Palladium–Polyamide Catalysts for the Hydrogenation of Some Unsaturated Hydrocarbons in the Liquid Phase

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The behavior of palladium–Nylon 66 and briefly, of some other palladium–polyamide fiber catalysts has been studied for the liquid phase hydrogenation of two 1-alkynes (1-pentyne and 1-octyne) and of two alka-1,3-dienes (penta-1,3-diene and isoprene) at 1 atm total pressure and between 50 and 70°C. The activity of the catalysts as a function of metal concentration of the catalyst or of the treating solution concentration was observed to pass through a maximum, which was not related either to a maximum palladium content of the nylon or of the chloropalladous acid treating solution. In addition, both catalyst activity and selectivity were observed to be strongly reactant and solvent dependent, in contrast to conventional supported palladium catalysts. In one polar solvent, catalyst selectivity was observed to be a function of the palladium content of the nylon. Olefin distributions for the first mole of hydrogen uptake were often significantly different to those observed for conventionally supported palladium, especially for the alka-1,3-dienes. A number of physical and chemical techniques were employed to try to characterize the catalysts, including chemical analysis, infrared studies, and temperature programmed reduction (TPR). From the results of the latter and the selectivity and olefin distribution data, it is concluded that the catalyst may well be a polyamide–palladium–chlorine complex, probably containing Pd(II) in a square coplanar arrangement of ligands. Some suggestions are made concerning (i) the possible nature and arrangements of the ligands and (ii) the possible mechanism of the reaction in the light of the observed product distributions, assuming that a square coplanar complex is involved.

INTRODUCTION

In the past few years, there have been a number of investigations concerning the use of natural and synthetic polyamides as supports for noble metals, particularly platinum, in the catalytic hydrogenation of various functional groups.

Japanese workers (*1–3*) and Harrison and Rase (*4*) provided evidence, though not unequivocal, that noble metal–polyamide catalysts possess unusual catalytic

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properties, possibly due to the metal being in some way associated with the regularly spaced amide groups. Indeed, Harrison and Rase proposed that a geometric effect operated in their studies using different types of nylon as a support for platinum.

More recently Dini *et al.* (*5*) have suggested that the catalytic species was a platinum atom complexed with two chlorine atoms and two amide groups. However, a later piece of work (*6*) provided strong indications of coordination of the platinum via the oxygen atoms in ε-caprolactam in a complex L_2PtCl_2. Nevertheless, it is worth pointing out that, although

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the evidence seems to be contradictory, the former preparations were carried out in aqueous media, whereas the latter were performed in nonaqueous media. Some Russian work appears to have been concerned with palladium physically deposited upon nylon rather than being chemically combined (7–10), but some later work has suggested complex formation (11–13) and the results suggest that a hydrido complex is involved. Nevertheless, some other recent work with platinum–nylon catalysts (14) led to the conclusions that the platinum was present as a complex and as small metal crystallites, and it may well be that the metal can be present in both zero-valent form and as higher oxidation states depending upon the temperature and conditions to which the catalyst is subjected.

The work reported here concerns the atypical behavior of some palladium–polyamide catalysts, compared with conventionally supported palladium catalysts, for the liquid phase hydrogenation of some 1-alkynes and alka-1,3-dienes.

EXPERIMENTAL

Materials

(a) *Nylons.* Nylon 66 was kindly supplied by I.C.I. Ltd. in the form of chopped fibers (1–2 mm long), as spun/stretched yarn, and spun/unstretched yarn. Other forms of nylon were all supplied as spun/stretched yarn, i.e., Nylon 6 (Courtaulds Ltd.), Nylon 11 (I.C.I. Ltd.) and Nylon–Nomex (Du Pont Ltd.). The spun yarns were chopped, as required, in a small unit built in this Department, to give fibers 1–2 mm in length and where possible all fibers were additive free.

(b) *Palladous chloride* (60% w/w Pd) was kindly provided by Johnson, Matthey and Company, Ltd.

(c) C$_5$- *and* C$_3$-*alkynes and* C$_5$-*alka*-1,3-*dienes* were used as supplied, glc analysis revealing no major hydrocarbon impuri-

ties. However, it is recognized that isoprene usually contains the stabilizer t-butyl catechol.

(d) *Solvents* were of Analar grade, where possible, but n-propanol and n-heptane were of G.P.R. grade. The latter contained a small amount of n-octane, for which allowance was made in reactions where n-octane was produced. However, apart from one special treatment of n-heptane (see results) all solvents were used as supplied.

(e) *Hydrogen* ($\geqslant$99.99% v/v) was used as supplied (B.O.C. Ltd. or Air Products Ltd.).

Catalyst Preparation

All catalysts were prepared from a suitably diluted stock solution of chloropalladous acid, which contained 5 g PdCl$_2$, dissolved in 50 cm^3 concentrated hydrochloric acid and made up to 500 cm^3 with distilled water.

