Selective Hydrogenation of Cyclooctadienes Using Colloidal Palladium in Poly(*N*-vinyl-2-pyrrolidone)

Hidefumi Hirai,* Hitoshi Chawanya, and Naoki Toshima
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received September 10, 1984)

Selective hydrogenation of 1,3-, 1,4-, and 1,5-cyclooctadiene to cyclooctene was carried out at 30 °C under atmospheric hydrogen pressure using colloidal palladium which was prepared by reducing palladium(II) chloride with refluxing methanol in the presence of poly(*N*-vinyl-2-pyrrolidone). The yields of cyclooctene were 99.9% and 97.8% for hydrogenation of 1,3- and 1,5-cyclooctadiene, respectively at the point that an equimolar hydrogen was uptaken by cyclooctadienes. The hydrogenation rate of 1,3- and 1,4-cyclooctadiene (R_1) is expressed as $R_1=k_1[H_2][Pd]$, and that of 1,5-cyclooctadiene (R_2) is expressed as $R_2=k_2[H_2]^{0.7}[Pd]$, where k_1 and k_2 are the rate constants. Alcohols were found to be good solvents for hydrogenation. In particular the fastest rate and the highest selectivity for monoene were observed in methanol among the solvents examined. Effect of bases on the monoene selectivity has also been investigated.

There have been numerous attempts to prepare highly dispersed metal catalysts supported on inorganic materials such as silica, alumina, and active carbon. Dispersion of the metal plays an important role in exhibiting high activity and selectivity of the catalyst.

On the other hand there are relatively little studies on colloidal metals homogeneously dispersed in a liquid phase. Rampino and Nord[1,2] reported that a colloidal dispersion of palladium with an average diameter of 700 Å was prepared by reducing aqueous palladium(II) hydroxide with molecular hydrogen in the presence of poly(vinyl alcohol).

Recently the present authors reported that colloidal noble metals were formed in good reproducibility by reducing the corresponding metal salts with primary or secondary alcohols or ethers in the presence of water-soluble vinyl polymers.[3,4] These colloidal metals were found to have smaller particle sizes (average particle diameters of 10—53 Å), and narrower particle size distributions than those prepared by reduction with molecular hydrogen. During the investigation of catalytic activity of the colloidal dispersions of noble metals, we have found that colloidal palladium prepared by reduction of palladium(II) chloride with methanol in the presence of poly(*N*-vinyl-2-pyrrolidone) catalyzes partial hydrogenation of cyclopentadiene,[5] and methyl esters of unsaturated fatty acid[6] to the corresponding monoenes. In the present paper we describe the selective hydrogenation of three isomers of cyclooctadiene to cyclooctene with the colloidal plladium.[7]

Experimental

Materials. Poly(*N*-vinyl-2-pyrrolidone) K-90 (Tokyo Chemical Industry Co. Ltd.; degree of polymerization, 3200) and palladium(II) chloride ($PdCl_2$) were used without further purification. 1,5-Cyclooctadiene, 1,3-cyclooctadiene, and cyclooctene were distilled under nitrogen before use. 1,4-Cyclooctadiene was prepared from 1,3-cyclooctadiene by bromination followed by reduction according to the literature.[8] All solvents were distilled and stored under nitrogen. Extra pure grade hydrogen (Nippon Oxygen Co. Ltd.; 99.99999% of purity) was passed through a Deoxo column (Nippon Engelhard, Ltd.) before use to remove trace amounts of oxygen. A commercial palladium catalyst used for comparison was 5% palladium on active carbon (Pd–C, Nippon Engelhard, Ltd.; surface area of Pd, 200 m^2/g-Pd).

Preparation of Colloidal Dispersion of Palladium. All manipulations were carried out under nitrogen atmosphere, using the solvents which were deaerated by purging with nitrogen.

Pd-PVP-MeOH/NaOH: Palladium(II) chloride (5.9 mg, 0.033 mmol) was dissolved in methanol (25 cm^3) by stirring the mixture overnight. Poly(*N*-vinyl-2-pyrrolidone) (151 mg, 1.36 mmol of monomeric units) was dissolved in methanol (20 cm^3). The combined mixture of these two solutions was gently heated with a water bath and brought to reflux. After the solution was refluxed for 30 min, a solution of sodium hydroxide (6.6 mg, 0.17 mmol) in methanol (5 cm^3) was added dropwise to the refluxing solution. The solution was refluxed for further 10 min to give a homogeneous dark brown dispersion of colloidal palladium protected by poly(*N*-vinyl-2-pyrrolidone).

