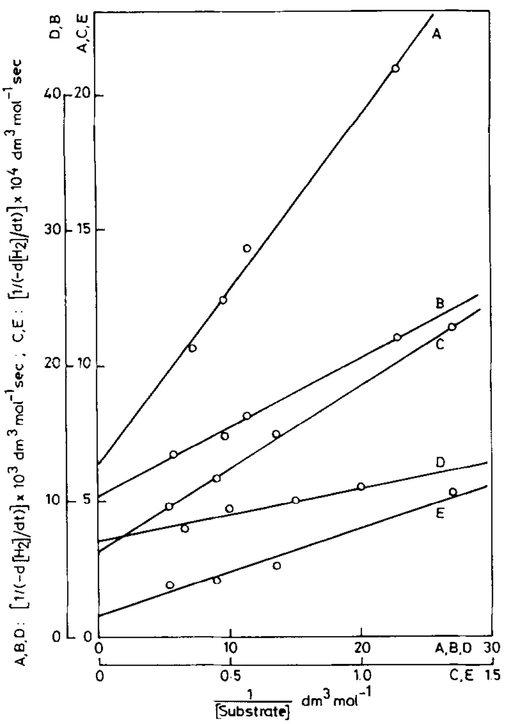


FIG. 6. Double reciprocal plots of rates versus substrate concentration at 1 atm H_2. Line A—2-Propyne-1-ol in methanol/benzene at 30°C with 7.8 mmol/dm^3 catalyst. Line B—Conditions same as A but at 25°C. Line C—Allyl alcohol in methanol/benzene at 25°C with 3.9 mmol/dm^3 catalyst. Line D—2-Butyne-1,4-diol in methanol/benzene at 30°C with 3.9 mmol/dm^3 catalyst. Line E—Conditions same as C but at 30°C.

mate k as well as K for the three substrates and the data obtained are in Table 6. The formation constant for complexation is largest for the alkyne diol and smallest for allyl alcohol. It is also clear that the terminal alkyne is reduced more slowly than the internal alkyne mainly due to the larger value of K for the latter. Coordination of the substrate with the metal is accompanied by negative enthalpy and entropy changes in all the three cases. It is also significant that allyl alcohol forms a stronger complex with the catalyst than styrene. Clearly more data on these as well as other types of substrates, mainly with respect to the stereochemistry of addition, is needed before we can speculate further.

Spectral Characterization of the Catalyst

The preparation of the catalyst by the oxidative addition method yielded material containing on the average 40–50 mg of Pd per gram of the polymer, the variation from batch to batch being not very pronounced. The ratio P/Pd was generally equal to 2. The ir spectrum of the polymer-supported catalyst in the region 650 to 4000 cm^{-1} consisted mainly of the typical polystyrene absorption bands. The ir spectrum of the catalyst in the region 100 to 600 cm^{-1} is reproduced in Fig. 7. It is not easy to locate the bands due to Pd–Cl(terminal) or Pd–P in the spectrum. However, the two strong bands in the region 500–550 cm^{-1} are due to Pd–C bond vibrations (*13*). Both freshly prepared as well as used catalyst could be stripped free of metal by a cyanide ion treatment in ethanol confirming that the catalysis is due to Pd(II).

Recycling Efficiency of the Catalyst

One of the ways in which the catalyst can lose palladium is by hydrogenolysis of the $\geqslant$C—Pd sigma bond during the course of the reaction. Another is loss of Pd brought about by acidic media or substrates. The latter was checked by the following experiment. With cinnamic acid as substrate the same sample of catalyst was recycled five times and the rates measured are given in Table 7. The activity of the catalyst drops

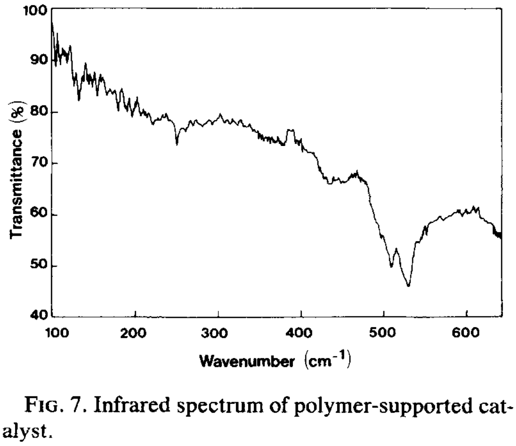


FIG. 7. Infrared spectrum of polymer-supported catalyst.

TABLE 6

Rate Parameters for the Reduction of Allyl Alcohol, 2-Propyne-1-ol, and 2-Butyne-1,4-diol in Methanol–Benzene (7 : 3) Medium

Substrate	Temp. (K)	k ($dm^3\ mol^{-1}\ sec^{-1}$)	E (kJ/mol)	K (dm^3/mol)	ΔH (kJ/mol)	ΔS (J/K/mol)
Allyl alcohol	298	2.143	189.6	0.496	−94.97	−324.4
	303	7.579		0.264		
2-Butyne-1,4-diol	298	7.762	21.35	47.73	−32.65	−77.43
	303	8.948		38.40		
2-Propyne-1-ol	298	3.196	65.64	20.08	−103.76	−323.3
	303	5.033		10.06		

TABLE 7

Efficiency of Recycling the Catalyst with Cinnamic Acid as Substrate in Methanol at 30°C and 1 atm H_2

Cinnamic acid ($mol \cdot dm^{-3}$)	Catalyst ($mol \cdot dm^{-3}$)	Fresh	Rate × $10^5\ mol \cdot dm^{-3}\ sec^{-1}$			
			I Cycle	II Cycle	III Cycle	IV Cycle
0.2	6.3×10^{-3}	1.7	1.75	1.65	1.55	1.45

to 85% of its initial value on being recycled four times. In the other type of experiment a 4-g sample of the catalyst was used over a period of 12 weeks for the reduction of several substrates involving all eight cycles. The Pd content of the catalyst was estimated at the completion of every two cycles and the data appear in Table 8. After eight cycles the metal content of the catalyst was found to be reduced to 83% of the original material. It is clear that the catalyst has a very good recycling efficiency if employed under neutral conditions. We are currently investigating reactions under higher H_2 pressures and temperatures and the recycling efficiency might be different under these conditions.

The main conclusions of the present study are the following: The oxidative addition reaction of a suitable palladium complex with the chloromethyl group of polystyrene can be used to prepare active polymer-supported Pd(II) catalysts for the hydrogenation of alkenes and alkynes under mild conditions. The catalyst has excellent recycling efficiency and is selective for the reduction of alkynes in presence of alkenes.

TABLE 8

Palladium Content of Catalyst at Various Stages of Recycling

	Fresh	Recycle No.			
		II	IV	VI	VIII
Pd content (mg/g of catalyst)	42	40	38	36	35

Note. Data refers to a 4-g batch of catalyst used for several substrates under various conditions for a period of 12 weeks.

The mechanism of reduction of most substrates shows that the unsaturated route is preferred.

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