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Kinetics on the Carbonylation of Cyclohexene in a Methanol Solution Catalyzed by Palladium(II) Chloride–Triphenylphosphine

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Methyl cyclohexanecarboxylate was obtained in high yields by the carbonylation of cyclohexene in a methanol solution using palladium(II) chloride–triphenylphosphine as the catalyst. The effects of variables, such as initial concentration of palladium(II) chloride, pressure of carbon monoxide, and temperature, upon the rate of carbonylation were examined kinetically. A probable reaction mechanism is proposed.

The synthesis of saturated esters from olefins, carbon monoxide and alcohol according to Eq. 1, has been described[1–6] using palladium complexes as catalysts.

$$\mathrm{RCH{=}CH_2 + CO + R'OH \rightarrow RCH(CO_2R')CH_3 + RCH_2CH_2CO_2R'} \qquad (1)$$

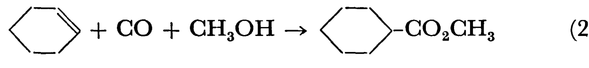
If water is used in place of alcohol, carboxylic acids are produced.[7] Tsuji *et al.*[8,9] proposed the mechanism shown in Scheme 1 for this reaction.

$$\begin{array}{l}
\mathrm{Pd + HCl} \\
\downarrow\uparrow \\
\left.\begin{array}{l}\mathrm{H\text{-}Pd\text{-}Cl} \\ \mathrm{RCH{=}CH_2}\end{array}\right\} \rightleftharpoons \mathrm{RCH_2CH_2PdClL_n} \underset{-\mathrm{CO}}{\overset{\mathrm{CO}}{\rightleftharpoons}} \\
\qquad\qquad \mathrm{RCH_2CH_2COPdClL_n} \rightleftharpoons \\
\qquad\qquad \mathrm{RCH_2CH_2COCl + Pd} \\
\qquad\qquad \downarrow \mathrm{R'OH} \qquad\qquad \text{L: Ligand} \\
\qquad\qquad \mathrm{RCH_2CH_2CO_2R' + HCl}
\end{array}$$

Scheme 1.

Fenton[7] considered the addition of alkoxycarbonyl or carboxyl complexes to olefins. However, very few kinetic studies have been reported on this reaction.

Methyl cyclohexanecarboxylate was obtained in high yields from cyclohexene, carbon monoxide, and methanol according to Eq. 2,



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using palladium(II) chloride–triphenylphosphine as the catalyst. This paper gives the result and a discussion on the mechanism of the reaction.

Results

Preliminary Investigation. Cyclohexene was chosen as the olefin substrate since it gives no isomer. The results of carbonylation of cyclohexene under various conditions are given in Table 1. When methanol was used as the solvent, methyl cyclohexanecarboxylate was obtained in *ca.* 50% yield, a significant amount of colloidal palladium metal being found in the resulting solution. Since the palladium metal recovered was inactive for the carbonylation of cyclohexene, the low yield is attributable to the deactivation of the palladium species. In the solution containing 20% (vol.) of methanol in benzene the yield of ester increased up to 96%, no palladium metal being found during the course of reaction. Deactivation of the palladium species was negligiable.

In addition to methyl cyclohexanecarboxylate, small amounts of cyclohexyl chloride, methyl 2-chlorocyclohexanecarboxylate, and a few unidentified compounds were obtained under the conditions (Table 1). However, the sum of amounts of the remaining cyclohexene and the ester produced accounted for over 98% of the charged cyclohexene. Thus, the amounts of the by-products were neglected.

The solubility of carbon monoxide in the reaction solution was measured, the result being shown in Fig. 1. Henry's constants which were determined from the slopes of linear plots in Fig. 1 are summarized in Table 3.

The effect of stirring speed on the rate of carbonylation was examined to eliminate the effect of diffusion of carbon monoxide into the reaction solution. The yields of ester were independent of the stirring speeds

TABLE 1. CARBONYLATION OF CYCLOHEXENE

Charge[a)]			Conditions			Analysis		Yield[d)] (%)	MB[e)] (%)
CHE[b)] (mmol)	MeOH (ml)	PhH (ml)	P_{CO} (atm)	Temp (°C)	Time (min)	CHE[b)] (mmol)	MCC[c)] (mmol)		
19.7	20	—	54— 38	100	300	—	9.21	46.7	—
24.4	20	—	176—146	100	320	—	14.3	58.7	—
9.86	1	20	44— 40	100	180	9.19	0.54	5.5	98.7
19.7	1	20	52— 47	120	300	16.3	3.19	16.2	98.7
19.7	5	20	49— 31	100	370	3.40	16.3	82.7	99.9
49.3	10	40	50[f)]	120	300	1.20	47.2	95.9	98.2

a) $\mathrm{PdCl_2}$ (1.0 mmol) and $\mathrm{PPh_3}$ (4.0 mmol) were also charged. b) Cyclohexene. c) Methyl cyclohexanecarboxylate. d) Based on the amount of initial CHE. e) Material balance = 100 × (Remaining CHE + Produced MCC)/(Initial CHE). f) The pressure was kept constant during the reaction.

