

Homogeneous Hydrogenation of Unsaturated Compounds Catalyzed by Pd Complexes

I. Scope and Effect of Variables

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The scope of activity and selectivity in hydrogenations of unsaturated compounds catalyzed by a number of Pd complexes has been explored. Monoolefins are both hydrogenated and hydroisomerized. Conjugated dienes are hydrogenated by a combination of 1,2 and 1,4 addition. Of variables affecting rates and product distributions, the nature of substrates was found to be most important and to determine the relative effect of other variables. Pretreatment of zerovalent Pd complexes with oxygen resulted in sizable rate increases. Observations have been rationalized on the basis of addition and elimination of Pd hydride species.

INTRODUCTION

Catalysis of homogeneous hydrogenation of unsaturated organic compounds has been the subject of considerable investigation (1). However, only few examples of such catalysis involve palladium species (2). This is somewhat surprising in view of the extensive use made of heterogeneous palladium hydrogenation catalysts (3) and the great variety of homogeneously catalyzed reactions involving palladium (4). We report here the results of our efforts to explore the ability of some palladium complexes to function as hydrogenation catalysts and to study some of the variables affecting these reactions.

METHODS

Catalysts

All Pd(II) complexes were prepared by addition of excess phosphine ligands (purchased (Strem) or prepared by literature

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procedures (14)) to PdCl₂ in dry alcoholic HCl. These species were reduced to the corresponding Pd(0) complexes by hydrazine or NaBH₄ in dry ethanol containing excess ligand under an atmosphere of dry argon. An alternate procedure for preparation of Pd(0) complexes was reduction of (φ₃P)₂PdCl₂ in the presence of excess ligands. Compounds were purified by dissolving in CH₂Cl₂ and reprecipitation by ethanol. New complexes were characterized by their elemental analyses and spectra.

All Pd(0) complexes were characterized by their ability to undergo oxidative addition reactions with alkyl and aryl halides and by the ability of these derivatives to insert CO. Details of preparation and characterization of previously unreported complexes will be described elsewhere. The zerovalent complexes were generally prepared immediately prior to use.

Sample Procedure for the Preparation of (φ₂PCH₂Pφ₂)₃Pd₂(I)

The entire procedure was carried out in a glove bag under argon. A mixture of 3.50 g (5 mmoles) (φ₃P)₂PdCl₂ and 3.84 g (10 mmoles) φ₂PCH₂Pφ₂ was sus-

pended in 50 ml dry ethanol. The mixture was warmed until all suspended material dissolved. Fifteen drops of anhydrous hydrazine were added to the light orange solution, immediately producing a deep red color and an orange precipitate. The hot suspension was filtered and the solid was washed with 25 ml dry ethanol. The product was purified by dissolving it in a minimum quantity of methylene chloride and immediately filtering the solution into cold ethanol. The reprecipitated solid was collected on a filter, washed with 25 ml portions of ethanol and pentane and dried under vacuum.

This procedure yielded 1.5 g (63%) of product, dec. 180–190°C. Analysis: Calculated for $C_{75}H_{66}P_6Pd_2$: C, 65.94; H, 4.87; P, 13.60; Pd, 15.55. Found: C, 65.88; H, 4.96; P, 13.49; Pd, 15.02.

Solvents, Substrates, and Gases

All solvents were dried, distilled, and stored under dry argon (>99.999%). Liquid and gaseous substrates were procured in the highest purities available, generally >99.5% and used without further purification. Hydrogen (99.95%) was not purified further. Liquid reagents were bubbled with dry argon immediately prior to use to remove dissolved air.

Apparatus and General Procedures

Hydrogenations were carried out in standard 2 oz aerosol compatibility bottles (Fischer-Porter) fitted with a needle valve and pressure gage. Catalysts, solvents, and liquid substrates were introduced into the bottles in a glove bag under an argon atmosphere. Except in experiments involving oxygen pretreatment, the bottles were sealed prior to removal from the bags. The bottles were attached to a manifold via Swage Loc fittings and charged with hydrogen. Contents were stirred magnetically. Products were analyzed by G.C. and/or M.S. when hydrogen absorption was complete or had declined notably (high conversions) or, in the case of very slow reactions, after some arbitrary time, usually not exceeding 1 week.

A qualitative comparison of rates is

based on the average specific conversion (moles substrate converted/Pd/hr) which may be viewed as an average catalyst turnover number for the total time each experiment was conducted.

RESULTS

The scope of hydrogenation activity and selectivity was examined with respect to substrates, solvents, additives, catalyst ligands, catalyst pretreatment, initial substrate/catalyst ratio, temperature, and pressure. Results for various unsaturated compounds are as follows:

Monoolefins

Under standard conditions (0.5 g catalyst, 50 ml solvent, saturated at 1 atm with gaseous substrate or plus 5 ml liquid substrate, 1 atm argon and initial hydrogen pressure of 100 psig, room temperature), conversion of ethylene to ethane was catalyzed by $(\phi_2PCH_2P\phi_2)_3Pd_2$ (I) in toluene. The reaction was followed (with several additions of ethylene and hydrogen) to a conversion of 150 moles ethylene/mole catalyst without any observed decrease in activity. No palladium metal precipitated and no oligomers were formed. Similar results were obtained in 5:1 toluene/benzonitrile. The corresponding Pd(II) complex, $(\phi_2PCH_2P\phi_2)PdCl_2$, although only sparingly soluble in toluene also catalyzed ethylene hydrogenation.

