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Selective Hydrogenation of Acetylenes to Olefins Catalyzed by Polymer-Bound Palladium(II) Complexes

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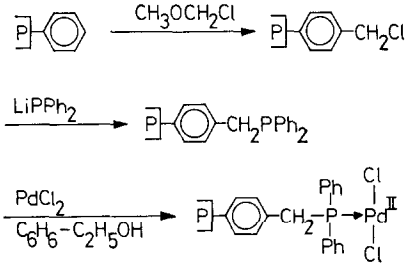
Semihydrogenations of 15 acetylenes to olefins catalyzed by polymer-bound palladium(II) complexes have been studied synthetically and mechanistically, and the hydrogenation of phenylacetylene has been studied kinetically. In the hydrogenation of isolated acetylenes, the catalyst generated corresponding olefins in high selectivities (above 92%). In the case of conjugated acetylenes, the catalyst generated corresponding conjugated olefins in relatively low selectivities (71–85%), whereas phenylacetylene was hydrogenated to styrene in a high selectivity (93%). A high activity of the catalyst was observed in oxygen-containing solvents such as dimethylformamide, tetrahydrofuran, dimethyl sulfoxide, and ethanol. The catalytic activity is affected more strongly by the π-acidity of acetylenes than their steric factor. The hydrogenation rate of phenylacetylene is expressed by the form: $R = k_2[H_2][A]$, where $[H_2]$ and $[A]$ are hydrogen and the catalyst concentrations, respectively. A mechanism for the hydrogenation is proposed on the basis of kinetic studies. Finally, it is summarily discussed what factors control the activity and the selectivity of the polymer catalyst for the hydrogenation of carbon–carbon double and triple bonds. This polymer-bound palladium complex was shown to be comparable in selectivity to cationic rhodium and the Lindlar catalysts.

INTRODUCTION

Organometallic complexes of palladium catalyze a large number of organic reactions under mild conditions and their chemistry is well explored and understood (*1*). However, there is relatively little study of hydrogenation catalyzed by the palladium complexes and their catalysis is not well understood (*2*). Divalent palladium complexes are in general labile to be reduced to palladium(0) species under hydrogenation conditions, consequently in many cases it is not very clear whether an active species in the hydrogenation is di- or zerovalent.

We have previously reported that a polymer-bound palladium(II) complex prepared by the reaction of palladium chloride with poly-4-diphenylphosphinomethylstyrene (Scheme 1) is an efficient and



SCHEME 1

recoverable catalyst for the heterogeneous hydrogenation of various olefins under mild conditions (*3*). The polymer–palladium complex especially shows a high activity and selectivity for the hydrogenation of

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conjugated dienes to monoenes. Furthermore, the complex is never reduced to a zerovalent species under the reaction conditions as shown in the study of a recovered polymer complex after hydrogenation by X-ray photoelectron spectroscopy (*3*). Hence the polymer–palladium complex is an appropriate catalyst system for studying the catalysis of palladium(II) complexes for the hydrogenation of unsaturated hydrocarbons.

In this work, we further examined the hydrogenation of acetylenes in order to review the catalysis of the polymer–palladium complex for the hydrogenation of unsaturated hydrocarbons.

It is well known that semihydrogenation of triple bonds over heterogeneous metal catalysts is the most convenient and widely employed route to *cis*-disubstituted olefins. Palladium (the Lindlar catalysts) is best for the above purpose among various metals (*4*). On the other hand, surprisingly very little work has appeared on the selective hydrogenation of acetylenes catalyzed by organotransition metal complexes (*2*, *5*). Schrock and Osborn have recently reported that cationic rhodium complexes selectively catalyze the hydrogenation of acetylenes to olefins and are superior to the Lindlar catalysts (*6*).

We have systematically carried out the hydrogenation of 15 acetylenes with the polymer-bound palladium(II) complexes. It has been found that the polymer complex is an efficient catalyst for the hydrogenation of acetylene to olefins and is comparable to the cationic rhodium and the Lindlar catalysts in selectivity. Furthermore, it has been summarily discussed what factors control the activity and selectivity for the hydrogenation of carbon–carbon unsaturated bonds.

EXPERIMENTAL

General

Gas–liquid chromatography measurements were made using a Yanaco G 180 chromatograph and a stationary phase of polyethylene glycol 6000 or *bis*[2-(2-methoxyethoxy)ethyl]ether. ^{13}C NMR spectra were obtained using a JNM FX-100 Fourier transform spectrometer. The hydrogenation apparatus and hydrogenation procedure were described previously (*3*).