(i) *Reflux temperature (100°C approx.) preparation.* Nylon fiber (0.5 g) was weighed into a conical flask containing 50 cm^3 distilled water, the flask being fitted with a reflux condenser and a dropping funnel containing 50 cm^3 suitably diluted stock palladium solution. The water and nylon fibers were brought to reflux temperature using a magnetic heater/stirrer unit and the palladium solution was added dropwise to the refluxing solution over a period of 15 min. On completion of the addition of the palladium solution, the contents of the flask were stirred and refluxed for a further 15 min (longer periods of treatment were unnecessary). The treated nylon, which varied in color according to the concentration of the treating solution, from almost colorless to golden brown, was filtered, washed copiously with distilled water and finally with methanol, followed by drying in air at 80°C. Apart from the very dilute treating solutions, all filtrates
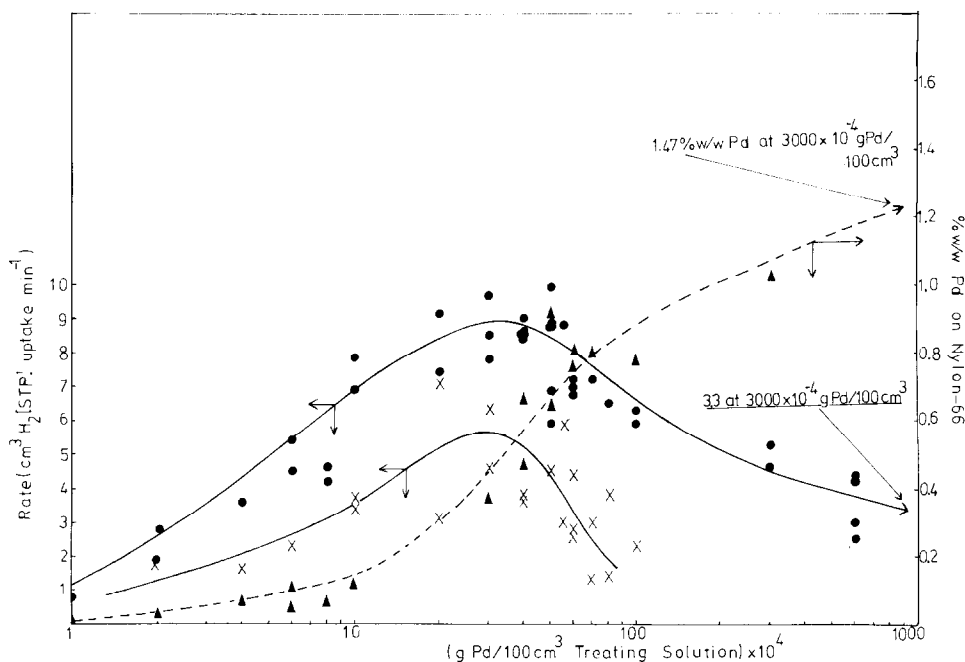
FIG. 1. Activity and metal concentration for Pd–Nylon-66 catalysts as a function of treating solution concentration. (●) n-propanol, (×) n-heptane.

contained unreacted $PdCl_4^{2-}$ and the treated fibers required no further treatment in order to activate them. When necessary a scaled-up process was used (2.5 g nylon fibers/500 cm³ solution) and this gave identical results within experimental error.

(*ii*) *Room temperature (20–25°C) preparation.* The scale of preparation was as above, but the nylon fibers were shaken with the treating solution for about 18 hr, after which they were filtered, acetone washed (the latter solvent did not remove complexed $PdCl_4^{2-}$), air dried at room temperature, and reduced in n-butanol (used for same reason as acetone above) at 70°C under hydrogen. The unreduced catalyst varied from pale straw to yellow-orange in color and after reduction from golden brown to dark brown, depending upon the concentration of treating solution. Catalysts prepared in this manner were similarly behaved to those produced at reflux temperatures, although greater

palladium concentrations on the nylon were obtainable at room temperature (Fig. 1), and this will be commented upon later.

Reactions

Reactions were carried out in 80 cm³ round-bottomed flasks, fitted with a suba-sealed side arm for sampling. The vessel was thermostated, agitated by a calibrated variable speed shaker, and connected to an automatic hydrogenation control unit that maintained the reaction at constant (usually ambient) pressure. Reaction products were analyzed using gas–liquid chromatography and the error involved was estimated as ±2%.

RESULTS

Catalyst Activity

A large number of catalysts were prepared at reflux temperature by varying the treating solution concentration, their

TABLE 1

Effect of Treating Solution Concentration on Selectivity of Pd–Nylon 66 Catalyst[a]

Treating solution concentration (g Pd $\times 10^{-4}$/100 cm³)	%w/w Pd on catalyst	Selectivity in	
		n-Propanol	n-Heptane
1.0	0.01	0.99	—
2.0	0.03	0.97	0.99
4.0	0.07	0.95	0.99
6.0	0.11	0.88	0.99
8.0	0.06	0.88	—
30.0	0.47	0.76	0.99
300.0	1.03	0.81	0.99
1800.0	1.3–1.4[b]	0.76	—

[a] Pressure = ambient; temperature = 70°C, catalyst weight = 0.1 g; solution = 20 cm³ 5% v/v 1-octyne/solvent.