Under the same conditions (I) catalyzed propylene hydrogenation but at a rate only 9% of that observed for ethylene. The activity was considerably lower in 1:1 toluene/ethanol and was suppressed completely in dichloromethane, although (I) is completely soluble in this solvent. Some sensitivity to catalyst structure was observed. Thus average specific conversion rates (moles substrate converted/mole Pd/hr) declined in the order (I) > $(\phi_2PCH_2CH_2P\phi_2)_2Pd$ (II) > $(\phi_2PCH_2CH_2CH_2P\phi_2)_2Pd$ (III).

The activity of (I) for catalyzing the hydrogenation of 1-butene was low, the conversion rate being only some 0.8% of that of ethylene. Selectivity was also poor. At 8.8% conversion, only 20.5% of the

product was *n*-butane. The remainder consisted of 56.8% *trans* and 22.7% *cis*-2-butenes. The ratio of *trans/cis* isomer (2.5) was lower than the equilibrium value (3.4). An increase of the temperature to 110°C had little effect on rate. Under these conditions, selectivity to *n*-butane increased to 25.8% while the *trans/cis* ratio of 2-butenes declined to 2.1.

Isobutene did not react.

A strong dependence of catalytic activity on substrate structure was also observed with cyclic olefins. Cyclohexene was neither hydrogenated nor disproportionated at room temperature or at 100°C. In contrast, (I) catalyzed the hydrogenation of cyclopentene to cyclopentane and of norbornene to norbornane. The reaction was approximately six times as fast in the latter case.

Acetylenes

In the presence of (I) under standard conditions, methyl acetylene was converted completely and rapidly to propylene which was then reduced more slowly to propane. Hydrogenation of 2-butyne was slower. The only product of reaction in this case was *cis*-2-butene which did not react further.

Conjugated Dienes

Results of hydrogenation experiments involving butadiene are summarized in Tables 1-3. Again, rates of hydrogenation catalyzed by (I) were affected strongly by the

reaction media, CH₂Cl₂ being particularly inhibiting. Selectivities to 1-butene, however, remained generally high. Except in acetic acid, *trans/cis*-2-butene ratios greater than equilibrium were obtained with these ratios decreasing at increasing conversion levels. This and the lower than equilibrium *trans/cis* ratio obtained in the hydrogenation of 1-butene indicate that 2-butene, formed by hydroisomerization, is relatively high in *cis* content while the 2-butene formed in the hydrogenation of butadiene is primarily *trans* and most likely is formed directly. The closeness of approach to equilibrium *trans/cis* ratio in acetic acid coupled with the low selectivity to 1-butene indicates extensive isomerization of primary product in this acidic medium.

Not surprisingly, both conversion rates and selectivities were found to be a function of catalysts employed. While selectivities to 1-butene were somewhat lower with Pd(II) than with Pd(0) catalysts, this effect does not seem due to enhanced isomerization activities as indicated by the high *trans/cis*-2-butene ratios obtained in these cases at less than 100% conversion. Further, catalytic activities in these cases do not depend on solubility since (ϕ_2 PCH(CH₃)P ϕ_2)PdCl₂ is only partially soluble and has a higher activity than (I) while (ϕ CN)₂PdCl₂, which is completely soluble in toluene, is essentially inactive. The Pt complex corresponding to (I) is inactive,

TABLE 1
HYDROGENATION OF BUTADIENE—EFFECT OF SOLVENTS^a

Solvent	Conversion		Products (%)				Selectivity		
	(%)	(moles/ Pd/hr)	1-C ₄ H ₈	<i>t</i> -2-C ₄ H ₈	<i>c</i> -2-C ₄ H ₈	<i>n</i> -C ₄ H ₁₀	%C ₄ H ₈	%1-C ₄ H ₈ / ΣC ₄ H ₈	<i>t</i> -2/ <i>c</i> -2 ^b
ϕ CH ₃	100	0.25	63.1	27.6	6.2	3.1	96.9	65.3	4.3
Diglyme	46.9	0.1	60.4	34.2	5.3	0.2	99.8	60.5	6.5
ϕ CN	100	0.28	61.4	28.6	6.8	—	100	61.4	4.2
HOAc	100	0.20	2.9	68.4	23.0	5.7	94.3	3.1	3.0
CH ₂ Cl ₂ ^c	13.8	0.026	62.3	37.7	—	—	100	62.3	

^a 50 ml solution, 7.4×10^{-3} M in (ϕ_2 PCH₂P ϕ_2)₃Pd₂, butadiene/Pd = 34. No pretreatment, 1 atm argon, initial hydrogen pressure = 100 psig, room temperature.

^b Equilibrium = 3.4.

^c Butadiene/Pd = 23.