Pd-PVP-MeOH/H$_2$O: A solution of palladium(II) chloride (5.9 mg) in methanol (25 cm^3) was combined with a solution of poly(*N*-vinyl-2-pyrrolidone) (151 mg) in water (25 cm^3). The mixed solution was refluxed over a water bath for 4 h, resulting in dark brown colloidal dispersion of palladium protected by poly(*N*-vinyl-2-pyrrolidone).

Electron Microscopy and Particle Size Determination. The sample film was prepared by evaporating a small amount of the colloidal dispersion of palladium to dryness on a collodion film which was coated with a carbon layer. The electron micrographs were taken at 100 kV at a magnification of 100000. The diameters of 200—900 particles of palladium in an arbitrarily chosen area were measured in an enlarged (4.4×) photograph. The particle size distribution and the number average particle diameter were determined on the basis of these results.

Hydrogenation of Cyclooctadienes. The reaction flask immersed in a thermostated water bath (30 °C) was evacuated and then flushed with hydrogen for 3—4 times. A solvent [(19−x) ml] and a colloidal dispersion of palladium (x ml) was then introduced into the flask and the mixed solution was stirred for 1 h to be saturated with hydrogen. A substrate diluted with a solvent for hydrogenation (1 cm^3) was injected into the reaction flask to start the reaction. Hydrogen uptake under a constant atmospheric pressure was monitored with a gas burette. Initial rates of hydrogenation (in H_2 mol/

Pd mol s) were calculated from the initial rates of hydrogen uptake.

The product was analyzed by GLPC with a flame ionization detector using helium as a carrier gas and a 30 m× 0.28 mmϕ glass capillary column coated with Silicone OV-101 at 55 °C

Kinetic Measurements. Initial rates of hydrogenation of cyclooctadienes with the colloidal palladium (Pd–PVP–MeOH/NaOH) were measured as a function of catalyst concentration, substrate concentration, and hydrogen pressure. Standard conditions are as follows: catalyst concentration=0.01 mmol dm^{-3} (0.1 mmol dm^{-3} for 1,5-cyclooctadiene), substrate concentration=25 mmol dm^{-3}, and hydrogen pressure=728 Torr (1 Torr≈133.322 Pa). Each variable was changed over the following range: catalyst, 0.002—0.01 mmol dm^{-3} (0.02—0.1 mmol dm^{-3} for 1,5-cyclooctadiene); substrate, 5—50 mmol dm^{-3}; hydrogen pressure, 180—728 Torr. The dependence of the rate on hydrogen pressure was measured in mixed gases of hydrogen and nitrogen at 1 atm. The concentration of hydrogen in the solution was determined from the partial pressure of hydrogen using Henry's law.

Under these reaction conditions, the hydrogenation rates were independent of the stirring rates of magnetic stirrers. Thus the reactions were not mass transfer limited.

Results

Preparation of the Colloidal Dispersion of Palladium. Palladium(II) chloride and poly(*N*-vinyl-2-pyrrolidone) were dissolved in methanol to form a yellow solution. After the solution was refluxed for 30 min, a methanol solution of sodium hydroxide was added to the refluxing solution, which caused a color change of the solution to dark brown. Further refluxing for 10 min gave a dark brown homogeneous dispersin of colloidal palladium, abbreviated as Pd–PVP–MeOH/NaOH.

When methanol/water (1/1, v/v) was used as a solvent instead of methanol in the case mentioned above, reduction of palladium ions took place even without addition of sodium hydroxide, resulting in a colloidal dispersion, Pd–PVP–MeOH/H_2O.

Electron micrographs of these colloidal dispersions (Figs. 1 and 2) show formation of well-dispersed palladium particles ranging from 10 to 120 Å in diameter. More than 98% of the particles in the colloidal dispersion, Pd–PVP–MeOH/NaOH, had a diameter below 30 Å, and the average diameter was determined to be 18 Å from the micrograph. In the colloidal dispersion of Pd–PVP–MeOH/H_2O 92% of the particles had a diameter below 30 Å, and the average diameter was determined to be 23 Å.