Materials

1-Phenyl-1-propyne (*7*), 1-phenyl-1-butyne (*7*), 1,5-hexadiyne (*8*), 1-hexen-5-yne (*8*), 2-methyl-1-buten-3-yne (*9*), 1-cyclohexyl-1-butyne (*7*), and cyclohexenylacetylene (*10*) were synthesized by the reported procedures or their modifications. Other acetylenes were commercially available. All were dried and purified before use. All solvents were dried and distilled under a nitrogen atmosphere. The polymer-bound palladium(II) complex (PC-5) was prepared by a method similar to that in our previous paper (*3*), where a phosphinated resin P-2 (no cross-linking, 2000–3000 molecular weight, 0.74-CH_2PPh_2 groups/benzene ring) in our previous paper (*3*) was used as a polymer ligand. Analysis showed C, 55.68; H, 4.34; Cl, 10.40; P, 6.53% for PC-5. A polymer-bound palladium complex PC-4 (P/Pd = 1.0, where Pd content was calculated by difference) in our previous paper (*3*) was used in Runs 7, 8, and 18, and PC-5 (P/Pd = 0.97, where Pd content was calculated by difference) in other and kinetic runs.

RESULTS AND DISCUSSION

Catalytic Hydrogenation of Acetylenes

The polymer-bound palladium(II) complex showed an effective catalytic activity for the hydrogenation of acetylenes at ambient temperature and pressure of 1 atm or below. Table 1 summarizes the results of hydrogenation of 15 acetylenes. The reactions were discontinued after the absorption of about 1 mole of hydrogen except for the cases in which the hydrogenation rates were extremely low. In most cases the rate

TABLE 1

Hydrogenation of Acetylenes[a]

Run	Acetylene	Reaction time (min)	Conversion (%)	Products (% yield)			Paraffin	Selectivity[b] (%)
				Olefins				
1	1-Heptyne	57	98	1-(90)	*cis*-2-(2)	*trans*-2-(1)	5	95
2	2-Heptyne	22	99	*cis*-2-(90)	*trans*-2-(4)	*cis*-3-(3)	2	98
3	Phenylacetylene	36	100		(93)		7	93
4	1-Phenyl-1-propyne	106	89	*cis*-(59)	*trans*-(4)		26	71
5	1-Phenyl-1-propyne[c]	100	89	*cis*-(64)	*trans*-(3)		22	75
6	1-Phenyl-1-butyne	81	93	*cis*-(62)	*trans*-(5)		26	67
7	1-Cyclohexyl-1-butyne	32	100	*cis*-(94)	*trans*-(5)		1	99
8	Cyclohexenylacetylene	27	100	Vinyl-cyclohexene (81)	Ethyl-cyclohexene (13)	Vinyl-cyclohexane (6)	0	81
9	2-Methyl-1-buten-3-yne	251	100	Isoprene (85)	Isopentene (15)		0	85
10	1,5-Hexadiyne	205	44	1-ene-5-yne (18)	1,5-diene (13)	1-ene (13)	0	41
11	1-Hexen-5-yne	400	90	1,5-diene (87)	1-ene (3)		0	97
12	Propargyl chloride	600	47		(47)		0	100
13	Propargyl alcohol	240	29		(29)		0	100
14	Propargyl alcohol[d]	247	93		(92)		1	99
15	2-Methyl-3-butyn-2-ol	35	97		(92)		5	95
16	3-Methyl-1-pentyn-3-ol	33	94		(91)		3	97
17	Acetylenedicarboxylic acid dimethyl ester	81	100	*cis*-(90)	*trans*-(2)		8	92

[a] Using catalyst, 7.00 mmol/liter; acetylene, 0.35 mol/liter; 1 atm of hydrogen in benzene-ethanol (1:1), [13-(volume of substrate)] ml at 25.0°C.

[b] Selectivity = (semihydrogenated products of the triple bond/products) × 100.

[c] Benzene was used as a solvent.

[d] Dimethylformamide was used as a solvent.

of hydrogen uptake was nearly constant until the reaction neared completion. In all the cases, only the hydrogenation products and their double bond isomers were obtained. Hydrogenolysis and oligomerization products were not observed.