[b] Estimated.

activity being tested by measuring the rate of 1-octyne hydrogenation at 70°C in both n-propanol and n-heptane. Despite the obvious difficulty in reproducing a given catalyst, a maximum activity was

TABLE 2a

Effect of Thiophen Addition on Activity (A) and Selectivity (S) of Pd–Nylon 66 Catalyst[a]

Vol. Thiophen added (μliter)	Thiophen/Pd	Temperature			
		50°C		70°C	
		S	A	S	A
(I)					
0	—	0.68	5.1	0 66	9.5
1	1.34	0.81	3.8	—	—
5	6.7	0.84	4.5	0.91	7.2
10	13.4	0.87	3.2	0.93	7.4
20	26.8	0.89	3.1	0.95	6.8
50	67	0.90	3.0	0.94	7.2
100	134	0.91	2.4	0.95	6.2
1000	1340	0.94	1.5	—	—
(II)					
0	—			0.99	9.7
1	22.5			0.99	9.3
5	112.5			0.99	8.7
10	225			—	—
20	450			0.99	8.5
50	1125			0.99	8.6
100	2250			—	—
1000	22500			—	—

[a] Pressure = ambient; solution = 20 cm³ 5% 1-octyne in n-propanol; catalyst weight = 0.2 g.

I = treating solution, 30 × 10⁻⁴ g Pd/100 cm³; catalyst = 0.5% w/w. II = treating solution 2 × 10⁻⁴ g Pd/100 cm²; catalyst = 0.03% w w

TABLE 2b

Effect of Triphenylphosphine on Activity (A) and Selectivity (S) of Pd–Nylon 66 Catalyst in n-Propanol[a]

PPh₃ (g)	PPh₃/Pd	S	A
0	—	0.82	12.0
0.1	40.4	0.91	4.5
1.0	40.4	0.95	2.2
1.0[b]	80.8	0.96	6.0

[a] Pressure = ambient; solution = 20 cm³ 5% v/v 1-octyne in n-propanol; temperature = 70°C; catalyst treating solution = 30 × 10⁻⁴ g Pd/100 cm³; catalyst = 0.5% w/w Pd.

[b] Catalyst weight = 0.1 g.

observed in both solvents (Fig. 1). In fact a plot of activity vs metal loading gives the same picture and it is clear that maximum activity does not correspond either to a maximum treating solution concentration or metal loading. The low metal loadings at low treating solution concentration may be due to metal deposition on the flask walls (this was observed particularly at low concentrations). If this had been avoidable, it is possible that the activity maximum would have occurred at a lower treating solution concentration than that actually observed (between 20 × 10⁻⁴ and 50 × 10⁻⁴ g Pd/ 100 cm³ solution). For more concentrated solutions, the metal may be inaccessible due to its incorporation in the fiber interior (see below).

Variation of Catalyst Activity and Selectivity[1] with Treating Solution Concentration

This effect was studied for 1-octyne hydrogenation in n-propanol and n-heptane. In the latter solvent high selectivities independent of metal concentration were observed, but the use of n-propanol gives high selectivities only at low treating solu-

[1] Selectivity = % olefin/% olefin + % paraffin during the first mole of hydrogen uptake.

tion concentrations (Table 1), i.e., $<5 \times 10^{-4}$ g Pd/100 cm³ solution, which corresponds to a palladium content of 0.1% w/w. The observed selectivities were determined by sampling throughout the first mole of hydrogen uptake, as were all the selectivities reported, and they remained essentially constant during that stage of the reaction.

It was thought that small quantities of sulphur in the n-heptane might have been giving selective catalyst poisoning, due to the latter solvent being derived from a petroleum source, thus resulting in high selectivity. Accordingly, a sample of n-heptane was allowed to stand for 24 hr over about 30 g 5% w/w Pd on charcoal, on which any poison should be chemisorbed. The filtered n-heptane gave identical results to the untreated solvent and furthermore, even the addition of 1000 μliter thiophen to 20 cm³ reaction solution, with n-propanol as solvent, did not result in a selectivity as high as in n-heptane or indeed as with low concentration catalysts used in n-propanol (Tables 1 and 2a). It is also clear that, over the whole range of poison addition, the thiophen/Pd ratio was greater than 1 and even with very large thiophen/Pd ratios, the catalyst activity was not destroyed and considerable improvement was effected in the selectivity for the 0.5% w/w catalyst (Table 2a, (I)).

The most selective catalyst was that prepared from a low concentration treating solution (Table 2a (II)), and the addition of poison could have no improving effect on an already high selectivity. The significant observation appears to be that the addition of thiophen to this catalyst has even less effect on its activity.

A limited number of experiments were carried out using triphenylphosphine instead of thiophen (Table 2b), and a similar effect was obtained for the 0.5% w/w Pd–Nylon 66 catalyst in that selectivity was improved at the expense of reduced ac-

tivity. The ability of triphenylphosphine to coordinate with transition metals is well known but the number of results reported is strictly limited, and it is not possible to draw any conclusions as to the interaction between the triphenylphosphine and the palladium.

Finally, it was observed that these catalysts have only a poor activity for 1-alkene hydrogenation and a virtually negligible activity for internal olefin hydrogenation. Consequently, reaction ceased when the 1-octyne had been consumed. Furthermore, the very dilute Pd–Nylon 66 catalysts (Table 2a (II)) were inactive for alka-1,3-diene hydrogenation.