TABLE 2
 HYDROGENATION OF BUTADIENE—EFFECT OF CATALYSTS^a

Catalyst	Conversion			Products (%)				Selectivity		
	Conc ($M \times 10^3$)	(%)	(moles/ Pd/hr)	1-C ₄ H ₈	<i>t</i> -2-C ₄ H ₈	<i>c</i> -2-C ₄ H ₈	<i>n</i> -C ₄ H ₁₀	%C ₄ H ₈	%1-C ₄ H ₈ / ΣC ₄ H ₈	<i>t</i> -2/ <i>c</i> -2
(ϕ_2 PCH ₂ P ϕ_2) ₃ Pd ₂	7.4	100	0.25	63.1	27.6	6.2	3.1	96.9	65.3	4.3
(ϕ_2 PCH(CH ₃)P ϕ_2) ₃ Pd ₂	7.2	100	0.30	48.3	32.7	6.7	12.3	87.8	55.0	4.9
(ϕ_2 PCH ₂ P ϕ_2)PdCl ₂	17.8 ^b	29.1	0.042	49.6	46.8	3.8	—	100	49.6	12.3
(ϕ_2 PCH(CH ₃)P ϕ_2)PdCl ₂	17.4 ^b	88.2	0.37	41.8	31.6	5.5	20.8	79.2	52.9	5.8
(ϕ_2 PCH ₂ CH ₂ P ϕ_2)PdCl ₂	17.4 ^b	17.6	0.072	49.5	40.3	2.3	8.0	92.0	53.9	17.5
(ϕ CN) ₂ PdCl ₂	26	14.4	0.04	44.8	51.4	4.2	—	100	44.8	12.2
(ϕ_2 PCH ₂ P ϕ_2) ₃ Pt ₂	6.4 ^b	1.2	0.004							

^a 50 ml toluene solution saturated with butadiene (0.52 moles/liter), no pretreatment, 1 atm argon, initial hydrogen pressure = 100 psig, room temperature.

^b Incompletely soluble.

indicating once again the hazards of drawing analogies between metals in the same subgroups for purposes of making predictions in homogeneous catalysis.

As shown below, the effect of additives depends on the particular substrate being studied. In the case of butadiene, thiophene is a weak poison, retarding the rate of hydrogenation and also, apparently, of isomerization with increasing concentration. On the other hand, pyridine and benzonitrile actually increase observed conversion rates, but have practically no effect on selectivity. Isopropylamine has no effect on conversion rate, but may inhibit product isomerization somewhat. Triphenyl phosphine and particularly CO are strong poisons.

Results with pentadienes are shown in Table 4. Again, the influence of substrate structures on conversion rates is clearly indicated. Thus, rates are in the order *trans*-1,3-pentadiene > isoprene > *cis*-1,3-pentadiene > 1,4-pentadiene. The considerable difference in *trans/cis*-2-pentene product ratios obtained from *trans*- and *cis*-1,3-pentadienes indicates that isomerization of the *cis* compound to *trans* prior to hydrogenation is unlikely even though some isomerization is evident. In the case of *trans*-1,3-pentadiene, loss of selectivity to 1-pentene and a decreasing *trans/cis*-2-pentene ratio at 100% conversion indicates secondary conversion of 1-pentene to *n*-pentane and 2-pentene. In the case of *cis*-1,3-

 TABLE 3
 HYDROGENATION OF BUTADIENE—EFFECT OF ADDITIVES^a

Additive	Conc (moles/ Pd)	Conversion		Products (%)				Selectivity		
		(%)	(moles/ Pd/hr)	1-C ₄ H ₈	<i>t</i> -2-C ₄ H ₈	<i>c</i> -2-C ₄ H ₈	<i>n</i> -C ₄ H ₁₀	%C ₄ H ₈	%1-C ₄ H ₈ / ΣC ₄ H ₈	<i>t</i> -2/ <i>c</i> -2
—		100	0.25	63.1	27.6	6.2	3.1	96.9	65.3	4.3
Thiophene	1.5	100	0.21	62.5	31.5	6.0	—	100	62.5	5.2
Thiophene	50	100	0.10	61.4	32.2	4.7	1.7	98.3	62.4	6.9
Isopropylamine	48	100	0.25	65.8	28.1	5.6	0.5	99.5	66.1	5.0
Pyridine	49	100	0.49	64.9	28.3	5.9	0.9	9.1	65.4	4.8
Benzonitrile	61	100	0.49	60.7	29.3	6.2	3.8	96.2	63.0	4.7
ϕ_3 P	15	21	0.044	69.4	30.6	tr	—	100	69.4	
CO	8	0								

^a 50 ml toluene solution, 7.4×10^{-3} M in (ϕ_2 PCH₂P ϕ_2)₃Pd₂, saturated with butadiene (butadiene/Pd = 35). No pretreatment, 1 atm argon, initial hydrogen pressure = 100 psig, room temperature.

TABLE 4
 HYDROGENATION OF PENTADIENES^a

Substrate	Conversion		Products (%)						Selectivity	
	(%)	(moles/ Pd/hr)	<i>t</i> -1,3-C ₃ H ₈	1-C ₃ H ₁₀	<i>t</i> -2C ₅ H ₁₀	<i>c</i> -2C ₅ H ₁₀	<i>n</i> -C ₆ H ₁₂	%C ₅ H ₁₀	%1-C ₃ H ₁₀ / ΣC ₅ H ₁₀	<i>t</i> -2/ <i>c</i> -2
<i>t</i> -1,3-Pentadiene	55.4	0.80	—	32.5	60.8	6.7	—	100	32.5	9.1
	100	—	—	15.9	65.4	10.2	8.5	91.5	17.4	6.4
<i>c</i> -1,3-Pentadiene	54.8	0.44	2.0	31.4	36.5	30.1	—	98.0	32.0	1.2
	91.0	—	1.0	30.2	38.3	30.6	—	99.0	30.2	1.3
1,4-Pentadiene	44.8	0.16	—	84.4	7.2	1.8	6.7	93.3	90.6	4.0
Isoprene	62.8	0.50	3-Me-1-C ₄ H ₇	2-Me-1-C ₄ H ₇	2-Me-2C ₄ H ₇	2-Me-C ₄ H ₉	2-Me-1	98.9	50.9	55.2
	91.5	—	22.5	27.7	48.7	1.1	1.2	98.8	50.2	56.7