With regard to activity, several observations can be made on the basis of the data in Table 1: (i) 2-heptyne is hydrogenated at a greater rate than 1-heptyne as 1-phenyl-1-butyne is hydrogenated faster than 1-phenyl-1-propyne; (ii) propargyl chloride and propargyl alcohol containing an electron-attracting substituent are hydrogenated very slowly; (iii) whereas 3-methyl-1-butyn-3-ol and 3-methyl-1-pentyn-3-ol, which contain such an electron-releasing substituent as methyl and ethyl groups on the α-carbon in propargyl alcohol, are hydrogenated at an extremely fast rate compared with propargyl alcohol itself; (iv) 1,5-hexadiyne and 1-hexen-5-yne are hydrogenated very slowly.

From the above results, it is clear that the activity of the palladium complex for acetylene hydrogenation depends more strongly on the electron density of triple bonds than on the steric hindrance about the bonds. The triple bonds are generally thought to have a strong π acidity and its strength is directly affected by the electron density. The bonding in acetylene complexes of the side-on type is usually viewed as involving a weak π-donor bond from the triple bond to the metal and a strong back-bond from filled metal orbitals to the π^* orbitals of the acetylene (*11*). The π^* orbitals are lowered by electron-attracting substituents, being able to accept electrons more easily from the filled metal orbitals (*12*). Therefore, the more the electron density in the triple bond decreases, that is to say, its π acidity becomes stronger, the more strongly the triple bond coordinates to the metal. Also, it is generally accepted that acetylenes containing electron-attract-

ing functional groups form the most stable complexes with noble metals (*12*). For example, the π acidity of 1-heptyne is thought to be stronger than that of 2-heptyne. It is consequently predicted that 1-heptyne coordinates much more strongly to the polymer complex than 2-heptyne. This is supported by the fact that although the rate of hydrogenation of 1-heptyne is smaller than that 2-heptyne, 1-heptyne was exclusively hydrogenated in the initial stage of competitive hydrogenation of 1- and 2-heptynes (Fig. 1). This behavior can be explained by the term "molecular queueing" which Crombie and Jenkins proposed in the competitive hydrogenation of but-3-ynoic acid and buta-2,3-dienoic acid over Pd-$BaSO_4$ (*13*). These results also suggested that the triple bonds coordinate too tightly to the palladium for hydrogenation, and consequently inhibit the catalysis to some degree.

In most cases the polymer catalyst remained dark green during the reaction, however 1,5-hexadiyne caused a dark green to brown color change to deactivate the catalyst completely after 200 min. This observation suggests that the diyne complexed the palladium as a bidentate ligand to destroy the active species.

This behavior of acetylenes resembles that of carbon monoxide which is also a strong π acid.

Next, with regard to selectivity for

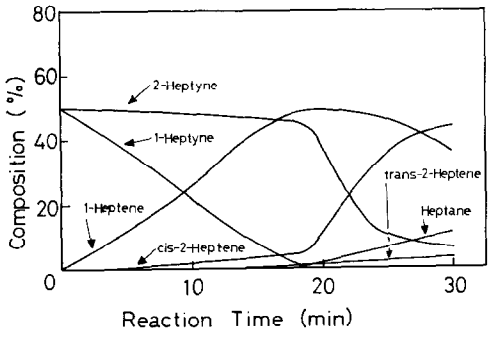


FIG. 1. Competitive hydrogenation of 1- and 2-heptyne (Run 18).

TABLE 2

Effect of Solvent on Phenylacetylene Hydrogenation[a]

Run	Solvent	Initial rate (ml/min)	
		Phenylacetylene	Styrene[b]
19	Dimethylformamide	2.83	8.04
20	Tetrahydrofuran	2.04	6.13
21	Dimethyl sulfoxide	1.54	0.09
22	Ethanol	1.46	7.74
23	Acetone	0.99	6.10
24	Nitromethane	0.92	0.10
25	Cyclohexane	0.87	0.22
26	Benzene	0.87	2.84
27	Ethyl acetate	0.55	2.08
28	Acetic acid	0.39	1.45
29	Methylene chloride	0.15	1.68
30	Chloroform	0.12	2.45

[a] Using catalyst, 5.00 mmol/liter; phenylacetylene, 0.70 mol/liter; 1 atm of hydrogen in 12 ml of solvent at 25.0°C.

[b] Quoted from our previous paper (Ref. (*3*)).

acetylene hydrogenation, several observations can be made except for the case of 1,5-hexadiyne in which the significant modification and the deactivation of the catalyst were observed: (i) the isolated triple bonds were hydrogenated to double bonds very selectively; (ii) except for phenylacetylene, the triple bonds in a conjugated system were hydrogenated to double bonds in a relatively low selectivity; (iii) internal acetylenes were selectively hydrogenated to *cis*-olefins.