These colloidal dispersions were so stable that no precipitates of palladium metal appeared and the catalytic activities were unchanged after storing the dispersions under air for a year.

Hydrogenation of Cyclooctadienes. The colloidal palladium, Pd–PVP–MeOH/NaOH, was effective as a catalyst for hydrogenation of 1,3-, 1,4-, and 1,5-cyclooctadiene at 30 °C under atmospheric hydrogen pressure. As shown in Table 1, the hydrogenation rate for 1,3-cyclooctadiene is the fastest among cyclooctadienes and the rate decreases in the order: 1,3-, 1,4-, and 1,5-isomer. For hydrogenation of 1,5-cyclooctadiene the colloidal palladium showed almost the same catalytic activity as that of 5% Pd–C. Typical curves of hydrogen uptake against time are shown in Fig. 3. In hydrogenation of 1,3-cyclooctadiene the rate of hydrogen uptake is very rapid until the amount of hydrogen uptake become equimolar to the charged amount of diene. At this point, however, the rate suddenly decreases

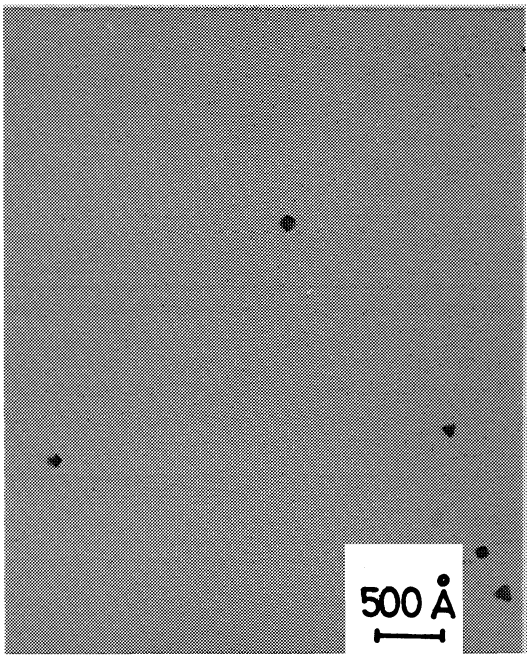


Fig. 1. Electron micrograph of colloidal palladium, Pd–PVP–MeOH/NaOH; original magnification, 100000×.

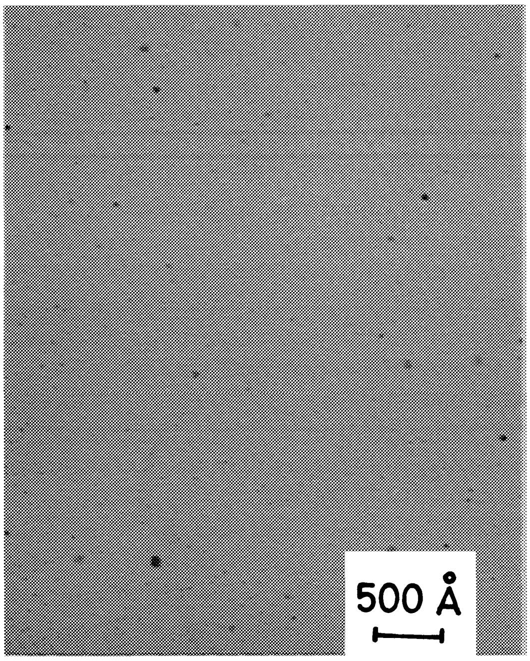


Fig. 2. Electron micrograph of colloidal palladium, Pd–PVP–MeOH/H_2O; original magnification, 100000×.

