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Phenylacetaldehyde and Carbon Monoxide as Effective Additives for the Selective Hydrogenation of Cyclooctadienes to Cyclooctene over Palladium Catalysts

Michio Higashijima, Hó Soc Man, and Shigeo Nishimura*
Department of Applied Chemistry, Tokyo University of Agriculture
and Technology, Koganei, Tokyo 184
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Three isomeric cyclooctadienes (1,5-, 1,4-, and 1,3-COD) were hydrogenated with phenylacetaldehyde (PAA)- or carbon monoxide (CO)-treated palladium black in tetrahydrofuran at 25 °C and atmospheric pressure of hydrogen. A complete depression of the hydrogenation of cyclooctene (COE) to cyclooctane (COA) was attained with both of the poisoned catalysts. By PAA the hydrogenation of 1,5-COD to COE was not hindered and the isomerization of 1,5-COD to 1,4-COD was greatly promoted, while the rate of hydrogenation of 1,4- and 1,3-COD decreased in the presence of PAA. By CO the hydrogenation and isomerization of 1,5-COD, as well as the hydrogenation of 1,4- and 1,3-COD, was suppressed. In the hydrogenation of 1,5-COD the PAA-treated palladium was more active and selective than was the CO-treated palladium for the formation of COE. The differences in the effects of these catalyst poisons are discussed on the basis of kinetic data concerning the individual and competitive hydrogenation of the three isomeric cyclooctadienes.

Many studies have been carried out on the selective hydrogenation of acetylenes and polyenes to monoenes with poisoned catalysts,[1] such as Lindlar's.[2] However, relatively few studies[1–4] have focussed on the selective hydrogentation of non-conjugated dienes to monoenes over heterogeneous catalysts. In a previous letter[5] it was briefly reported that phenylacetaldehyde is especially effective as a catalyst poison among various aldehydic compounds in the selective hydrogenation of 1,5-COD and methyl linoleate to the corresponding monoenes over palladium catalysts. The exact nature of its effectiveness, however, has yet to be clarified. Since phenylacetaldehyde may decarbonylate to produce carbon monoxide and toluene on the catalysts, we are interested in the poisoning action of carbon monoxide in this type of selective hydrogenation. Although the effect of carbon monoxide has been studied in selective hydrogenation,[6] to our knowledge it has not yet been reported concerning the hydrogenation of 1,5-COD.

In this paper, two poisoned catalysts, phenylacetaldehyde-treated palladium (PAA-Pd) and carbon monoxide-treated palladium (CO-Pd), are compared concerning the hydrogenation of 1,5-COD as well as the hydrogenation of 1,4- and 1,3-COD, both of which may be significant intermediates during 1,5-COD hydrogenation. On the basis of the kinetic data concerning both individual and competitive hydrogenation of the three isomeric COD's, the effects of PAA and CO were characterized quantitatively; the differences in their effects are discussed in terms of the obtained results.

Experimental

Materials. 1,3- and 1,5-COD were commercial samples, which were purified through activated alumina and then distilled under nitrogen before use. 1,4-COD was prepared according to the procedure of Moon and Ganz[7] by bromination of 1,3-COD followed by reduction and purification as a silver nitrate complex. The 1,4-COD obtainied by this procedure had a purity of ca. 85%, the main impurities being 1,3- and 1,5-COD. However, 1,4-COD with a 99.9% purity (GLC analysis) was obtained by further repeating the purification procedure with the silver nitrate complex. Tetrahydrofuran was distilled in the presence of lithium aluminum hydride under nitrogen and stored in a refrigerator under nitrogen.

Catalyst. Palladium black was prepared by the hydrogen reduction of palladium(II) hydroxide and was then washed well with warm distilled water, as described previously.[8] The catalyst was shaken under an atmospheric pressure of hydrogen in tetrahydrofuran for 20 min before adding the substrate.