The Activity and Selectivity of Nylon 66 Supported Catalysts in Various Solvents

This investigation was carried out with catalysts prepared from a treating solution containing 30×10^{-4} g Pd/100 cm³ solution, i.e., that solution giving optimum activity. The results are presented in Table 3, and there is a wide range of activity and selectivity. Although no attempt has been made to correct rates for vapor pressure differences of the various solvents, it is not thought that the range of activities can be explained simply in terms of hydrogen concentration differences in the various solvents. In any case the selectivity differences provide strong evidence for some kind of solvent effect and such a variation is contrary to the experience of other workers (15–18), who have observed high selectivities for olefin formation over a number of conventional palladium catalysts for conditions similar to those employed in this work (some of those results are quoted in Table 3).

The olefin distributions determined during the first mole of hydrogen uptake are of even greater interest (Table 4). 1-Pentyne and 1,3-pentadiene, where comparison is possible with conventional catalysts, give somewhat similar pentene

TABLE 3

Activity and Selectivity of Pd–Nylon 66 Catalysts for Various
Reactant/Solvent Systems[a]

Solvent	Organic Reactant							
	Isoprene (50°C)		1,3-Pentadiene (50°C)		1-Pentyne (50°C)		1-Octyne (70°C)	
	A	S	A	S	A	S	A	S
n-Propanol	4.5	0.69	21.0	0.84	12.0	0.66	24.0	0.67
n-Heptane	0.5	0.77[b]	0.5	0.68[b]	4.1	0.94	18.0	0.99
D.M.F.	6.2	0.86	10.6	0.81	5.6	0.80	15.0	0.79
Glacial acetic acid	17.0	0.99	17.0	0.99	9.4	0.98	20.0	0.96
M.E.K.	0.5	0.53	2.1	0.70	1.3	0.59	0.8[c]	0.86[c]
Ethyl acetate	0.5	0.39[b]	1.8	0.65	1.8	0.82	1.0[c]	0.85[c]
1,4-Dioxan	8.9	0.98	7.3	0.95	2.5	0.92	6.7	0.86
Ref. (18)		0.98						
Ref. (15)				0.94 to 0.99		0.97		
Ref. (16)		0.97 to 0.98		0.98 to 0.99		0.95 to 0.98		

[a] Pressure = ambient; catalyst weight = 0.3 g; solution = 20 cm³ 5% v/v reactant in solvent; A = activity (cm³ H_2(S.T.P.)min⁻¹); D.M.F. = dimethylformamide; M.E.K. = methyl ethyl ketone.

[b] Measured at low conversions.

[c] At 50°C.

distributions, although some pentene distributions might be thought to be significantly different. Isoprene, on the other hand, really stands out in that there is a wide variation of selectivity (Table 3) and, furthermore, the methylbutene distribution is very different from those obtained with conventional palladium catalysts (Table 4); it is not thought that the differences can be ascribed to unremoved t-butyl catechol stabilizer since one reference (16) refers to work carried out in these laboratories with the same batch of isoprene for which the methylbutene distributions are similar to those reported by other workers with conventional catalysts. In particular the Pd–Nylon 66 catalysts give larger quantities of 2-methyl-2-butene than do conventional palladium catalysts. It is also true that when the selectivity of the Pd–Nylon 66 catalysts is high, i.e., in acetic acid and 1,4-dioxan, the amount of

2-methyl-2-butene produced is somewhat lower.

Other Forms of Nylon as a Support for Palladium

This study was limited by lack of availability of large quantities of flocked nylon in any other form but Nylon 66. The treating solution employed was that giving optimum activity with Nylon 66, i.e., 30 × 10⁻⁴ g Pd/100 cm³, and it is recognized that the optimum treating solution may vary from one type of nylon to another.

Further work is clearly required, but it is interesting that a Pd–Nylon 11 catalyst gave activities greater than those for Pd–Nylon 6, even though its metal concentration was lower (Table 5). Pd–Nylon 11 also gives selectivities greater than those for Pd–Nylon 66, but this may be a result of its lower metal concentration (cf. Table 1 for Pd–Nylon 66). Nylon–

TABLE 4

Initial Olefin Distribution for Pd–Nylon 66 Catalysts and
Various Reactant/Solvent Systems[a]

Organic reactant	Initial olefins	Initial olefin distribution (%) in							
		PrⁿOH	n-C⁷H₁₆	D.M.F.	HAc	EtAc	M.E.K.	1,4-DN	CH₃OH
1-Pentyne	1-P	87.0	100	88.5	98.0	95.0	79.0	97.0	—
	t-2-P	8.0	—	7.0	2.0	4.0	13.0	1.5	—
	c-2-P	5.0	—	4.5	—	1.0	8.0	1.5	—
1-Pentyne	1-P	96–100	100						99.0[b]
	t-2-P	0–3	—						—
	c-2-P	0–1	—						—
Ref.		(16)	(16)						(15)[b]
1,3-PD	1-P	21.0	23.0	32.0	39.0	24.0	22.0	38.0	—
	t-2-P	59.0	77.0	49.0	45.0	59.0	60.0	46.0	—
	c-2-P	20.0	—	19.0	16.0	17.0	18.0	16.0	—
1,3-PD	1-P	33–38	35						32–38
	t-2-P	45–46	48						50–60
	c-2-P	16–22	17						7–11
Ref.		(16)	(16)						(15)
Isoprene	3-M-1-B	7.0	—	13.0	16.0	—	—	20.0	—
	2-M-1-B	15.0	—	23.0	30.0	12.0	11.0	26.0	—
	2-M-2-B	78.0	100	64.0	54.0	88.0	89.0	54.0	—
Isoprene	3-M-1-B	22.5	26–29						26.0
	2-M-1-B	29.6	30–37						31.3
	2-M-2-B	47.8	33–44						42.7
Ref.		(16)	(16)						(18)[b]