^a 50 ml toluene solution, 7.4×10^{-3} M in (ϕ_2 PCH₂P ϕ_2)₃Pd₂, 1 M in substrate; no pretreatment, 1 atm argon, initial hydrogen pressure = 100 psig, room temperature.

pentadiene, selectivity to 1-pentene remains uniformly high to very high conversions indicating, as shown in greater detail below, preferential complexing of diene as compared to monoolefin. The same conclusion can be drawn from the relatively low conversion rate of 1,4-pentadiene which reacts essentially as isolated monoolefin. In the case of isoprene, the somewhat greater selectivity to 2-methyl-1-butene can be rationalized on the basis of more facile hydrogenation of the less hindered double bond. Here as with butadiene, considerably less than equilibrium 2-methyl-2-butene formation indicates substantial 1,4 addition of hydrogen.

Hydrogenation of isoprene was studied in some detail. An examination of the effect of initial substrate/catalyst ratio on conversion rates and selectivities is summarized in Table 5. As shown, conversion rates decline with decreasing isoprene/catalyst ratio. Sensitivity to this parameter indicates the necessity of caution in making rate comparisons between different catalysts or substrates. However, the conclusion drawn from the effect of substrate structure on conversion rates, that substrate complexing is important in these hydrogenations and quite likely is part of the rate determining step, appears valid. The sharp decrease in selectivity to 1-pentenenes at low substrate/catalyst ratios may be due to isomerization of primary products in the

absence of competing diene. However, the unaltered high selectivity to pentenes and lack of change in the relative amounts of 2-methyl-1- and 3-methyl-1-butenes indicates that some enhancement of 1,4 addition under these circumstances is more likely.

One of the more interesting findings of this study is the effect of catalyst pretreatment on conversion rates and selectivities. Results for isoprene are shown in Table 6.

Based on the known chemistry of zero-valent Pt group metal complexes (5), a dissociation equilibrium in solution with formation of a coordinatively unsaturated species can be assumed. The increase in conversion rate without selectivity change when (I) was presoaked in toluene under argon for 24 hr prior to introduction of substrate and hydrogen conforms to this expectation. The relatively minor additional rate enhancement observed when the presoak period was extended to 72 hr, indicates that the dissociation equilibrium is essentially established during the first 24 hr. The lack of effect on both rate and selectivity of hydrogen presoak indicates that hydrides are not preformed.

A truly remarkable increase in conversion rate was obtained when (I) was exposed to oxygen prior to hydrogenation. The specific conversion rate increased by two orders of magnitude and further re-

TABLE 5
HYDROGENATION OF ISOPRENE—EFFECT OF SUBSTRATE/CATALYST^a

Initial isoprene/Pd	Conversion		Products (%)				Selectivity		
	(%)	(moles/ Pd/hr)	3-Me-1- C ₄ H ₇	2-Me-1- C ₄ H ₇	2-Me-2- C ₄ H ₇	2-Me- C ₅ H ₈	%C ₆ H ₁₀	%1-C ₆ H ₁₀ / ΣC ₆ H ₁₀	2-Me-1 2 + 3-Me-1
50 ^b	31.3	0.32	17.2	27.6	54.6	0.6	99.4	45.1	61.6
25 ^c	51.9	0.27	17.2	26.8	55.2	0.8	99.2	44.3	60.8
12.5 ^d	55.0	0.14	18.6	27.2	53.8	0.4	99.6	46.0	59.4
5 ^e	96.8	0.10	17.5	28.5	52.9	1.1	98.9	46.6	61.9
2.5 ^f	61.6	0.065	15.1	21.2	63.6	—	100	36.3	58.5
1.6 ^g	9.6	0.01	9.6	16.0	74.4	—	100	25.6	62.5

^a 50 ml toluene solution, no pretreatment, 1 atm argon, initial H₂ pressure = 100 psig, room temperature.

^b 0.2 M isoprene, (φ₂PCH₂Pφ₂)₃Pd₂: 2 × 10⁻³ M; ^c 4 × 10⁻³ M; ^d 8 × 10⁻³ M.

^e 0.02 M isoprene, (φ₂PCH₂Pφ₂)₃Pd₂: 2 × 10⁻³ M; ^f 4 × 10⁻³ M; ^g 6 × 10⁻³ M.