Phenylacetaldehyde- and Carbon Monoxide-treated Palladium Catalysts (PAA-Pd and CO-Pd). After a prereduction of unpoisoned palladium (Pd 2 mg) in the solvent for 20 min at 25 °C under atmospheric pressure of hydrogen, PPA (4.0—32.0 µl) or CO (40—100 µl) was added to the catalyst suspension with a gas-tight syringe, and then vigorously shaken for 20 min for PAA (10 min for CO) before adding the substrate.

Hydrogenation. High-purity hydrogen gas (Nippon Sanso Co.) was used without further purification. The substrate (50 µl) was hydrogenated in a small glass bottle with 2.0 mg of the catalyst in 1.60 ml of tetrahydrofuran at 25 °C under atmospheric pressure of hydrogen throughout the experiments.

Analysis of Reaction Mixture. The reaction mixture was taken into a microsyringe through a silicone rubber stopper during the course of hydrogenation and subjected to gas chromatography (3.75 m×3 mmϕ glass column with 10% PEG 20 M on Chromosorb W at 80 °C for the products from 1,5-COD). For the products of the hydrogenation of PAA, a fused-silica capillary column of SPB-1 (Superco Co., Ltd., 30 m, 0.53 mm ID, 1.0 µl film thickness) was used at 70—200 °C programmed at 6 °C min^{-1} with 5 ml min^{-1} nitrogen.

Results and Discussion

Hydrogenation Routes of 1,5- and 1,4-COD over Various Palladium Catalysts. Figures 1 and 2 show typical diagrams for the product distibution vs. the reaction time in the hydrogenation of 1,5-COD and 1,4-COD, respectively, over various palladium catalysts.

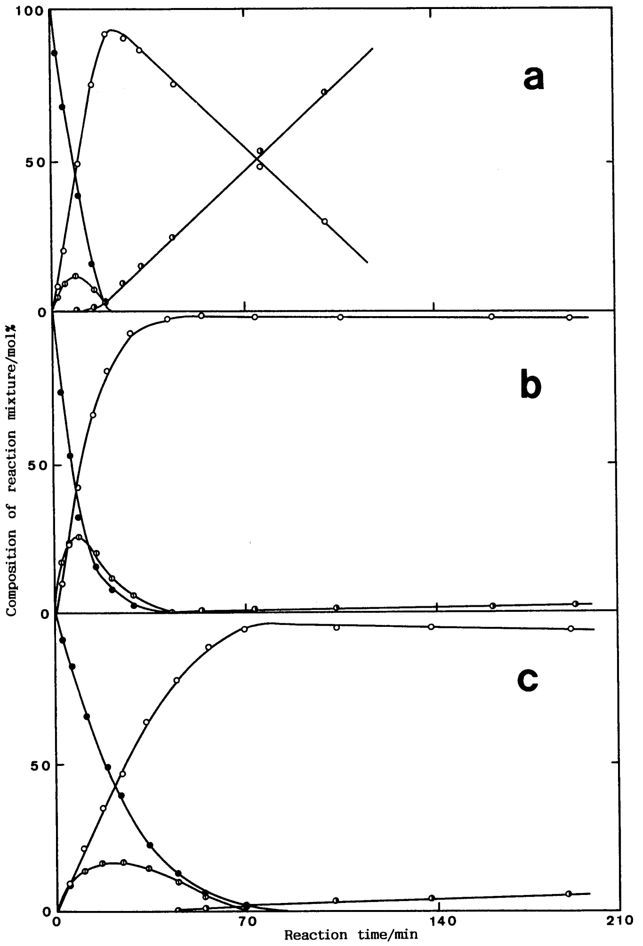


Fig. 1. Hydrogenation of 1,5-COD over various palladium catalysts. The points are experimental values and the curves show simulations using the values given in Table 1. For the reaction conditions, see footnote a) in Table 1. ●: 1,5-COD, ⦶: 1,4-COD, ○: COE, ◑: COA. **a**: Hydrogenation with Pd, **b**: Hydrogenation with PAA-Pd, **c**: Hydrogenation with CO-Pd.