Table 1. Hydrogenation of cyclooctadienes with colloidal palladium[a)]

Substrate	c[b)]	r[c)]	Product composition/%[d)]			
	mol dm^{-3}	s^{-1}	1,5-COD	1,4-COD	COE	COA
1,3-COD	0.01	35	0.0	0.0	99.9	0.1
1,4-COD[e)]	0.02	4.6	1.7	3.5	94.0	0.8
1,5-COD	0.1	1.4	0.4	0.3	97.8	1.5
1,5-COD	0.1[f)]	1.2	0.4	0.2	94.2	5.2
COE	0.1	0.07				

a) Hydrogenation conditions: temperature, 30 °C; total pressure, 1 atm; [substrate]=25 mmol dm^{-3}; solvent, methanol (20 cm^3); catalyst: Pd-PVP-MeOH/NaOH. COD=cycloocadiene, COE=cyclooctene, COA=cyclooctane. b) Concentration of palladium. c) Initial rate of hydrogen uptake in (H_2mol/Pd mol s). d) The composition of the reaction mixture when the amount of hydrogen uptake becomes equimolar with charged diene. e) Containing 6.9% of 1,5-COD. f) Commercial 5% Pd-C was used as a catalyst.

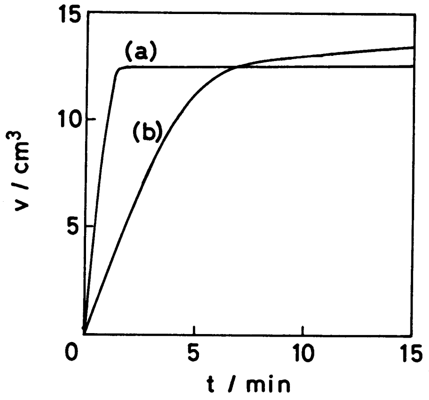


Fig. 3. Hydrogen uptake (v) in the hydrogenation of 1,3- (a) and 1,5-cyclooctadiene (b) with Pd-PVP-MeOH/NaOH. [COD]=25 mmol dm^{-3}: [Pd]= 0.01 (a) and 0.05 (b) mmol dm^{-3}.

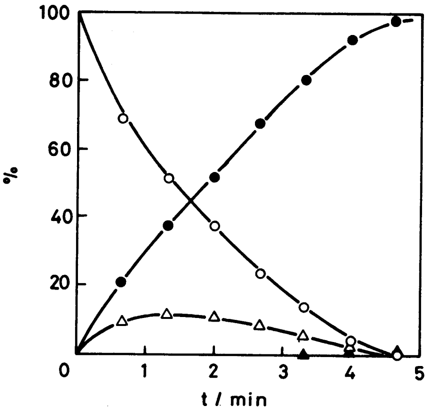


Fig. 4. Composition of the reaction mixtures on hydrogenation of 1,5-cyclooctadiene with a Pd-PVP-MeOH/NaOH catalyst in methanol at 30 °C under a total pressure of 1 atm of hydrogen. [Pd]=0.1 mmol dm^{-3}: [1,5-COD]=25 mmol dm^{-3}. ○: 1,5-COD, △: 1,4-COD, ●: COE, ▲: COA.

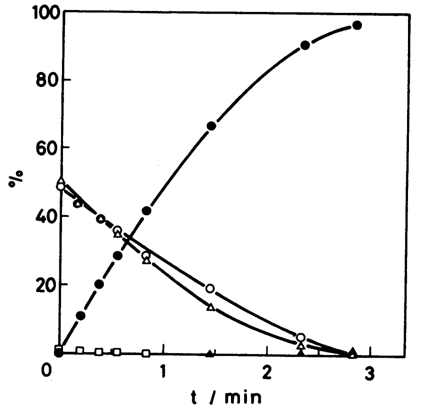


Fig. 5. Composition of the reaction mixtures on hydrogenation of 1,4- and 1,5-cyclooctadiene with a Pd-PVP-MeOH/NaOH catalyst in methanol at 30 °C under a total pressure of 1 atm of hydrogen. [Pd]=0.1 mmol dm^{-3}: [1,4-COD]+[1,5-COD]=25 mmol dm^{-3}.

○: 1,5-COD, △: 1,4-COD, □: 1,3-COD, ●: COE, ▲: COA.

to 1/570 of the initial rate. The conversion of 1,3-cyclooctadiene was complete at this point and cyclooctene was produced in a 99.9% yield.

In hydrogenation of 1,5-cyclooctadiene (curve b) the change in the rate at an equimolar hydrogen uptake is rather small compared with the case of 1,3-cyclooctadiene (curve a). The yield of cyclooctene is 97.8% in hydrogenation of 1,5-cyclooctadiene. This value is considerably higher than that in the hydrogenation with 5% Pd-C (94.3%).