TABLE 6
HYDROGENATION OF ISOPRENE—EFFECT OF PRETREATMENT^a

Catalyst	Additive (moles/Pd)	Pretreatment (hr)	Reaction time (hr)	Conversion		Products (%)						Selectivity	
				(%)	(moles/Pd/hr)	3-Me-1- C ₄ H ₇	2-Me-1- C ₄ H ₇	2-Me-2- C ₄ H ₇	2-Me- C ₄ H ₈	%C ₆ H ₁₀	%1-C ₈ H ₁₀ / ΣC ₈ H ₁₀	2-Me-1 2 + 3-Me-1	
(φ ₂ PCH ₂ φ ₂) ₂ Pd ₂	—	—	48	31.3	0.32	17.2	27.6	54.6	0.6	99.4	45.1	61.6	
	—	Ar(24) ^b	24	42.8	0.89	17.8	28.5	53.0	0.5	99.5	46.4	61.6	
	—	Ar(72) ^b	24	44.3	0.92	18.3	27.8	54.0	—	100	46.1	60.2	
	—	H ₂ (2.5) ^c	24	14.7	0.30	19.7	27.9	52.4	—	100	47.6	58.5	
	—	O ₂ (+) ^d	1	100	50	4.2	23.0	58.9	13.9	86.1	31.6	84.5	
	—	O ₂ (1)	3	100	—	2.6	15.3	72.3	9.8	90.2	19.8	85.5	
	H ₂ O ^e	—	17	21.0	0.60	19.5	26.2	54.3	—	100	45.7	57.4	
	H ₂ O ^e	O ₂ (+) ^d	1	100	50	—	16.6	74.1	9.3	90.7	18.3	100	
	H ₂ O ^e	O ₂ (1)	1	100	—	0.4	12.4	72.2	15.0	85.0	15.0	96.9	
	(φ ₂ PCH ₂ CH ₂ φ ₂) ₂ Pd	—	—	48	100	3.58	21.2	26.2	50.5	2.1	97.9	48.5	55.4
—	—	24	100	4.15	19.8	26.7	52.6	0.9	99.1	46.8	57.0		
—	Ar(24) ^b	1	93.5	93.5	28.9	26.0	44.5	0.6	99.4	55.2	47.4		
—	O ₂ (+) ^d	1	22.8	22.8	13.5	20.6	65.9	—	100	34.1	60.4		
Thiophene (100)	—	—	—	—	—	—	—	—	—	—	—	—	
(φ ₂ PCH ₂ CH ₂ φ ₂) ₂ Pd	—	—	48	26.3	0.55	18.3	24.3	56.8	0.8	99.2	42.9	57.0	
—	—	48	22.1	0.46	18.1	23.6	58.4	—	100	41.7	56.5		

^a 50 ml toluene solution 0.2 M in isoprene, 2 × 10⁻³ M in catalyst; initial H₂ pressure = 100 psig, room temperature.

^b Catalyst solution stirred under argon before addition of isoprene.

^c Catalyst solution stirred under hydrogen before addition of isoprene.

^d Assembled in air.

^e Saturated with water.

action of product olefins also was enhanced considerably.* Longer oxygen pretreatment appeared to raise the isomerization activity of the catalyst relative to hydrogenation. On the basis of speculation that water formed by hydrogenation of residual oxygen might be responsible for this large increase in activity, an experiment was carried out in toluene saturated with water under strictly anaerobic conditions. In this case, some enhancement of conversion rate of the same order of magnitude as presoak under argon was found, but without any change in selectivity. Exposure of this system to oxygen again led to a two orders of magnitude increase in conversion rate with both hydrogenation and product isomerization increases.

Similar effects were noted with (II) which catalyzed the hydrogenation of isoprene with a higher specific rate than (I). It is of interest that in this instance, oxygen pretreatment led to increased selectivity to 3-methyl-1-butene, chiefly at the expense of 2-methyl-2-butene, either due to inhibition of isomerization or 1,4 addition. Thiophene again retarded the conversion rate. However, 2-methyl-2-butene formation was enhanced. In view of the retardation of isomerization by thiophene found with butadiene, this most likely indicates enhancement in the relative rate of 1,4 addition.

Interestingly, argon presoaking did not enhance the conversion rate in catalysis by (III) and, if anything, had a slight retarding effect.

Catalysis of isoprene hydrogenation by (I) also was examined at 45, 60, and 90°C. The greatest conversion rate under otherwise standard conditions was observed at 60°C. No notable effect on selectivity as a function of temperature was found. The effect of initial hydrogen partial pressure in the range studied (50–150 psig) was negligible.

* The effect appears to be irreversible; i.e., the oxygen pretreated catalyst continued to display enhanced activity in subsequent experiments without further exposure to oxygen.

Monocyclic Dienes

Catalysis of hydrogenation of cyclohexadienes by (I) (Table 7) depends strongly on conjugation. Thus, 1,3-cyclohexadiene was hydrogenated with good selectivity to cyclohexene at approximately the same rate as isoprene. Since cyclohexene was neither hydrogenated nor disproportionated under these conditions, the small amounts of benzene and cyclohexane formed must be the result of diene disproportionation. In contrast to observations with butadiene, isopropylamine had a decidedly inhibiting effect in this case.

Hydrogenation of 1,4-hexadiene in the presence of (I) was not observed under standard conditions except in the presence of acidic co-catalysts such as acetic or *p*-toluenesulfonic acids. Some isomerization to 1,3-cyclohexadiene, probably an intermediate, was noted in these cases. Addition of ethanol at elevated temperatures also led to slow hydrogenation and relatively more disproportionation, an effect also found in catalysis by $(\phi_2\text{PCH}_2\text{P}\phi_2)\text{PdCl}_2$ at room temperature. After oxygen pretreatment, (I) showed considerable activity in hydrogenation of 1,4-cyclohexadiene which was retarded only slightly by thiophene. At elevated temperatures, (II) catalyzed hydrogenation, isomerization, and disproportionation of the 1,4 diene but at low overall rate. Pretreatment of (II) with oxygen increased rates at room temperature to levels comparable to those found with (I) under the same conditions.