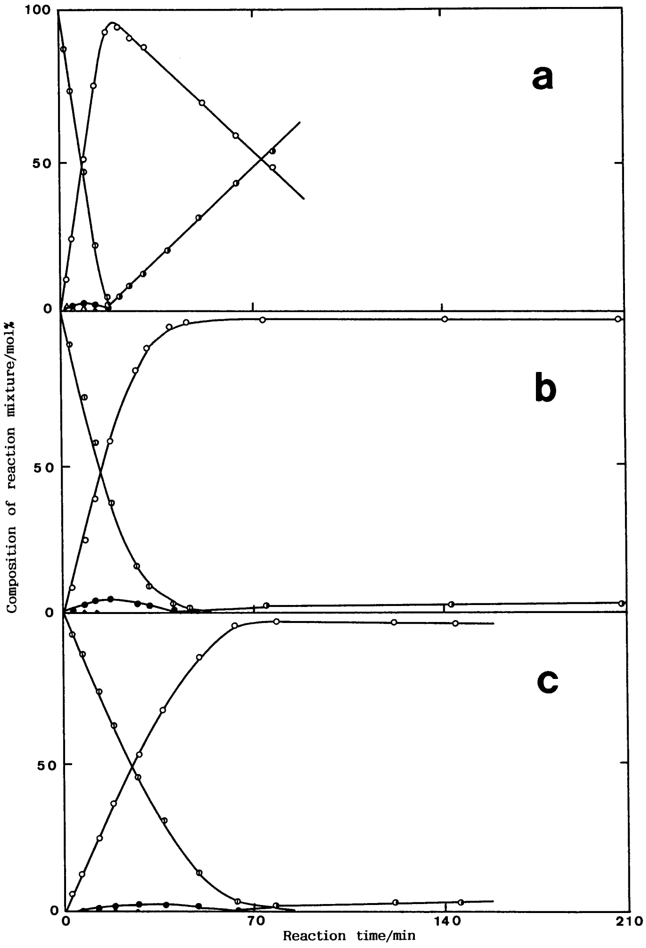


Fig. 2. Hydrogenation of 1,4-COD over various palladium catalysts. △: 1,3-COD. For other indications, see the footnotes in Fig. 1.

In the hydrogenation of 1,5-COD, isomerization to 1,4-COD always occurred simultaneously along with direct hydrogenation to COE. In the hydrogenation of 1,4-COD isomerization to 1,5- and 1,3-COD occurred together along with direct hydrogenation to COE, though the isomerized products were detected only in small amounts (Fig. 3). From the results given in Fig. 3, the selectivity for the 1,3- or 1,5-COD desorbed from the catalyst surface (*f*) and the relative reactivity of each isomerized COD to 1,4-COD (*K*) were evaluated by applying Eq. 1,[9] except for the 1,3-COD formed with the poisoned catalysts, where the amounts were too small to apply the following equation.

$$C_{\mathrm{i}} = \frac{f}{K-1}\left(C_{1,4} - C_{1,4}{}^{K}\right) \qquad (1)$$

C represents the concentration of each substrate; subscripts i and 1,4 refer to the 1,3- or 1,5-COD formed by