Initial hydrogenation rate of cyclooctene with colloidal palladium was 1/20 of that of 1,5-cyclooctadiene, and was almost the same as the rate of the second stage (after equimolar hydrogen uptake) in hydrogenation of the diene.

Formation of 1,4-cyclooctadiene in the early stage of hydrogenation of 1,5-cyclooctadiene (shown in Fig. 4) indicates that the hydrogenation is accompanied by isomerization. No other hydrogenated product than cyclooctene is observed at the initial stage of the reaction. Cyclooctane is produced after consumption of most diene.

No isomerization occurred when a methanol solution of 1,5-cyclooctadiene and the colloidal dispersion of palladium was stirred under nitrogen.

1,4-Cyclooctadiene is hydrogenated at 3.3 times the rate of hydrogenation of 1,5-cyclooctadiene (Table 1). While, in hydrogenation of equimolar mixture of 1,4- and 1,5-cyclooctadiene, initial rate of consumption of 1,4-cyclooctadiene is only 1.3 times that of 1,5-cyclooctadiene as shown in Fig. 5.

Kinetics of Hydrogenation of Cyclooctadiene. Initial rates of hydrogenation of 1,3-, 1,4-, and 1,5-

cyclooctadiene were measured as a function of catalyst concentration, substrate concentration, and hydrogen pressure. The rate for 1,3- and 1,4-cyclooctadiene increased linearly with increasing catalyst concentration and hydrogen pressure, and were independent of substrate concentration. Thus, the rate, R, is expressed in the following form:

$$R = k_1[\mathrm{H_2}][\mathrm{Pd}] \qquad (1)$$

where k_1 is a rate constant. The value of k_1 was determined to be 4.86×10^3 and 1.06×10^3 $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ for 1,3- and 1,4-cyclooctadiene, respectively.

The rate of hydrogenation of 1,5-cyclooctadiene increased linearly with increasing catalyst concentration and was independent of substrate concentration. However, dependence on hydrogen pressure deviated from linear relationship. The hydrogenation rate, R, is expressed in the following form:

$$R = k_2[\mathrm{H_2}]^{0.7}[\mathrm{Pd}] \qquad (2)$$

where k_2 is a rate constant.

Effects of Solvents. Hydrogenation of 1,5-cyclooctadiene with colloidal palladium, Pd–PVP–MeOH/NaOH, was carried out using various solvents, as listed in Table 2. For the experiments in solvents without methanol, methanol used for the preparation of the colloid was evaporated under vacuum, and then resulting residues were re-dissolved in the solvent for hydrogenation. Catalytic activity of the colloidal palladium was confirmed not to change by the treatment of evaporation and re-dissolution.

The highest rate of hydrogenation was observed in methanol. In ethanol and 1-propanol the rates were found to be a little lower than that in methanol, but selectivities for formation of monoene were almost the same.

Colloidal palladium protected by poly(*N*-vinyl-2-pyrrolidone) was insoluble in ethyl acetate and tetrahydrofuran, but it became soluble in the presence of a small amount of methanol. In these mixed solvents hydrogenation rate and selectivity are considerably lower than those in methanol.

Table 2. Effect of solvents on hydrogenation of 1,5-cyclooctadiene[a)]

Solvent (cm³)	r[b)]	Product composition/%[b)]			
	$\mathrm{s^{-1}}$	1,5-COD	1,4-COD	COE	COA
Methanol(20)[c)]	1.6	0.5	0.4	96.6	2.5
Ethanol(20)[c)]	1.3	0.0	0.0	94.8	5.2
1-Propanol(20)[c)]	1.2	0.5	0.2	96.3	3.0
Ethyl acetate(17) /Methanol(3)	0.4	5.7	2.1	89.6	2.6
Tetrahydrofuran(17) /Methanol(3)	0.2	1.3	0.9	94.0	3.8

a) Hydrogenation conditions: temperature 30 °C; total pressure: 1 atm; [Pd]=0.1 mmol $\mathrm{dm^{-3}}$; [COD]=25 mmol $\mathrm{dm^{-3}}$; catalyst, Pd–PVP–MeOH/NaOH. b) Abbreviations: See legend of Table 1. c) The catalyst solution was evaporated and re-dissolved in the hydrogenation solvent.