It is very significant that the replacement of an acetylenic hydrogen in phenylacetylene with a methyl or an ethyl group caused a lowering of the olefin selectivity. These selectivities are discussed later in some detail in connection with a reaction mechanism.

The selectivities observed here are comparable to those of the best catalyst systems for the selective hydrogenation of acetylenes to olefins reported earlier, homogeneous cationic rhodium and the Lindlar catalysts. For example, the former reduces

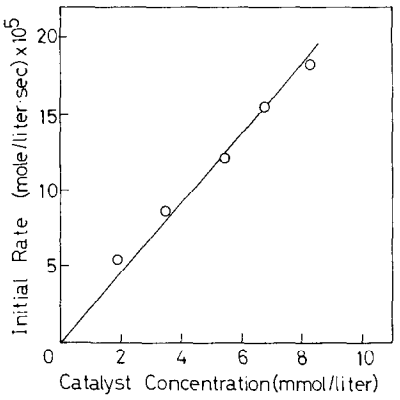


FIG. 2. Dependence of hydrogenation rate of phenylacetylene on catalyst concentration with 0.35 *M* phenylacetylene at 25.0°C.

2-heptyne to 2-hexene with 92 to 99% selectivities (*6*), and the latter rarely shows the selectivity above 90% (*4*). Furthermore, this polymer catalyst is superior to the homogeneous rhodium catalysts in handling, because of its heterogeneity.

Table 2 lists the initial rates of hydrogenation of phenylacetylene in a variety of solvents with those of styrene in our previous paper (*3*) in order to reveal solvent effects on both hydrogenations. The activity did not vary much with changes of solvent, compared with the case of styrene. The relatively high activity was observed in such oxygen-containing solvents as dimethylformamide, tetrahydrofuran, and ethanol, similar to the case of styrene. It is remarkable that moderate activity was observed in dimethyl sulfoxide, nitromethane, and cyclohexane in which the hydrogenation of styrene was extremely slow presumably because of either very strong or very weak coordination of solvent to the palladium complex. These facts show that the coordination strength of phenylacetylene to the metal is larger than that of dimethyl sulfoxide or nitromethane. It also seems that phenylacetylene itself behaves as a solvent toward a reaction intermediate. That is to say, the palladium species tend to be more strongly solvated with phenylacetylene itself than some solvents, because phenylacetylene coordinates much more strongly to the metal than the solvents.

Quantitative Measurements of Hydrogenation of Phenylacetylene

The overall rates of hydrogenation of phenylacetylene have been measured and the dependence on catalyst concentration, hydrogen pressure, substrate concentration, and temperature has been investigated. Benzene–ethanol (1:1) was used as a solvent. The hydrogenation product was only styrene under the quantitative measurement conditions. The details of the measurements are the same as those reported earlier (*3*).

A plot of the rate of hydrogen consumption against catalyst concentration is shown in Fig. 2. The rate increases linearly with increasing catalyst concentration. This indicates that a mass-transfer effect could be neglected in the reaction conditions. Furthermore, the rate seems to be hardly controlled by diffusion because the polymer is not crosslinked and is not beaded. A plot of the rate against hydrogen pressure is shown in Fig. 3. The rate increases linearly with increasing hydrogen pressure. The lack of dependence of the rate on phenylacetylene concentration can be seen from

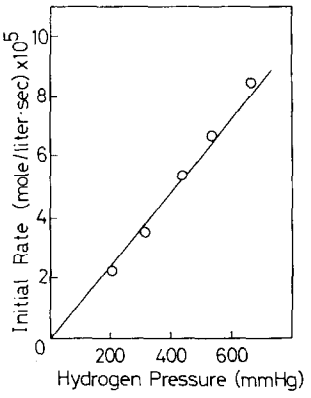


FIG. 3. Dependence of hydrogenation rate of phenylacetylene on hydrogen pressure with 5.15 m*M* catalyst and 0.35 *M* phenylacetylene at 25.0°C.

Fig. 4. The rate does not depend on the substrate concentration and is constant. Rates were measured at three temperatures 0.0, 12.5, and 25.0°C for various concentrations of phenylacetylene. The rates were constant at each temperature. The constant values and rate constants derived from them are given in Table 3. From an Arrhenius plot, which is linear, a value of the activation energy E_a was obtained and the values of some kinetic parameters are given in Table 4.