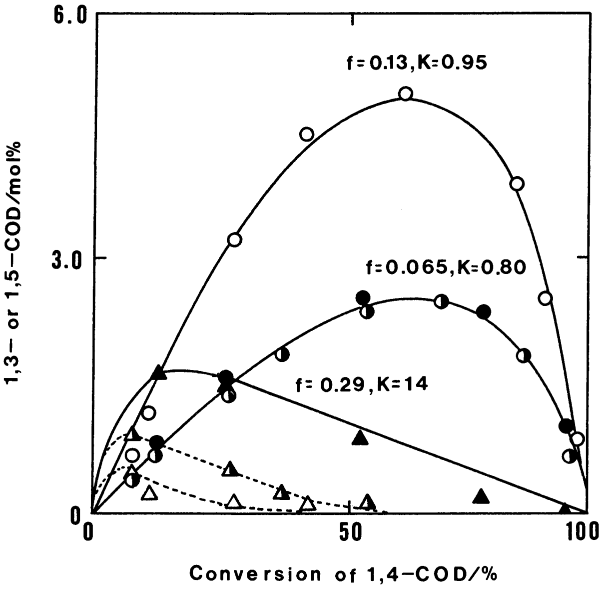
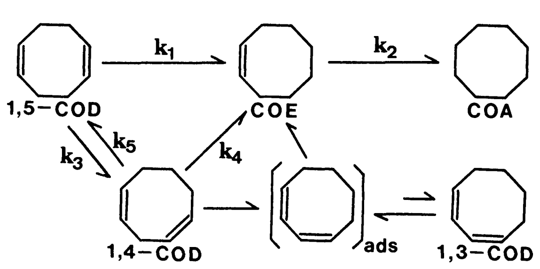


Fig. 3. Formation of 1,5- and 1,3-COD during the hydrogenation of 1,4-COD. Pd (●: 1,5-COD, ▲: 1,3-COD), PAA-Pd (○: 1,5-COD, △: 1,3-COD), CO-Pd (◑: 1,5-COD, ◭: 1,3-COD).

isomerization and 1,4-COD, respectively. The solid lines in Fig. 3 are theoretical curves for the estimated values of *K* and *f*. With all the catalysts, the values of *K* for the intermediate 1,5-COD are rather small and isomerization to 1,5-COD occurs only to small extents. On the other hand, the occurrence of more isomerization to 1,3-COD than expected from the values of *f* would be probable, since the adsorption–desorption equilibrium concerning the 1,3-COD formed by isomerization would not be established under these circumstances. According to these observations, the hydrogenation routes of 1,5-COD over palladium can be described as shown in Scheme 1, where the subscript "ads" represents 1,3-COD which is adsorbed on the catalyst.

Determination of Reaction Variables for the Hydrogenation of 1,5-COD. By assuming the establishment of adsorption–desorption equilibrium for both the reactant and the intermediates in Scheme 1, except for 1,3-COD, the Langmuir–Hinshelwood model was applied to a simulation of the reaction time vs. the composition of the reaction mixture (solid lines in Figs. 1 and 2). In these simulations rate constant k_4 involves that for the hydrogenation of the 1,3-COD produced by isomerization of 1,4-COD. First, rate constants k_1, k_3, and k_2 in 1,5-COD hydrogenation as well as k_5 and k_4 in 1,4-COD hydrogenation were determined using all experimental data. In these determinations, the ratios of the adsorption coefficients ($b_{1,4}/b_{1,5}$ and $b_{COE}/b_{1,5}$) were selected so as to best fit the varying composition of the reaction mixture during the course of hydrogenation. Subscripts 1,4, 1,5, and COE refer to 1,4-COD, 1,5-COD, and cyclooctene, respectively.



Scheme 1. Hydrogenation routes of 1,5-cyclooctadiene with palladium catalysts.

Table 1 summarizes the kinetic data thus obtained for the hydrogenation of 1,5-COD over unpoisoned and poisoned catalysts. With PAA-Pd, k_1 did not change (or even increased) compared to k_1 with Pd; however, a remarkable decrease in k_1 was observed over CO-Pd. The isomerization of 1,5- to 1,4-COD (k_3) as well as the isomerization of 1,4- to 1,5-COD (k_5) significantly increased over PAA-Pd, while both k_3 and k_5 decreased with CO-Pd. The increase in the maximum yield of 1,4-COD over CO-Pd, compared to the case with Pd, results from greater decreases in k_1 and k_4 relative to the decrease in k_3. The hydrogenation rate constant of COE (k_2)

Table 1. Kinetic Data for the Hydrogenation of 1,5-Cyclooctadiene over Pd Catalysts/Effects of Phenylacetaldehyde and Carbon Monoxide