[a] Pressure = ambient; temperature = 50°C; solution = 20 cm³ 5% v/v reactant in solvent; catalyst weight = 0.3 g; 1,3-PD = 1,3-pentadiene; 1-P = 1-pentene; t-2-P = trans-2-pentene; c-2-P = cis-2-pentene; 3-M-1-B = 3-methyl-1-bentene; 2-M-1-B = 2-methyl-1-butene; 2-M-2-B = 2-methyl-2-butene; PrⁿOH = n-propanol; D.M.F. = dimethylformamide; HAc = acetic acid; EtAc = ethyl acetate; M.E.K. = methylethylketone; 1,4-DN = 1,4 dioxan.

[b] No solvent or none indicated and temperature = 20°C.

Nomex was difficult to treat because of its chemical inertness, due no doubt to its aromatic backbone, and it may be behaving similarly to a low concentration Pd–Nylon 66 catalyst.

Physical and Chemical Investigation of the Catalysts

Total surface area measurements, using a dynamic method for Nylon 66 fibers, gave a surface area of 0.4 m² g⁻¹, which was in good agreement with an area of 0.2 m² g⁻¹ based on scanning electron microscope studies; the latter technique also confirmed that the fibers possess no pore structure. Attempts to measure the metal surface area by CO chemisorption both in these laboratories and those of Johnson, Matthey and Company, Ltd. were unsuccessful. Either the palladium is inaccessible or is present in a form which does not chemisorb CO. These measurements were made with the "dry" fibers

TABLE 5

Activity (A) and Selectivity (S) of Various Pd–Nylon Catalysts
for Some 1-Alkyne/Solvent Systems[a]

| Nylon | wt% Pd on Nylon | 1-Octyne | | | | | | 1-Pentyne | | | | | |
| | | a | | b | | c | | a | | b | | c | |
		A	S	A	S	A	S	A	S	A	S	A	S
Nylon 66	0.47	12.0	0.99	16.0	0.67	10.0	0.79	2.7	0.94	8.0	0.66	3.7	0.80
Nylon 6	0.40	2.7	0.90	6.1	0.78	5.4	0.81	1.6	0.96	6.0	0.91	9.1	0.79
Nylon 11	0.12	11.4	0.87	13.3	0.92	10.7	0.87	10.7	0.83	7.1	0.99	10.5	0.87
Nylon–Nomex	0.03	1.6	0.90	1.5	0.99	1.8	0.99	1.3	0.97	1.1	0.99	1.6	0.99

[a] Temperature = 50°C; solution = 20 cm³ 5% v/v 1-alkyne in solvent; catalyst weight = 0.2 g; a = n-heptane; b = n-propanol; c = dimethylformamide; A = cm³ H_2(S.T.P.) min⁻¹.

and it may be that the presence of a solvent is essential for the operation of the catalyst. Electron probe microanalysis (Johnson, Matthey and Company, Ltd.) studies revealed that palladium was present both on the exterior surface and in the interior of the fiber (diameter = 2×10^{-3} cm, approximately). This observation gives support to the idea that inaccessibility of the palladium is a factor contributing to the activity pattern (Fig. 1). Some temperature programmed reduction (TPR) studies based on the system reported by Jenkins et al. (19) have proved interesting, although the results at this stage are qualitative. A fresh Pd–Nylon 66 catalyst, prepared by the reflux method, took up hydrogen rapidly at room temperature. In fact it was not possible to record the event, which occurred as the cell was stabilizing. However, during programming at 5°C/min from 20°C, hydrogen was evolved at 65°C, thus confirming previous hydrogen uptake. The catalyst was then heated at the above rate to various temperatures between 100°C and 200°C, no further hydrogen uptake being observed, and on cooling rapidly, two hydrogen uptake peaks were recorded, the first being the larger of the two. On reprogramming, a single hydrogen evolution peak was observed at 65°C and when

cooled rapidly from temperatures above 100°C hydrogen was readsorbed as two peaks again; this process could be repeated many times.

For the sake of comparison, a sample of charcoal impregnated with chloropalladous acid, representing a similar quantity of palladium, was also subjected to TPR. In this case the fresh catalyst, which also contained some water, did not reduce until a temperature between 160 and 180°C. On cooling from 200°C a single hydrogen chemisorption peak was obtained and on reprogramming there was no sharp hydrogen evolution peak at 65°C, the indications being that hydrogen was being eluted slowly over a range of temperature. Recooling from temperatures above 100°C resulted in a single hydrogen uptake peak, attributable to chemisorption. A sample of palladium oxide, also representing a similar quantity of palladium, was reduced at 90°C, and on cooling from 180°C an almost negligible hydrogen chemisorption peak was obtained, followed by a very large uptake peak ascribed to β-PdH$_{0.6}$ formation. This indicated the presence of bulk palladium, necessary for the formation of the β-PdH$_{0.6}$. On reprogramming, the β-PdH$_{0.6}$ decomposed at 65°C. Evidently the H$_2$PdCl$_4$-impregnated charcoal consisted of palladium in very small par-

ticulate form, since there was insufficient bulk to allow β-hydride formation.