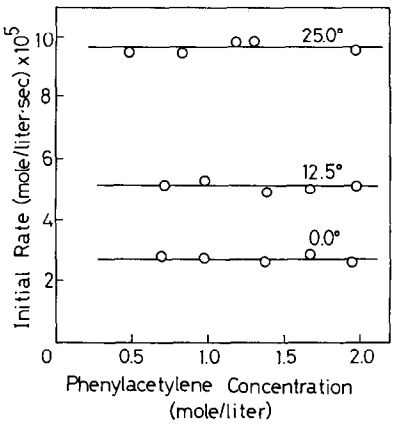


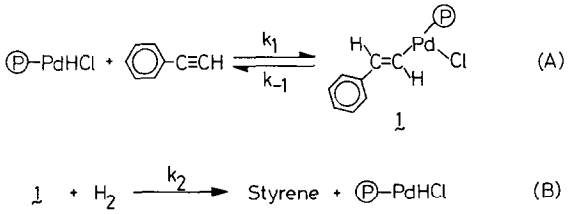
FIG. 4. Dependence of hydrogenation rate of phenylacetylene on substrate concentration with 5.15 m*M* catalyst at 25.0°C.

Discussion of Kinetic Results

A palladium hydride species, which was formed by the pretreatment of the polymer palladium complex with hydrogen in the presence of a solvent, seems to be an active species in the hydrogenation of phenylacetylene, as well as in the case of olefin hydrogenations (*3*).

Ⓟ-$PdCl_2$ + H_2 → Ⓟ-PdHCl + HCl.

By analogy with the reaction mechanism of olefin hydrogenations, we can present a formal scheme containing Pd–H species for the hydrogenation of phenylacetylene (Scheme 2). The triple bond adds to the



SCHEME 2

palladium hydride to form a σ-styryl complex, followed by the attack of hydrogen to give styrene and the palladium hydride. The regio-manner of addition of Pd–H bond to the triple bond is discussed later in detail. Using the principles of steady state, the rate R is

$$R = -\frac{d[S]}{dt} = \frac{k_1 k_2 [S][H_2][A]}{k_{-1} + k_1[S] + k_2[H_2]}, \quad (1)$$

where k_1, k_{-1}, and k_2 are the rate constants for the reaction equations A and B (Scheme 1), $[H_2]$ is the concentration of hydrogen in the solution, and $[S]$ and $[A]$ are the substrate and the catalyst concentrations, respectively. If $k_1[S] \gg k_{-1} + k_2[H_2]$, Eq. (1) reduces to the simple form

$$R = -\frac{d[S]}{dt} = k_2[H_2][A]. \quad (2)$$

Here, the above assumption is thought to be reasonable from the facts that the coordination strength of phenylacetylene to the palladium is very large and that the styryl complex is predicted to be relatively stable toward the reverse reaction, β

TABLE 3

Data Derived from Plot of Rate against Phenylacetylene Concentration for Different Values of Reaction Temperature

Temperature (°C)	Constant value (mol liter^{-1} sec^{-1}) $\times 10^5$	Rate constant k_2 (liter mol^{-1} sec^{-1})
0.0	2.75	1.96
12.5	5.15	3.47
25.0	9.70	6.06

elimination of Pd–H. The rate equation reasonably accommodates the experimental data for phenylacetylene hydrogenation.

The activation enthalpy, the activation entropy, and the frequency factor at 25°C for the hydrogenation (Table 4) resemble those for hydrogenations of styrene and 1,3-cyclooctadiene (*3*), suggesting that the hydrogenation of phenylacetylene proceeds through a pathway similar to those of the olefins. The rate constant is smaller than those for styrene, 1,3-cyclooctadiene, and cyclohexene. This seems to result from the solventlike poisoning effect of phenylacetylene itself based on its unusual coordination strength mentioned before. The high isotope effect ($k_2^H/k_2^D = 2.5$) suggests that synchronous formation of Pd–H and C–H bonds does not easily take place in the second reaction stage B in Scheme 2.

The Origin of Selectivities

The reaction mechanism in Scheme 2 is also applicable to the hydrogenation of internal acetylenes. The double-bond configuration of produced olefins is determined by the manner of addition of the palladium hydride to a triple bond to give a σ-vinyl complex at the first reaction stage A; *cis*-addition of the palladium hydride to the triple bond leads to a *cis*-olefin and *trans*-addition to a *trans*-olefin because the *cis–trans* isomerization of the σ-vinyl complex does not occur under reaction conditions used here (*15*) and because the following reaction (the second stage) proceeds with retention of the geometry (*16*). The polymer palladium complex selectively generated *cis*-olefins (Runs 2, 4–7, 17). Therefore, the addition of the palladium hydride to the triple bonds seems to be exclusively a *cis* manner.