Additive	k_1	k_2	k_3	k_4	k_5	COE_{MAX}	$1,4\text{-}COD_{MAX}$	$b_{1,4}/b_{1,5}$[d]	$b_{COE}/b_{1,5}$[d]
	$\times 10^3$ mol min^{-1} (g-Pd)$^{-1}$[c]					%	%		
None[a]	10.0	1.70	7.0	12.7	0.66	93.5	11.2	2.2	0.14
PAA[b]	13.6	0.02	30.0	8.3	1.10	98.4	26.1	4.8	0.87
CO[b]	4.0	0.08	4.4	4.3	0.29	96.2	17.1	2.4	0.35

a) 1,5-COD (4×10^{-4} mol) was hydrogenated in THF (1.6 ml) over 2 mg of Pd at 25 °C and 1 atm H_2. b) After prereduction of the catalyst for 20 min with H_2, the catalyst was treated with PAA (196.6 μmol) for 20 min or CO (3.08 μmol) for 10 min. c) For the rate constants k_i's see Scheme 1. d) Ratios of the adsorption coefficient of 1,4-COD or COE to that of 1,5-COD employed in simulations.

Table 2. Hydrogenation of Isomeric Cyclooctadienes over Unpoisoned and Poisoned Palladium Catalysts

Additive	Substrate	k_D[a]	COE_{MAX}	Isomerization to 1,4- or 1,5-COD	b_{COE}/b_{COD}[b]
		$\times 10^3$ mol min^{-1} (g-Pd)$^{-1}$	%	%	
None	1,3-COD	20.0	98.8	0	0.03
	1,4-COD	12.7	95.2	5.2	0.06
	1,5-COD	17.0	93.5	41.2	0.14
PAA[c]	1,3-COD	5.0	99.4	0	0.06
	1,4-COD	8.3	98.3	13.3	0.18
	1,5-COD	43.6	98.4	68.8	0.87
CO[c]	1,3-COD	3.4	99.7	0	0.16
	1,4-COD	4.3	98.0	6.7	0.15
	1,5-COD	8.4	96.2	52.4	0.35

a) Disapperance rate constants of COD's. For 1,5-COD, k_D is k_1+k_3. b) Ratios of the adsorption coefficient of COE to those of COD's. c) See the footnote b) in Table 1.

became very small and the reaction was almost brought to a halt over both the poisoned catalysts. The maximum yield of COE was 96.2% over CO-Pd and 98.4% over PAA-Pd, which were greater than that with Pd (93.5%)

Disapperance Rate Constand (k_D) and Relative Strengths of Adsorption of Isomeric COD's. Table 2 summarizes the rate data for the hydrogenation of isomeric COD's over unpoisoned and poisoned catalysts. In all of the cases the disapperance rate constants of the COD's (k_D) decreased with the poisoned catalysts, except for 1,5-COD with PAA-Pd, where the rate greatly increased due to a remarkable increase in the rate of isomerization to 1,4-COD. The effects to decrease k_D were in the order 1,3>1,4>1,5 with respect to the substrates. The degrees in the decrease of k_D were always greater with CO-Pd than with PAA-Pd.

According to the data from a computer simulation, the ratios of the strength of adsorption ($b_{1,4}/b_{1,5}$ and $b_{COE}/b_{1,5}$) were 2.2 and 0.14, respectively, over Pd (Table 1); $b_{COE}/b_{1,3}$ was also evaluated to be 0.03 from the results of the hydrogenation of 1,3-COD over Pd (Table 2 and Fig. 4). Thus, the order in the strength of adsorption is 1,3-COD (33.3)>1,4-COD (15.7)>1,5-COD (7.1)>COE (1), where the relative values are given in parentheses.