Under standard conditions, (I) did not catalyze the hydrogenation of 1,3-cyclooctadiene during 168 hr and gave only 0.5% conversion of 1,5-cyclooctadiene during the same time.

It is interesting that when ethylene was added to nonreactive substrates such as 1,4-cyclohexadiene or the cyclooctadienes, it was hydrogenated normally.

Norbornadiene

Despite the fact that norbornadiene is unconjugated and could be considered hindered, hydrogenation of this substrate proceeded at a relatively rapid rate (Table

TABLE 7
HYDROGENATION OF CYCLOHEXADIENES^a

Substrate (M)	Catalyst (M × 10 ⁻³)	Solvent	Additive (moles/Pd)	Pretreat- ment	Conversion		Products (%)		
					(%)	(moles/ Pd/hr)	1,3-Cyclohexadiene	Cyclohexene	Cyclohexane
1,3-cyclohexadiene, 1.04	(ϕ_2 PCH ₂ P ϕ_2) ₃ Pd ₃ , 7.4	ϕ CH ₃			100	0.58	95.5	1.3	3.2
	(ϕ_2 PCH ₂ P ϕ_2) ₃ Pd ₃ , 7.4	ϕ CH ₃	Isopropylamine (48)		11.1	0.065	99.5		0.5
	(ϕ_2 PCH ₂ P ϕ_2) ₃ Pd ₃ , 7.4	ϕ CH ₃			0				
1,4-cyclohexadiene, 1.06	(ϕ_2 PCH ₂ P ϕ_2) ₃ Pd ₃ , 7.4	HOAC			9.1	0.1	90.1	4.4	5.5
	(ϕ_2 PCH ₂ P ϕ_2) ₃ Pd ₃ , 7.4	ϕ CH ₃ ^b			1.4	0.007	71.5		28.5
	(ϕ_2 PCH ₂ P ϕ_2) ₃ Pd ₃ , 7.4	EtOH			80.2	44	93.4	4.9	1.7
0.22	(ϕ_2 PCH ₂ P ϕ_2) ₃ Pd ₃ , 2	ϕ CH ₃		O ₂ (+) ^c	64.1	35	93.0	4.8	2.3
	(ϕ_2 PCH ₂ CH ₂ P ϕ_2) ₃ Pd, 11	ϕ CH ₃ ^d	Thiophene (50)		11.1	0.073	37.8	7.2	13.5
0.22	(ϕ_2 PCH ₂ CH ₂ P ϕ_2) ₃ Pd, 2	ϕ CH ₃ ^d		O ₂ (+) ^c	73	62	95.3	3.0	1.8
1.06	(ϕ_2 PCH ₂ P ϕ_2) ₃ PdCl ₂ ^e , 17.8	ϕ CH ₃ ^f			22.2	0.11	71.5	7.2	21.3

^a 50 ml solution, initial H₂ pressure = 1.00 psig, room temperature unless specified.

^b 82°C.

^c Assembled in air.

^d 150°C.

^e Incompletely soluble.

^f 65°C.

TABLE 8
 HYDROGENATION OF NORBORNADIENE^a

Catalyst ($M \times 10^{-3}$)	Initial norbornadiene/ Pd	Pretreat- ment (hr)	Reaction time (hr)	Conversion		Products (%)	
				(%)	(moles/ Pd/hr)	Norbornene	Norbornane
$(\phi_2\text{PCH}_2\text{P}\phi_2)_3\text{Pd}_2$, 7.4 2.0	66		48	94.3	1.3	67.0	31.4
	65		24	92.2	2.5	90.5	1.2
	65	Ar(24)	24	99.2	2.7	81.0	11.1
$(\phi_2\text{PCH}_2\text{CH}_2\text{P}\phi_2)_2\text{Pd}$, 11.0	89		264	98.6	0.33	25.6	73.2
$(\phi_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}\phi_2)_2\text{Pd}$, 10.8 ^b	91		240	57.7	0.22	70.0	21.2
$(\phi_3\text{P})_4\text{Pd}$, 8.6	114		288	81.8	0.32	70.8	27.9
	114	O ₂ (0.5)	20	98.1	5.6	33.2	60.1

^a 50 ml toluene solution, initial H₂ pressure = 100 psig, room temperature.

^b Incompletely soluble.

8). In this case, products consisted of norbornene and norbornane plus small amounts of a material which was not identified. Catalysis by (I) resulted in high selectivity to norbornene to conversion levels in excess of 90%. The specific conversion rate of norbornene was sufficiently high so that at these levels, the monoolefin competed effectively.

At the same norbornadiene/catalyst ratio, but a lower than standard catalyst concentration, the specific conversion rate increased; an observation generally considered as evidence of catalyst dissociation (1b). This effect was of the same magnitude as found in presoaking under argon. In contrast to observations with isoprene, the conversion rate declined as the number of methylene groups between phosphorus atoms in the diphosphine ligands increased. In the presence of tetrakis(triphenylphosphine) palladium (0), the observed conversion rate was similar to that obtained with the mononuclear chelated phosphine complexes (II) and (III). Again a rate increase was found after pretreatment with oxygen but the effect was only of one rather than the usual two orders of magnitude.

Unconjugated Dienes

Results with 1,4-pentadiene already have been discussed. Conversion rates of longer

chain α - ω -dienes (Table 9) were ca. 0.1 of those observed for the 1,4 diene under anaerobic conditions with considerable isomerization in evidence. The effect of oxygen pretreatment on conversion rates was particularly pronounced with both hydrogenation and isomerization enhancement evident.