TABLE 4

Kinetic Data (at 25°C) for the Hydrogenation of Phenylacetylene

$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	k_2^H/k_2^D	Frequency factor A
7.0	−32	2.5	2.3×10^6

Semihydrogenations of isolated triple bonds to double bonds were accomplished very selectively (Runs 1, 2, 7, 12–17). It is believed that the high selectivity is due to the selective coordination of the triple bonds to the complex and this occurs because the coordination strength of triple bonds is much greater than that of double bonds as mentioned in an early section.

On the other hand, the hydrogenation of triple bonds in a conjugated system did not give such successful results (Runs 4–6, 8, 9). The same trend for triple bonds versus the conjugated system is also observed for the Lindlar catalysts (*4*). However, reasons for this phenomenon are not very clear. Here,

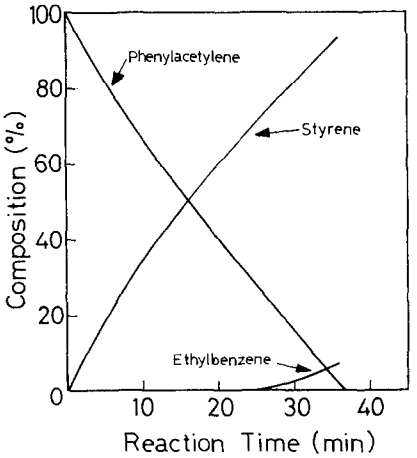


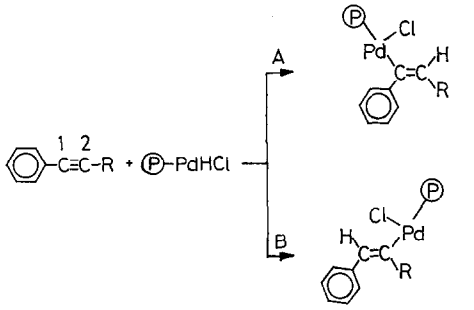
FIG. 5. Hydrogenation of phenylacetylene (Run 3).

it should be noteworthy that phenylacetylene with the conjugation of a triple bond with a phenyl group was exceptional; styrene was formed in a high selectivity (Run 3). These results seem to give a clue to the origin of the selectivity for the hydrogenation of triple bonds in a conjugated system to double bonds.

The hydrogenation profiles of phenylacetylene and 1-phenyl-1-butyne are shown in Figs. 5 and 6, respectively. In the former, the formation of ethylbenzene was not observed until the consumption of phenylacetylene was almost complete, while in the latter, 1-phenylbutane was produced at a constant ratio to 1-phenyl-1-butene from the start of the reaction. Profiles similar to this were also observed in the hydrogenations of 1-phenyl-1-propyne, cyclohexenylacetylene, and 2-methyl-1-buten-3-yne. These facts suggest that the hydrogenation pathway of phenylacetylene should be different from that of other conjugated acetylenes.

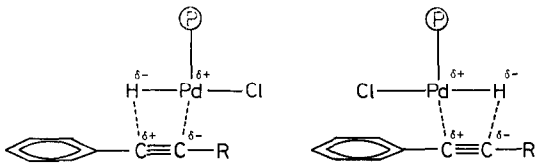
1-Cyclohexyl-1-butyne, which has a similar carbon skeleton to 1-phenyl-1-butyne but has no conjugated double bond, was hydrogenated to 1-cyclohexyl-1-butene in a high selectivity dissimilar to 1-phenyl-1-butyne (Runs 6, 7). Also, cyclohexenylacetylene, which has a similar carbon skeleton to phenylacetylene and yet has a conjugated double bond, was hydrogenated to vinylcyclohexene in a low selectivity dissimilar to phenylacetylene (Runs, 3, 8). These facts show that a conjugated double bond plays an important role in determining the selectivity and that the role of the double bond is different according to the kind of acetylenes.