Competitive Hydrogenation of 1,5- or 1,4-COD against 1,3-COD. The competitive hydrogenation of 1,4- or 1,5-COD against 1,3-COD has been carried out (Fig. 5). With Pd, the relative reactivities (K) of 1,3-COD against 1,4-COD and 1,5-COD were evaluated to be 2.94 and 6.22, respectively, from the slopes of a linear relationship of $\log(C_{1,3,0}/C_{1,3})$ vs. $\log(C_{1,4,0}/C_{1,4})$ or $\log(C_{1,5,0}/C_{1,5})$.[10)]

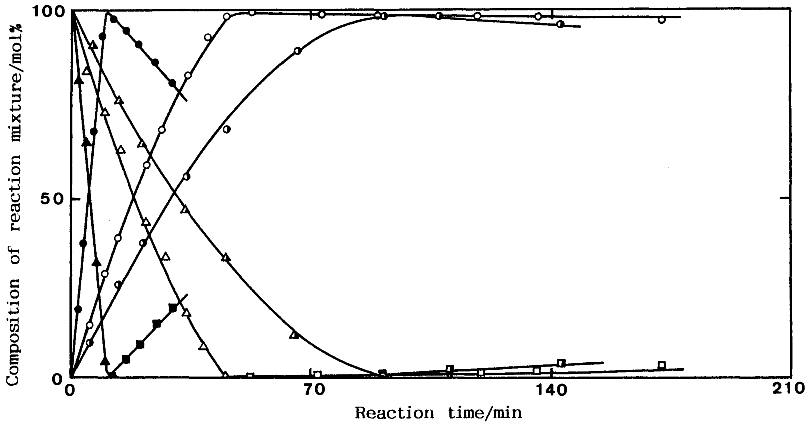


Fig. 4. Hydrogenation of 1,3-COD over various palladium catalysts. Pd (▲: 1,3-COD, ●: COE, ■: COA), PAA-Pd (△: 1,3-COD, ○: COE, □: COA), CO-Pd (◭: 1,3-COD, ◑: COE, ◨: COA). The points are experimental values and the curves were derived from simulations using the values given in Table 2. For the reaction conditions, see footnote a) in Table 1.

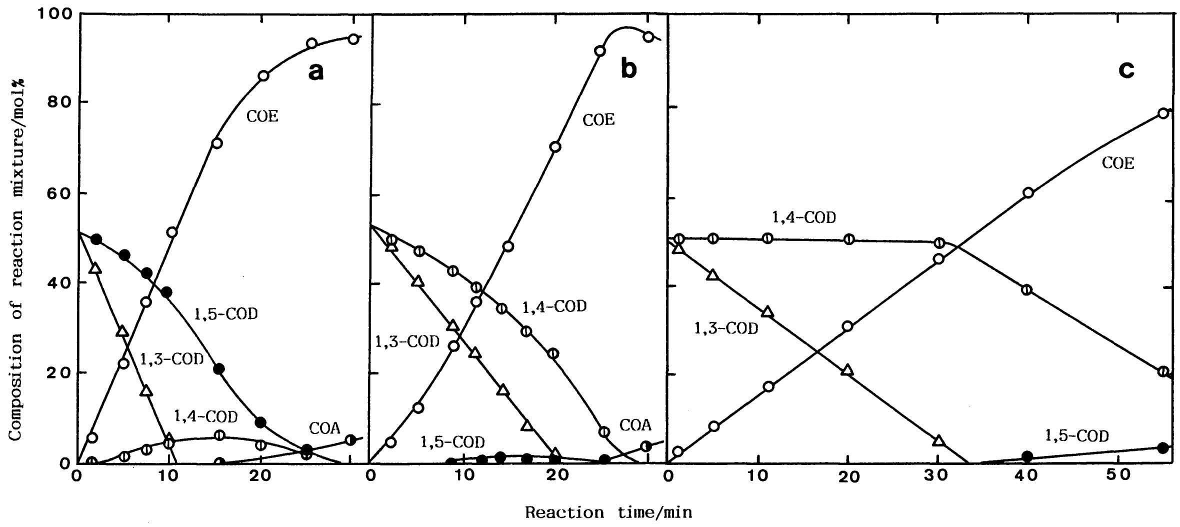


Fig. 5. Competitive hydrogenation of 1,4- or 1,5-COD aginst 1,3-COD. **a**: 1,5- vs. 1,3-COD with Pd. **b**: 1,4- vs. 1,3-COD with Pd. **c**: 1,4- vs. 1,3-COD with Pd-PAA. An equimolar mixture of two COD's (4×10^{-4} mol) was hydrogenated under the reaction conditions described in Table 1.