Effects of Additives. As mentioned above, colloidal palladium, Pd–PVP–MeOH/NaOH, exhibits considerably higher selectivity for formation of monoene than a Pd–C catalyst. Difference in sizes of palladium particles and interaction between palladium and the protective colloid have been considered to play important roles in exhibiting high selectivity of the colloidal palladium.[5,6)] In addition, base added in preparation of the colloidal palladium (Pd–PVP–MeOH/NaOH) may have some effect on the selectivity. In order to clarify this effect, hydrogenation of 1,5-cyclooctadiene was carried out in the presence of additives using colloidal palladium, Pd–PVP–MeOH/$\mathrm{H_2O}$, as a catalyst. In Fig. 6 the yield of cyclooctene is plotted against the degree of hydrogenation which is calculated as [(yield of cyclooctene)+(yield of cyclooctane)×2]. In the absence of additives the yield of cyclooctene reaches a maximum value of 95—96%, which is smaller by 2% than one with the base-added colloid (Pd–PVP–MeOH/NaOH).

On addition of sodium hydroxide the yield of cyclooctene over the Pd–PVP–MeOH/$\mathrm{H_2O}$ catalyst increased by 0.7% at a degree of hydrogenation of 95—100%. The yield of cyclooctene also increased by addition of triethylamine instead of sodium hydroxide, while it did not change by addition of sodium chloride or hydrochloric acid.

Addition of hydrochloric acid into the solution for hydrogenation with the colloid prepared by addition of base (Pd–PVP–MeOH/NaOH) decreased the yield of cyclooctene from 96.5% to 94.5% at the degree of hydrogenation of 100%.

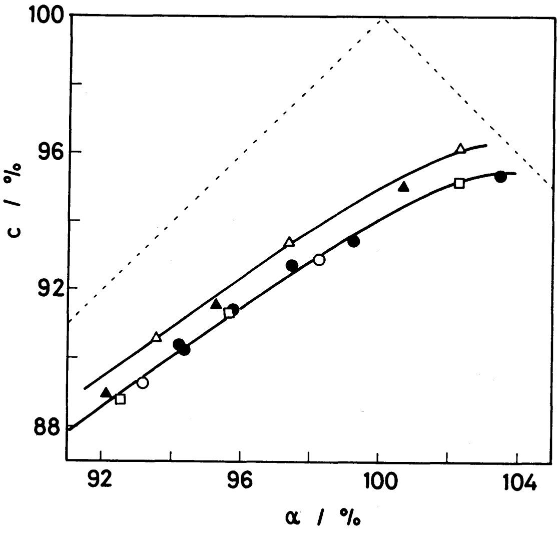


Fig. 6. Effect of additives on the hydrogenation of 1,5-cyclooctadiene with Pd–PVP–MeOH/$\mathrm{H_2O}$. Yield of cyclooctene (c) is plotted as a function of degree of hydrogenation (α). The dotted line shows the yield of cyclooctene at the complete selectivity. [Pd]=0.1 mmol $\mathrm{dm^{-3}}$: [1,5-COD]=25 mmol $\mathrm{dm^{-3}}$. Amount of additives=10 μmol; additives: ●: none, △: NaOH, □: HCl, ▲: $\mathrm{Et_3N}$, ○: NaCl.