Therefore, we predicted that the regiospecific addition of the palladium hydride to the triple bond is one important factor controlling the selectivity for the semihydrogenation of triple bonds in a conjugated system. Here, we take up the hydrogenations of phenylacetylene and 1-phenyl-1-butyne. Two regio-manners of the addition are considered for such unsymmetrically substituted acetylenes. As shown in Scheme 3, one is manner A in



SCHEME 3

which the palladium adds to carbon 1 and the other B, where the palladium adds to carbon 2. The selection of A or B is mainly governed by two factors, an electron density on the acetylenic carbons 1 and 2, and a steric hindrance about the triple bond. Here, lets assume that the palladium hydride is a three-coordinate complex where the hydrogen and the chlorine ligands are *trans*, and that the addition of Pd–H to the triple bond proceeds through a four-centered transition state as shown in Scheme 4.

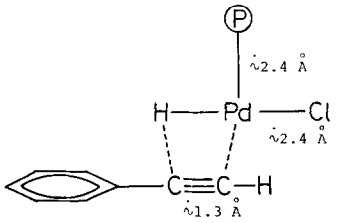


SCHEME 4

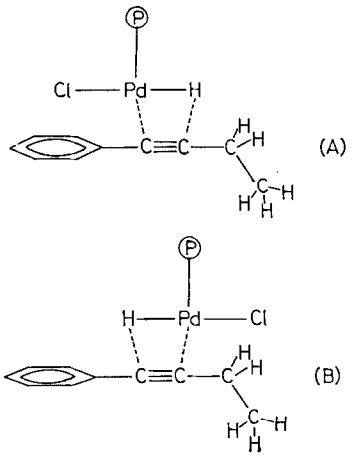
The palladium is commonly thought to have a more positive charge than the hydrogen in the Pd–H bond. According to the results of ^{13}C-NMR spectra of the acetylenes (Table 5), carbon 2 has a slightly more negative charge than that of carbon 1 in both phenylacetylene and 1-phenyl-1-butyne. However, the degree of polarization is small. From only the standpoint of the electronic effect, the palladium, therefore, prefers to add to carbon 2 in both cases.

On the other hand, the favored manner of

addition drastically changes between two cases from the point of a steric effect. Here, it should be noted that the hydrogen and the chlorine ligands in the palladium hydride complex are monoatomic, respectively, and that the phenyl-C(1)–C(2)–R bond is nearly linear. One of the acetylenic carbons is also thought to coordinate to the palladium through a vacant site in a square plane. As shown in Schemes 5 and 6, the



SCHEME 5



SCHEME 6

degrees of interaction of the chlorine ligand with acetylenic hydrogen, phenyl, and ethyl groups in the acetylenes should be compared mutually on evaluating steric effects.

In the case of phenylacetylene, the degree of interaction of the chlorine with the hydrogen is clearly smaller than that with the ethyl group. Therefore, the palladium prefers to add to carbon 2 as shown in Scheme 5, while the steric effects become complex in the case of 1-phenyl-1-butyne. Scheme 6 shows molecular models: A, in

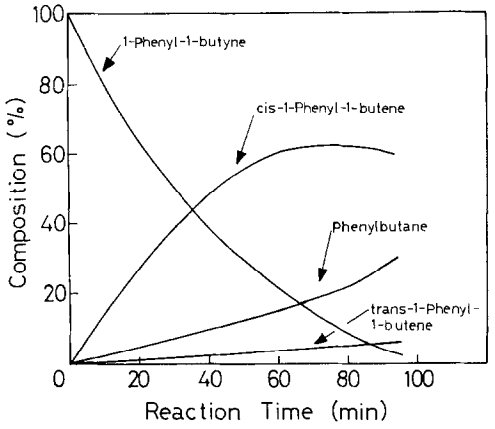


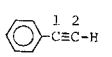
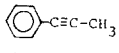
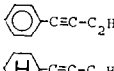
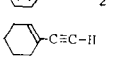
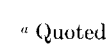
FIG. 6. Hydrogenation of 1-phenyl-1-butyne (Run 6).

which the palladium adds to carbon 1 and B, in which the palladium adds to carbon 2. The degree of interaction of the chlorine ligand with the phenyl group in model A is smaller than that with the ethyl group in model B. This is based on the facts that there is no hydrogen bound to α-carbon in the phenyl group and that in model B the chlorine ligand is very close to the hydrogens bound to α-carbon in the ethyl group. Consequently, the palladium preferentially adds to carbon 1 as model A.