By employing the values in Tables 1 and 2, the values of K can also be calculated from the relationship $K=k_{1,3}/k_i \times b_{1,3}/b_i$, where subscript i refers to 1,4- or 1,5-COD. The k_D values of 20.0, 12.7, and 17.0 for 1,3- 1,4-, and 1,5-COD, respectively, were used for the respective k's. The K values of 1,3-COD against 1,4- and 1,5-COD (thus calculated) were 3.1 and 5.5, respectively. These values were in fairly good accordance with the corresponding values of 2.94 and 6.22 evaluated from competitive hydrogenation with Pd. That the order in the strengh of adsorption is 1,3->1,4->1,5-COD can also be seen from the results in Fig. 5 (compare Fig. 5a with Fig. 5b), where the hydrogenation of 1,3-COD always occurs preferentially and is depressed more effectively by 1,4-COD than by 1,5-COD. It is noted that, in contrast to hydrogenation with Pd, with PAA-Pd neither 1,4-COD nor 1,5-COD is hydrogenated at all until 1,3-COD is completely consumed, as shown in Fig. 5c for the case of a competitive hydrogenation of 1,3- and 1,4-COD. The relative reactivity of 1,3- to 1,4- or 1,5-COD thus becomes very large in the presence of PAA during competitive hydrogenation. Such a phenomenon is not observed with CO-Pd, though the value of K in the competitive hydrogenation of 1,3-COD against 1,5-COD is as great as 18. Since the relative rate constant of 1,3-COD to 1,4- or 1,5-COD becomes smaller in the presence of PAA (see Table 2), the results (with the observation mentioned above) suggest that 1,3-COD is apparently adsorbed on the catalyst more strongly in the presence of PAA.

During the hydrogenation of 1,4-COD, 1,3-COD was detected in much smaller amounts over PAA-Pd and CO-Pd (see Fig. 3). Since the isomerization of 1,4- to 1,3-COD is not depressed by PAA or CO, the smaller amonts of 1,3-COD detected with the poisoned catalysts also support the view that 1,3-COD is adsorbed relatively more strongly in the presence of PAA or CO than over unpoisoned Pd. By the computer simulation, the value of $b_{1,4}/b_{1,5}$ was estimated to be 4.8 with PAA-Pd, compared to 2.2 with Pd (Table 1). Since the simulation of 1,4-COD includes the reactive 1,3-COD which is produced on the catalyst surface by isomerization of 1,4-COD, the effect of the 1,3-COD to increase the estimated value of $b_{1,4}/b_{1,5}$ becomes greater with PAA-Pd than with Pd, as expected from the results mentioned above.

Table 3 shows the effects of varying the amounts of PAA and CO in the hydrogenation of 1,5-COD. High maximum yields of COE were always attained with PAA-Pd, irrespective of the amounts of added PAA, even when the hydrogenation of COE was not completely depressed. Thus, the high maximum yields of COE over PAA-Pd can not be explained by the depression in the rate of hydrogenation of COE alone. The extensive isomerization to 1,4-COD, and probably further to 1,3-COD, would be a more important factor. These isomerized dienes, which are more strongly adsorbed than 1,5-COD, may prevent the adsorption of COE more effectively over PAA-Pd than over Pd, since the rate of hydrogenation of 1,4-COD, and especially of 1,3-COD, are greatly depressed in the presence of PAA. These characteristics observed with PAA-Pd are not very pronounced over CO-Pd, which gave a lower COE maximum yield of 96.2% in the hydrogenation of 1,5-COD, although a high COE maximum yield of 98.8% was obtained in the hydrogenation of 1,4-COD.