Trienes

Hydrogenation of 1,3,5-heptatriene to a mixture of 1-heptene (40.2%), *cis* (3.9%) and *trans*-2-heptene (39.4%), and five unidentified products was catalyzed by (I) under standard conditions. The rate was similar to that of *trans*-1,3-pentadiene. Cycloheptatriene was hydrogenated at about 20% of this rate.

Miscellaneous Reductions

The ability of (I) to catalyze hydrogenation of several substrates other than olefins was explored briefly. Propionaldehyde in toluene at 80°C was converted to ethane and ethylene. Decarbonylation also was found in the absence of hydrogen, presumably by oxidative addition of the aldehyde to (I) to form an acyl, a reaction found to be reversible in the case of corresponding methyl palladium complexes. Similarly, conversion of vinyl chloride to a mixture of ethyl chloride, ethylene, and ethane is consistent with hydrogenation to

TABLE 9
 HYDROGENATION OF UNCONJUGATED DIENES^a

Substrate (<i>M</i>)	Initial substrate/Pd	Pretreat- ment	Conversion		Products (%)	%C _n H _{2n}	Selectivity %1-C _n H _{2n} / ΣC _n H _{2n}
			(%)	(moles/ Pd/hr)			
1,5-Hexadiene, 0.86	58		3.9	0.014	1-Hexene (79.5) <i>t</i> -2-Hexene (7.7) <i>c</i> -2-Hexene (2.6) 3-Hexene (5.1) <i>n</i> -Hexane (5.1)	94.9	83.8
	0.2	O ₂ (+) ^b	100	100	1-Hexene (36.7) <i>t</i> -2-Hexene (22.8) <i>c</i> -2-Hexene (12.7) 3-Hexane (3.2) <i>n</i> -Hexane (24.6)	75.4	48.6
1,9-Decadiene, 0.54	36		5.2	0.012	1-Decene (44.4) 2-Decene (19.2) <i>n</i> -Decane — Unidentified (36.5)	100	44.4
	0.2	O ₂ (+) ^b	99.2	98	1-Decene (12.7) 2-Decene (35.6) <i>n</i> -Decane (43.9) Unidentified (7.8)	56.1	22.6

^a 50 ml toluene solution, (φ₂PCH₂Pφ₂)₃Pd₂ catalyst, initial H₂ pressure = 100 psig, room temperature.

^b Assembled in air.

ethyl chloride, oxidative addition to form an ethyl palladium complex and reductive elimination of ethylene or hydrogenolysis to ethane. This path is supported by reaction of (I) with ethyl chloride to yield ethane and ethylene.

Under similar conditions, 3-chloro-2-methyl-1-propene was converted to 2-methyl propene and propane as well as π-methylallyl palladium chloride dimer.

Neither cyclopropane nor naphthalene were hydrogenated.

DISCUSSION

It is evident from the preceding results that observed rates and products in hydrogenations catalyzed by palladium complexes depend on ligands, the oxidation state of the central metal atom, substrates, solvents and other constituents of reaction mixtures. Of these, the nature of substrates appears to be most important and, in fact, determines the relative effect of other vari-

ables. Therefore, it can be assumed that complexing of substrates is an important step in the reaction sequence. However, whether π, σ, or, in appropriate cases, π-allyl complexes are involved cannot be decided from the data presented so far.

Another likely event is dissociation of zerovalent palladium complexes in solution prior to complexing with substrates. The positions of these pre-rate determining equilibria and the rates at which they are achieved is expected to be a function of solvents and of other molecules present. Thus, results with various additives can be interpreted as due to competition for complexing sites on the central metal atom of the catalyst between ligands, solvent, additives and substrate (Eqs. 1-3). Rate acceleration by additives can be viewed as formation of weak complexes in a step analogous to solvation and, as far as substrates are concerned, creation of a coordinatively unsaturated site. Formation of too stable a complex in this step leads to poisoning.



where L = ligand, S = solvent, A = additive, ol = substrate.

Another possibility (favored by a referee) is that the observed effects might be due to ligand replacement by additives leading to complexes with different electronic and, therefore, catalytic properties. This explanation seems less satisfactory for the following reasons:

1. Pyridine and benzonitrile, ligands with very different electronic properties, have the same effect on the rate of conversion of butadiene catalyzed by (I) and have no effect on selectivity.

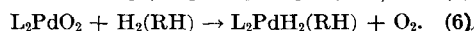
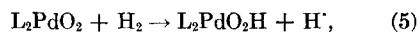
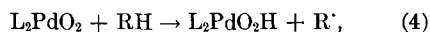
2. The effect of additives is substrate dependent. For example, isopropylamine has essentially no effect in the hydrogenation of butadiene but is strongly inhibiting in the hydrogenation of 1,3-cyclohexadiene.

3. The level of inhibition in methylene chloride, a noncomplexing solvent, is similar to that found on addition of $\phi_3\text{P}$, an excellent ligand. Moreover, a complex containing this ligand, $(\phi_3\text{P})_4\text{Pd}$, was found to be a moderately active catalyst.