It would seem that the Pd–Nylon 66 might possess some properties associated with very small Pd particles and some associated with bulk Pd in view of the two hydrogen uptake peaks on cooling. However, X-ray diffraction studies did not reveal any sharp diffraction lines associated with bulk Pd, although diffraction patterns become difficult to obtain at very low concentrations. It is significant that the fresh Pd–Nylon 66 catalyst takes up hydrogen at room temperature, whereas chloropalladous acid treated charcoal does not, yet each catalyst had been subjected to similar conditions during preparation. The fresh Pd–Nylon 66 catalyst activates readily at room temperature, yet evolves hydrogen at 65°C as though bulk metal had been formed. This seems highly unlikely in view of the mild conditions and the low metal loading of the catalysts ($<1\%$ w/w); thus, significant agglomeration seems unlikely. Even so, the results are equivocal and neither prove nor disprove the existence of a Pd(II) complex, yet they suggest that the system is unusual. Finally, it should be pointed out that the conditions experienced by the catalyst during TPR were far different from those during reaction, in which temperature was never greater than 70°C, and in the presence of a solvent, the hydrogen concentration at the catalyst surface would be less than that in the TPR cell with the 5% H_2/Argon stream. Even if a Pd(II) complex is formed, prolonged catalyst use at temperatures above 100°C might well cause its gradual reduction to Pd(0), and many of the investigations involving benzene hydrogenation have employed temperatures in the range 100 to 200°C.

Attempts to study the Pd–Nylon 66 catalysts using ESCA were unrewarding because of sample charging, which is unfortunate since this technique would other-

wise have revealed the chemical state of the palladium.

The Pd–Nylon 66 fibers themselves failed to provide any meaningful infrared reflectance spectra but a sample of Nylon 66 film treated with chloropalladous acid gave (i) a strong Pd–Cl signal and (ii) a strong H_2O signal when the sample had just been placed in the cell. The latter signal gradually disappeared as the sample warmed up in the cell, and if the sample was then removed and allowed to stand in air, the H_2O signal returned when reexamined in the ir unit; untreated nylon did not exhibit this behavior.

Finally, chemical analysis of the catalysts by Johnson, Matthey and Company, Ltd. showed that the Pd–Nylon 66 produced at room temperature, but unreduced, had a Cl–Pd ratio of 3:1. Similar analysis of the reduced room temperature prepared catalyst or of the reflux temperature preparation gave a Cl–Pd ratio of 1:1.

DISCUSSION

In view of the results obtained, it is suggested that a fresh catalyst contains palladium as a square coplanar Pd(II) complex and some possible reaction sequences are suggested which are in accord with such a hypothesis and which explain the product distributions and selectivities. However, it must be emphasized that they are speculative.

The results obtained by other workers have indicated that metal complexes and/or zerovalent metal dispersed in an unusual way might be responsible for the undoubtedly atypical catalytic behavior of these catalysts. Indeed, it is very likely that the more concentrated the metal becomes, and the more extreme the operating conditions, the greater will become the chance of forming agglomerates of metal atoms.

The observation of an activity maximum at a particular treating solution concentration (Fig. 1) is in agreement with some of
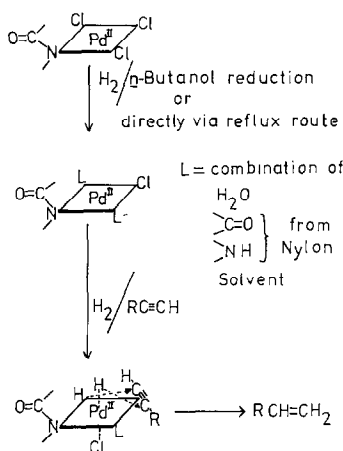
FIG. 2. Possible reaction sequence for 1-alkynes over low concentration catalysts.

the observations of Harrison and Rase (4). In part, the electron probe microanalysis results explain the existence of a maximum activity or more reasonably an upper limit to activity if palladium begins to enter the fiber interior as treating solution concentration increases (a further possibility will be discussed later).

The unusual activity and selectivity results suggest that, under the relatively mild conditions employed, the palladium is present as a Pd(II) complex and not as zerovalent metal. The appearance of the catalyst and the results of chemical analysis provide some support for this view. It is known that palladium salts exists as square coplanar complexes and the first step (at room temperature or reflux temperature) in the catalyst preparation is probably

$$\text{(I)}$$
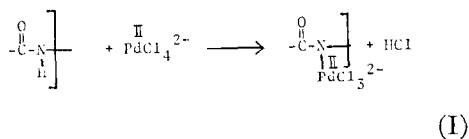
This would be in agreement with the results of chemical analysis of the unreduced catalyst prepared at room temperature. The second stage of the room temperature preparation involves reduction

by hydrogen in a solvent and could occur as follows:

$$\text{(II)}$$
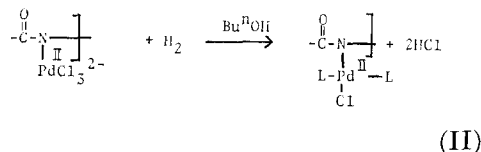
where L = suitable ligands, the possible nature of which will be discussed below.