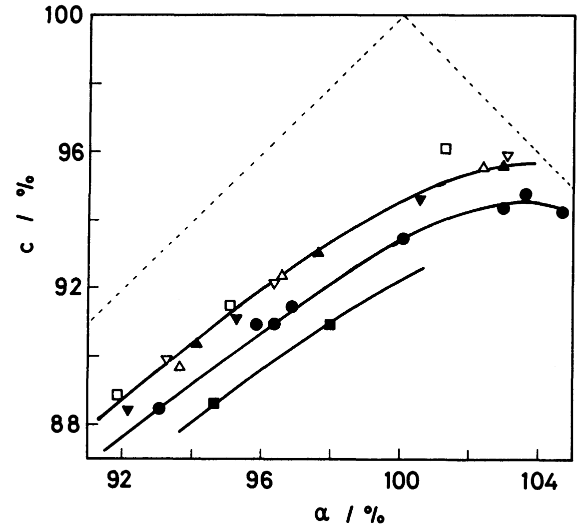


Fig. 7. Effect of additives on the hydrogenation of 1,5-cyclooctadiene with Pd–C catalyst. Yield of cyclooctene (*c*) is plotted as a function of degree of hydrogenation (*α*). Pd–C, 4.3 mg; [1,5-COD]=25 mmol dm^{-3}. Additives (amount in μmol): ●: None, △: NaOH(10), ▽: NaOH(20), □: NaOH(40), ▲: KOH(10), ▼: Et_3N(10), ■: HCl(10).

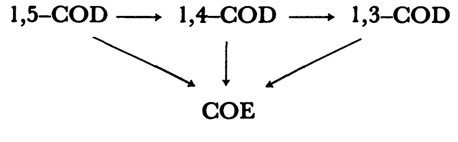
Effects of Additives on the Hydrogenation with Pd–C. Effects of addition of base and acid in the hydrogenation with 5% Pd–C are illustrated in Fig. 7. In the absence of additives the yield of cyclooctene reaches a maximum value of 94—95% at a degree of hydrogenation of 104%. This value in yield is smaller by 3% than that with the base-added colloid and by 1% than that with the water-added colloid.

The yield of cyclooctene increased by 1% on addition of a base such as sodium hydroxide, potassium hydroxide, and triethylamine, but decreased by 1% on addition of hydrochloric acid.

Discussion

Selectivity for the Formation of Cyclooctene. In the first stage of hydrogenation of 1,5-cyclooctadiene with the colloidal palladium, Pd–PVP–MeOH/NaOH, hydrogenation of cyclooctene to cyclooctane was inhibited and cyclooctene was produced in a high yield. However, after most of the diene was consumed, hydrogenation of cyclooctene occurred at an appreciable rate. This fact strongly suggests that adsorption of diene on the catalytic site is much stronger than that of monoene, and thus the adsorption of monoene is completely suppressed in the presence of diene.

Formation of 1,4-cyclooctadiene in hydrogenation of 1,5-cyclooctadiene (Fig. 4) shows that this reaction occurs with accompanying isomerization of nonconjugated dienes to conjugated diene as follows (COD, cyclooctadiene; COE, cyclooctene):



1,3-Cyclooctadiene was not detected in the reaction mixtures, probably because the rate of hydrogenation of 1,3-cyclooctadiene was much higher than that of the isomerization of 1,4-cyclooctadiene to 1,3-cyclooctadiene.

The yield of cyclooctene in hydrogenation of 1,5-cyclooctadiene was 97.8% with the colloidal palladium, and 94.2% with Pd–C. This difference in selectivity is relatively small compared with that in the hydrogenation of cyclopentadiene, in which the yield of cyclopentene is 98.7% with colloidal palladium and 82.6% with Pd–C.[5] Relatively high selectivity for cyclooctene formation in the hydrogenation of 1,5-cyclooctadiene with Pd–C may be explained by the considerably small hydrogenation rate of cyclooctene. Unusually low hydrogenation rate of cyclooctene has also been reported by Jardine *et al.*, and was related to the lower heat of hydrogenation due to the severe transannular interactions in cyclooctane.[8]

In hydrogenation of equimolar mixtures of 1,4- and 1,5-cyclooctadiene, 1,4-cyclooctadiene was consumed 1.3 times as fast as 1,5-cyclooctadiene. These rates of consumption of 1,5- and 1,4-cyclooctadiene were 0.85 and 0.3 times of the rate of the separate hydrogenation, respectively. Large inhibition effect of 1,5-cyclooctadiene in the hydrogenation of 1,4-cyclooctadiene indicates that the adsorption of 1,5-cyclooctadiene on the catalyst is stronger than that of 1,4-cyclooctadiene.

Kinetics of Hydrogenation of Cyclooctadienes. Zero order with respect to substrate and positive order with respect to hydrogen indicate that diene is more strongly adsorbed on the surface of catalysts than hydrogen, and consequently the surface coverage of diene is larger than that of hydrogen.