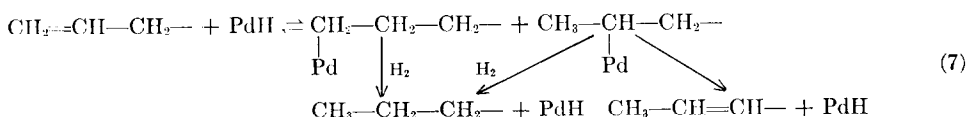
Normal hydrogenation of ethylene in the presence of nonreactive substrates, such as 1,4-cyclohexadiene and cyclooctadienes indicates lack of complex formation for these substrates rather than formation of complexes which are too stable to react further.

Catalyst pretreatment also very likely affects pre-rate determining steps. Thus, presoaking of catalysts in inert atmosphere allows time for establishment of ligand dissociation equilibria. The effect of oxygen, in some cases, has been explained as promoting such dissociation by converting dissociating phosphine ligands to phosphine oxides (6). However, in the present case, it seems that the effect is much larger than can be accounted for on this basis as the magnitude of rate effects due to presoaking, donor additives and readdition of phosphines is not as great as that found on exposure to oxygen. More-

over, while ir spectra of oxygen pretreated catalysts indicate the presence of phosphine oxides and complexed oxygen, complexes containing chelating diphosphines do not catalyze the autoxidation of excess phosphines. Therefore, while oxygen transfer to ligands does take place, the resulting complexes are not extensively dissociated or exchanged. In the case of $(\phi_3\text{P})_4\text{Pd}$ which is known to dissociate readily in solution (5) and to catalyze the autoxidation of phosphines (7), the effect of oxygen pretreatment on hydrogenations catalyzed by this material is not quite as large. A tentative conclusion, which also has been reached for catalysis by rhodium (8), is that oxygen pretreatment leads to formation of new species which are more active catalysts. Possible alternatives to the effect being due merely to a change of ligands are substrate activation via hydrogen abstraction by complexed oxygen (7a, 9) (Eq. 4) hydrogen activation by dissociation via hydroperoxide formation (10) (Eq. 5) or facilitation of either hydrogen or substrate complex formation by oxygen displacement (11) (Eq. 6).



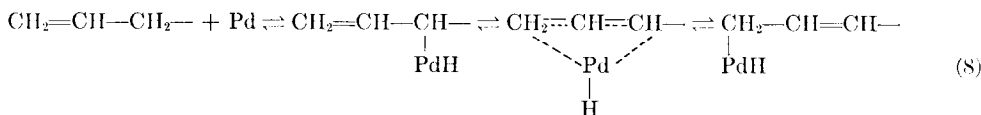
In view of these possibilities, it is unclear from the data presented whether hydrogen is complexed dissociatively or indeed, whether it is complexed at all. However, on the basis of many other studies of homogeneously catalyzed hydrogenations, it can be assumed tentatively that the actual catalysts are palladium hydrido species. Such species may be formed from gas phase hydrogen, from solvents or substrates, or possibly by interaction of palladium with ligand phenyl groups (12). The simplest mechanistic scheme for reaction of monoolefins involves 1,2 addition of Pd-H across the double bond. Reelimination in the direction opposite to addition leads to isomerization, and hydrogenolysis of the Pd-C bond yields hydrogenated products (Eq. 7).



This scheme is compatible with the finding that $\text{CH}_3\text{Pd}(\phi_2\text{PCH}_2\text{P}\phi_2)\text{X}$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}$), formed by oxidative additions of methyl halides to (I), reacts with hydrogen to yield methane while addition of ethyl halides results in formation of ethylene.

version rates is expected to be complex and likely varies considerably as a function of substrate.

Lack of disproportionation of cyclohexene and the relatively minor effect of thiophene on rate is evidence that catalysis in these cases is homogeneous and



Isomerization via π -allyl formation (Eq. 8) is also possible, and this route may be favored at elevated temperatures or when reactions are catalyzed by Pd(II) species.

In the case of conjugated dienes, hydrogenation may proceed via 1,2 PdH addition coupled with π -allyl formation or by a combination of 1,2 and 1,4 Pd-H additions (Eq. 9).

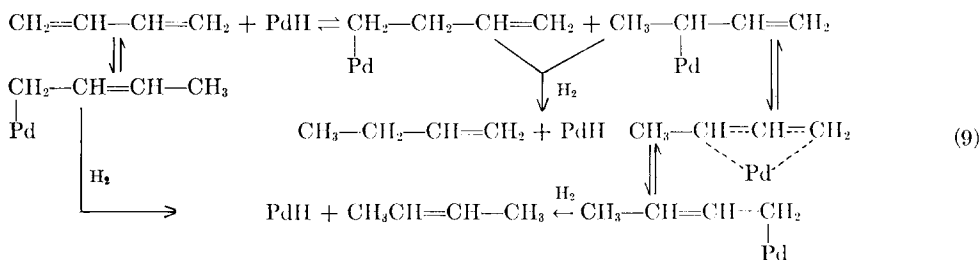
is not due to metallic palladium which may have formed but gone unnoticed.

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Of these possibilities, direct 1,4 addition appears least likely as the 2-butene initially produced from butadiene is mostly *trans* rather than *cis* which would be expected to be favored by this route (13).

The apparent rate maximum as a function of temperature found in catalysis of isoprene hydrogenation by (I) is consistent with the expectation that while catalyst dissociation and hydride addition should be speeded up, olefin complex formation should be suppressed and hydride elimination favored at elevated temperatures. Thus the precise effect of temperature on overall con-

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