In the case of the reflux temperature route, the same $Pd:Cl$ ratio is obtained (1:1) but no hydrogen is involved and some kind of hydrolytic process seems likely. A number of possible routes could occur and the process is just depicted as

$$\text{(III)}$$
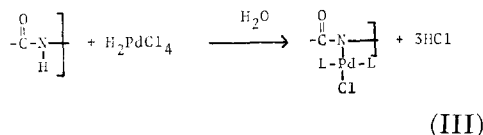
This route could be very complex, but it is known that a solution containing $Pd^{II}Cl_4^{2-}$ with $pH > 1$ undergoes hydrolysis and can even give rise to precipitation of hydroxy species if the pH increases too much; in fact the pH of the standard treating solution was 1–2 depending upon the temperature. It is suggested that these factors indicate the reason for it being possible to complex more palladium with nylon at room temperature than at reflux temperature, since the nature of the reacting species may vary from $Pd^{II}Cl_4^{2-}$ to hydroxy species for which the equilibrium may be different.

The nature of the above species is not very different from those proposed by Dini et al. (5) for Pt–Nylon 6 catalysts prepared in aqueous solutions. As pointed out earlier, the later evidence obtained by Dini et al. (6) suggesting that the platinum is bound via the oxygen groups in the nylon in no way contradicts their earlier work or indeed our own, since nonaqueous media were used in that later work.

It is further suggested that the behavior of low concentration Pd–Nylon 66 cata-

lysts may be explained in terms of isolated metal complexes, which are capable of giving only very selective behavior with alkynes because alkenes are insufficiently strongly complexed and diolefins cannot complex; neither mono- nor diolefins reacted on the low concentration catalysts. The nature of the ligand L is purely speculative, although the infrared evidence suggests water as a possibility. However, other possibilities are (i) other amide and (ii) other carbonyl groups in the same or adjacent nylon chains, and this is shown very simply in Fig. 2 as a possible reaction sequence. Certainly six to seven atom chains should be capable of entering into this kind of cyclic configuration without undue strain. This would explain the inertness of Nylon–Nomex, with its more rigid structure. Indeed almost any combination of the above ligands is likely, including even the reaction solvent.

The less selective behavior of the more concentrated catalysts can be explained if it is assumed that there will be more adjacent catalytic sites, so that an alkyne could interact with two sites simultaneously. Thus, in a polar solvent or at least a weakly interacting solvent it may be possible for the simultaneous addition of two molecules of hydrogen to occur [Fig. 3, step (a)], giving poor selectivity. If a nonpolar solvent such as n-heptane, a polar solvent plus thiophen or glacial acetic acid is used, high selectivity is regained and Fig. 3, step (b) indicates that this could occur via deactivation of half of a pair of sites. In the case of thiophen, this itself becomes a ligand, and in the case of n-heptane this solvent does not allow easy interchange of ligands. The peculiar ability of glacial acetic acid to promote high selectivity may be due to its carbonyl group being able to reinforce or replace those of the nylon. However, ethyl acetate and methyl ethyl ketone contain carbonyl groups, yet poor selectivity was observed in those solvents. The individual solvent
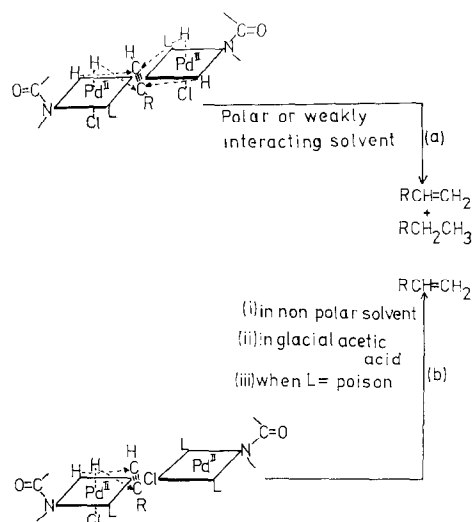

FIG. 3. Possible reaction sequence for 1-alkynes over high concentration catalysts.

effects are difficult to explain in any detail at present but it does appear that the degree of interaction of the solvent with the complex has a profound effect on activity and selectivity.

The low activity of the more concentrated catalysts may be caused by the formation of bridged species of the type
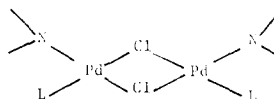
The latter may possess little or no activity and readily explains the existence of an activity maximum, rather than a limiting activity by incorporation of palladium into the fiber interior. Bridged species are well known in transition metal complexes, and palladium chloride itself exists as
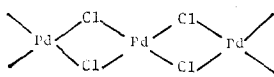
The behavior of the dienes is only easily understood by proposing a two-site coordination complex (Fig. 4). This allows the explanation of low selectivities because simultaneous addition of two molecules of hydrogen is possible, this being difficult
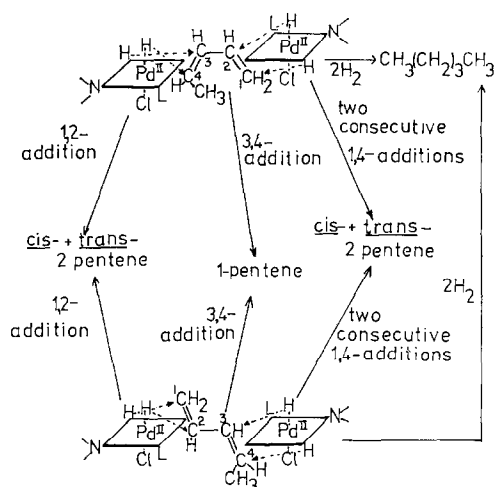
FIG. 4. Possible reaction sequence for dienes.