Reactions of PAA on Palladium and the Selectivity of 1,5-COD Hydrogenation. In the hydrogenation of 1,3- and 1,4-COD, decreases of the hydrogenation rates as well as high selectivities for COE were observed over both of the poisoned catalysts. It is interesting that the disapperance rates were depressed to greater extents by the poisons in the case of more strongly adsorbed 1,4- and 1,3-COD. From the described results, many characteristic features of the PAA-Pd catalyzed hydrogenation of 1,5-COD, which differ from CO-Pd catalyzed hydrogenation, could be pointed out. With PAA-

Table 3. Effects of Varying Amounts of Phenylacetaldehyde and Carbon Monoxide in the Hydrogenation of 1,5-Cyclooctadiene

Additive	Amount of PAA[a]	Residual PAA[b]	Toluene produced[c]	Selectivity for toluene[d]	k_D[e]	k_2[f]	Isomerization to 1,4-COD	COE_{MAX}
	µmol	µmol	µmol	%	$\times 10^3$ mol min^{-1} (g-Pd)$^{-1}$		%	%
None	—	—	—	—	17.0	1.70	41.2	93.5
PAA[h]	32.4	13.5	2.18	10.53	21.0	1.20	66.7	97.8
PAA	85.5	60.4	3.89	15.50	41.0	0.11	73.2	98.0
PAA	128.2	103.5	6.14	24.90	43.0	0.06	69.8	98.1
PAA	196.6	165.5	8.37	26.91	43.6	0.02	68.8	98.4
PAA	273.5	243.7	10.30	36.58	30.0	—[i]	73.3	—
CO[h]	1.32	—	—	—	9.6	0.96	48.0	96.6
CO	3.08	—	—	—	8.4	0.08	52.4	96.2
CO	4.40	—	—	—	5.7	—[i]	53.8	—

a) Amount of added PAA to 2 mg of Pd. b) Unreacted PAA after pretreatment of the catalyst with PAA for 20 min. c) Amount of toluene produced during the treatment of the catalyst with PAA. d) Proportion of toluene in the products from PAA. e) Disapperance rate constant of 1,5-COD. f) Rate constant of the hydrogenation of COE. h) See the footnote b) in Table 1. i) The hydrogenation was incomplete even after 5 h.

Pd the isomerization to 1,4-COD (k_3) is greatly increased and k_1 is not influenced (or even increases). However, it was observed that a part of PAA decomposes to produce toluene on the catalyst after pretreatment with PAA. Considerable amounts of phenethyl alcohol and ethylbenzene were also detected in the solvent at the same time. The residual PAA in the reaction mixture was not further hydrogenated in cases where the hydrogenation of COE was completely depressed. Little influence of the by-products on the hydrogenation was confirmed. However, when PAA was added together with 1,5-COD at the same time to the catalyst suspension, the hydrogenation of PAA to phenethyl alcohol occurred extensively with COE hydrogenation after 1,5-COD had been completely converted. In this case, the rate of hydrogenation of COE gradually decreased as the reaction of PAA proceeded. Thus, the decomposition of PAA, which may give CO with toluene, seems to be essential to completely depress the hydrogenation of COE.

It is noted, however, that the addition of CO decreases k_D effectively, even at a much lower amount than that corresponding to the amount of toluene formed from PAA (see Table 3). Further, upon decreasing the amount of CO to 1.32 μmol hydrogenation of COE starts to occur, even thought the hydrogenation of 1,5-COD is seriously depressed, even by such a small amount of CO. There is a possiblilty that a by-product other than CO is produced from PAA on the catalyst together with toluene, even though other products such as methanol and formaldehyde were not detected in the solvent by GLC analysis. Another interpretation of the effect of PAA is that the state of CO formed from PAA on the catalyst is different from that when CO is added to the catalyst. In order to understand the effects of PAA and CO more exactly, further studies are required concerning the influence of these catalyst poisons on adsorbed hydrogen.

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