Dependence of the rate on the hydrogen pressure was the first order in the hydrogenation of 1, 3- and 1, 4-cyclooctadiene, but deviated from the first order in the hydrogenation of 1,5-cyclooctadiene. This divergence from linear relationship can be associated with the extent of accompanying isomerization. As shown in Fig. 4, the yield of 1,4-cyclooctadiene reaches the maximum value of 12% in hydrogenation of 1,5-cyclooctadiene at the hydrogen pressure of 728 Torr. As the hydrogen pressure was decreased from 728 to 371 Torr, the maximum value increased from 12 to 15%. This fact indicates that the proportion of the diene hydrogenated *via* the isomerization to 1,4-isomer increased by decreasing hydrogen pressure.

Effect of Additives. In the hydrogenation with the water-added colloid (Pd–PVP–MeOH/H_2O), selectivity for monoene incrcased by addition of sodium hydroxide and triethylamine. On the other hand, the selectivity decreased by addition of hydrochloric acid in the hydrogenation with the base-added colloid (Pd–PVP–MeOH/NaOH). These results suggest that hydroxide ion have some effects on the selectivity. In accordance with this assumption, addition of sodium chloride had no effect on the selectivity. Similar effects of addition of bases were also observed with Pd–C. This suggests that bases affect the selectivity not through changes in the state of polymer which protects colloidal palladium, but through direct interactions between palladium metals and hydroxide ions.

McQuillin *et al.* have reported that hydrogenation of 2-butyne-1,4-diol, 2-butene-1,4-diol, and mesityl oxide over Pd–C in ethanol was retarded by the addition of a base such as potassium hydroxide.[9] The effect of base on the monoene selectivity in the present study is also interpreted in terms of inhibition effect of base. As a hydroxide ion is more strongly adsorbed on the catalytic site than monoene, but more weakly is than diene, addition of the ion may inhibit the adsorption of monoene more strongly than that of diene. As a result, monoene selectivity is enhanced with the addition of a base.

By the way discussed above, the base added in preparation contributes to the high selectivity of the base-added colloid (Pd–PVP–MeOH/NaOH). Other factors for the high selectivity may involve the particle size of the palladium particles and the interaction between palladium and the polymer or the support. Thus, in the hydrogenation of cyclopentadiene, the selectivity increased with decreasing size of palladium particles, and with addition of poly(*N*-Vinyl-2-pyrrolidone) to Pd–C and Pd-black.[5]

The difference in activity with solvents (Table 2) is also interpreted by the adsorption of solvent molecules on catalytic sites. On the palladium catalyst, hydrocarbon groups have been reported to be adsorbed more strongly than oxygen atoms.[10] Higher alcohols, ethyl acetate, and tetrahydrofuran act as a kind of inhibitor because of a large portion of hydrocarbon groups in a molecule. Thus, the hydrogenation rate is relatively slow in these solvents. The high hydrogenation rate in methanol can be due to a small hydrocarbon group of methanol and, therefore, a weak inhibiting character of methanol.

References

1) L. D. Rampino and F. F. Nŏrd, *J. Am. Chem. Soc.*, **63**, 2745 (1941).

2) L. D. Rampino, K. E. Kavanagh, and F. F. Nord, *Proc. Natl. Acad. Sci., U.S.A.*, **29**, 246 (1943).

3) H. Hirai, Y. Nakao, and N. Toshima, *J. Macromol. Sci., Chem.*, **A12**, 1117 (1978).

4) H. Hirai, Y. Nakao, and N. Toshima, *J. Macromol. Sci., Chem.*, **A13**, 727 (1979).

5) H. Hirai, H. Chawanya, and N. Toshima, *Reactive Polymers*, in press.

6) H. Hirai, H. Chawanya, and N. Toshima, *Nippon Kagaku Kaishi*, **1984**, 1027.

7) This work has been published in a communication: H. Hirai, H. Chawanya, and N. Toshima, *Makromol. Chem., Rapid Commun.*, **2**, 99 (1981).

8) I. Jardine and F. J. McQuillin, *J. Chem. Soc. (C)*, **1966**, 458.

9) F. J. McQuillin, W. O. Ord, and P. L. Simpson, *J. Chem. Soc.*, **1963**, 5996.

10) J. Iijima and K. Mitsui, *Nippon Kagaku Kaishi*, **85**, 687 (1964).