to envisage with a single site. This is illustrated in Fig. 4 by *cis-* and *trans-*1,3-pentadiene and it is expected that a diene will be less strongly complexed than an alkyne. This is supported by the fact that thiophen addition completely inhibits the reaction. The large quantity of 2-methyl-2-butene generated with isoprene in reactions of lower selectivity (Tables 3 and 4) must occur via 1,4 addition of hydrogen from the complex via two successive insertions of isoprene (as illustrated by 1,3-pentadiene in Fig. 4). Again the unusual ability of glacial acetic acid and 1,4-dioxan to give high selectivity may arise as a result of an ability to interact with the sites involved in hydrogen activation. Thus, the diene could complex via two sites but only one may have a complexed hydrogen molecule. Certainly, there is more 1,2 and 3,4 addition in the case of the latter two solvents.

The ability of thiophen or triphenylphosphine to give improved selectivity in *n*-propanol is explicable if they act as coordinating ligands and the more bulky triphenylphosphine ligand may well affect activity more than thiophen.

Further work is clearly required to confirm (a) the nature of the ligands involved with the palladium and (b) the role of the solvent. However, it is concluded that a palladium(II)–polyamide complex is formed initially rather than Pd(0), which may be produced gradually under more severe conditions via breakdown of the complex. The reaction mechanisms suggested are speculative and should be investigated in more detail, perhaps with appropriate isotope techniques. Nevertheless, this work has indicated that the catalytic properties of these palladium–polyamides can be unusual and agrees in that respect with the results of other workers. It would certainly be helpful to prepare catalysts in both aqueous and nonaqueous solvents and with polymers containing other possible ligands, e.g.,

$$\overset{\diagdown}{\underset{\diagup}{}}C{=}O$$

only, as in Terylene and $-C{=}N$ as in polyacrylonitrile.

REFERENCES

1. Izumi, Y., *Bull. Chem. Soc. Japan* **32**, 932 (1959).
2. Akamatsu, A., Izumi, Y., and Akabori, S., *Bull. Chem. Soc. Japan* **34**, 1067 (1961).
3. Akamatsu, A., Izumi, Y., and Akabori, S., *Bull. Chem. Soc. Japan* **34**, 1302 (1961).
4. Harrison, D. P., and Rase, H. R., *Ind. Eng. Chem. Fund.* **6**, No 2, 161 (1967).
5. Dini, P., Dones, D., Montelatici, S., and Giordano, N., *J. Catal.* **30**, 1 (1973).
6. Dini, P., Bart, J. C. J., and Santoro, E., *Inorg. Chim. Acta* **17**, 97 (1976).
7. Sokolskii, D. V., *Russ. J. Phys. Chem.* **40**, No. 3, 394 (1966).

8. Tyurenkova, O. A., *Russ. J. Phys. Chem.* **43**, No. 8, 1167 (1969).

9. Tyurenkova, O. A., and Volkova, V. E., *Russ. J. Phys. Chem.* **43**, 1587 (1969).

10. Tyurenkova, O. A., and Zhakin, V. P., *Russ. J. Phys. Chem.* **44**, 210 (1970).

11. Radadkina, E. N., Kushetsova, T. V., Teleshev, A. T., Rozhdestvenskaya, I. D., and Kalechits, I. V., *Kinet. Katal.* **15**, No. 4, 969 (1974).

12. Rasadkina, E. N., Rozhdestvenskaya, I. D., and Kalechits, I. V., *Katal. Reakts. Zhidk. Faze* **3**, 658 (1974).

13. Rasadkina, E. N., Rozhdestvenskaya, I. D., and Kalechits, I. V., *Kinet. Katal.* **17**, No. 4, 916 (1976).

14. Bernard, J. C., Hoang-Van, C., and Teichner, S. J., *J. Chim. Phys.* **72**, 729, 735 and 1217 (1975); **73**, 799 and 988 (1976).

15. Bond, G. C., and Rank, J. S., *in* "Proceedings of the Third International Congress on Catalysis, 1964," Vol. 2, p. 1225.

16. Ahmad, M. M., Ph.D. thesis, University of Birmingham, 1974.

17. Bond, G. C., and Wells, P. B., *Advances in Catal.* **15**, 92 (1964).

18. Kazanskii, B. A., Gostunskaya, I. V., and Granat, A. M., *Izvest. Akad. Nauk SSSR Otdel. Khim. Nauk* 670 (1953).

19. Jenkins, J. W., McNicol, B. D., and Robertson, S. D., *Chem. Technol.* 316 (1977).