In the case of phenylacetylene, both electronic and steric effects lead to the

TABLE 5

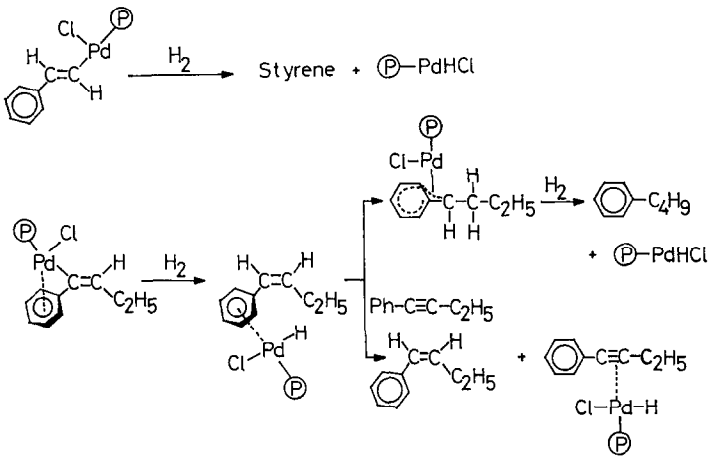
Chemical Shifts of Acetylenic Carbons in ^{13}C-NMR Spectra of Acetylenes

Acetylene	Chemical shift (ppm)	
	C(1)	C(2)
	83.3[a]	77.7[a]
	85.9	80.0
	91.6	80.2
	83.8	81.4
	85.6	74.6

[a] Quoted from Ref. (*18*).

addition of palladium to carbon 2. On the other hand, in the case of 1-phenyl-1-butyne the two effects lead to the different additions, respectively. Since the degree of polarization in the triple bond is small and, in general, organotransition metal complex-induced reactions are more strongly affected by a steric effect, the addition of palladium to carbon 1 seems to be more favorable for 1-phenyl-1-butyne.

Next, we consider σ-vinyl complexes formed by the addition of the palladium hydride to the triple bonds as shown in Scheme 7. In the σ-vinyl complex from



SCHEME 7

phenylacetylene, the palladium is too far apart to interact with the phenyl ring, so that the complex is attacked with hydrogen only to give styrene and the palladium–hydride complex. In the case of 1-phenyl-1-butyne, a different situation is encountered. In the σ-vinyl complex, the palladium is adjacent to the phenyl ring and may interact with the ring through one vacant coordination site. The σ-vinyl complex is attacked with hydrogen to give 1-phenyl-1-butene and the hydride complex. However, the produced 1-phenyl-1-butene may be maintained in the coordination sphere of the palladium complex by the interaction of the metal with the phenyl ring. In the following reaction stage, the maintained 1-phenyl-1-butene either is added by the palladium hydride to give a final product 1-phenylbutane or is replaced by 1-phenyl-1-butyne to give a free 1-phenyl-1-butene. From both facts (a) a triple bond coordinates much more strongly to the palladium complex than a double bond, (b) the palladium hydride adds very rapidly to a π-bonded conjugated olefin (*3*), it is appropriate for both of the above reaction routes to occur competitively. In this manner, both 1-phenyl-1-butene and 1-phenylbutane are simultaneously produced at a constant ratio from the very initial stage of the reaction. Consequently, the selectivity becomes lower.

These reaction pathways can reasonably interpret the results obtained for the hydrogenations of phenylacetylene and 1-phenyl-1-butyne. A similar mechanism, not involving a free olefin intermediate, has been suggested for the hydrogenation of 1-hexyne over borohydride-reduced catalysts (*17*). We believe that the selectivity for semihydrogenation of a triple bond in a conjugated system to a double bond is determined by the regio-manner of addition of the palladium hydride to the triple bond as mentioned above.

CONCLUSION

From this and prior studies (*3*), we might conclude:

(i) The polymer-bound palladium(II) complex is a highly efficient catalyst for both the selective hydrogenation of conjugated dienes to monoenes and that of acetylenes to olefins under mild conditions.

(ii) The activity of the complex for olefin hydrogenations increases with decreasing steric hindrance about a double bond and with increasing stability of the half-hydrogenated state formed by the addition of Pd–H to the bond.

(iii)The activity for acetylene hydrogenations increases with decreasing strength of π-acidity of a triple bond.

(iv) Conjugated dienes are hydrogenated to monoenes very selectively because of the selective coordination of the dienes to the complex.

(v) Isolated acetylenes are hydrogenated to monoenes because of the selective coordination of the acetylenes to the complex.

(vi) The selectivity of conjugated acetylenes to conjugated olefins is controlled by the regio-manner of addition of Pd–H to the acetylenes.

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