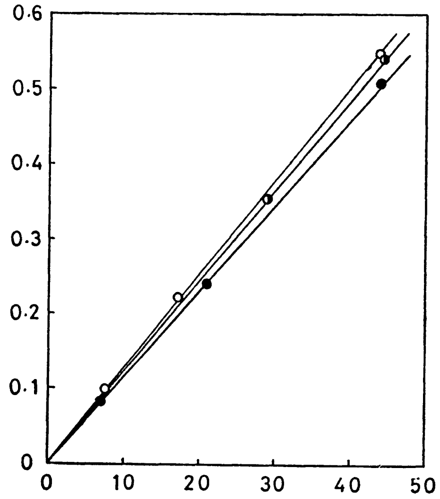


Fig. 1. Solubility of CO.
Cyclohexene 10 ml, MeOH 20 ml, PhH 80 ml, Mesitylene 10ml. Temp: ○ 120, ◑ 110, ● 100 °C.

between 600 and 1000 rpm. Thus, all the kinetic experiments were carried out at about 750 rpm.

Kinetics. The following variables were examined kinetically: initial concentrations of palladium(II) chloride, cyclohexene, and methanol, pressure of carbon monoxide, temperature, and molar ratio of triphenylphosphine to palladium(II) chloride.

A typical time *vs.* yield curve is shown in Fig. 2. The plot of time *vs.* $X=\ln[(\text{CHE})_0/\{(\text{CHE})_0-(\text{MCC})\}]$, where $(\text{CHE})_0$ and (MCC) represent the concentrations of initial cyclohexene and ester produced, gives a straight line after the induction period of 30—60 min as shown in Fig. 3. Thus, except for the induction period of 30—60 min, the empirical formula $X=X_c(t-t_0)$ can be used, where t is reaction time and X_c and t_0 are constants characteristic of the observed straight line. All the kinetic results given in terms of empirical formulas are summarized in Table 2.

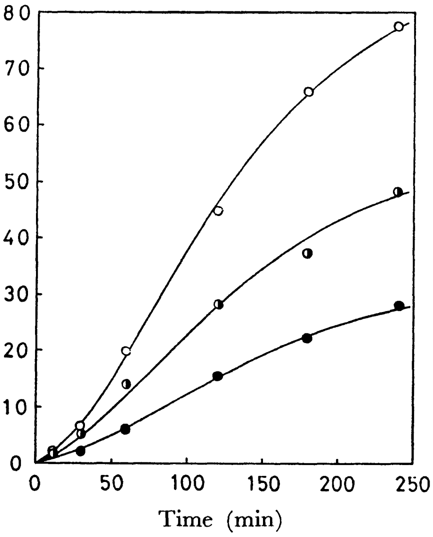


Fig. 2. Time *vs.* yield curve.
$PdCl_2$: ○ 1.66×10^{-2}, ◑ 8.38×10^{-3}, ● 4.83×10^{-3} mol l^{-1}. Other conditions were shown in Table 2. Curves were calculated according to Eq. 19.

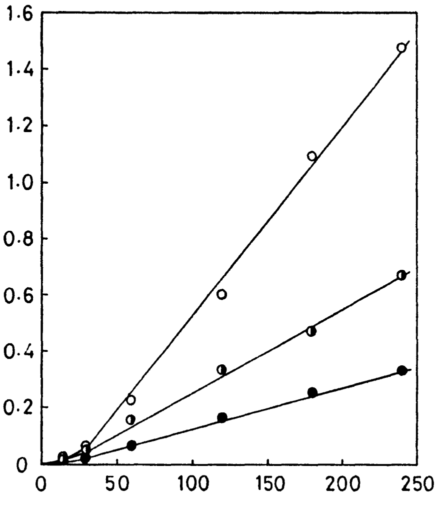


Fig. 3. Time *vs.* X.
Conditions were the same as those in Fig. 2.

TABLE 2. KINETIC DATA

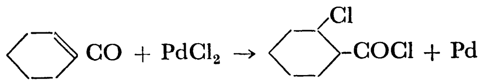
Variables			Empirical equation $X=X_c(t-t_0)$ $X_c\times10^3$	t_0
MeOH Concn[a]	4.12	(mol l^{-1})	7.01	28
	2.07		7.02	28
$PPh_3/PdCl_2$[b]	3.01	(mol/mol)	7.11	28
	4.04		7.01	28
	7.84		6.93	27
CHE Concn[c]	0.822	(mol l^{-1})	7.01	28
	0.657		6.82	28
	0.493		6.94	28
$PdCl_2$ Concn[d]	1.66×10^{-1}	(mol l^{-1})	7.01	28
	8.38×10^{-3}		3.12	12
	4.83×10^{-3}		1.53	19
CO Press.[e] 120 °C	44.5	(atm)	7.01	28
	19.5		4.79	28
	10.5		2.98	30
108 °C	44.5		3.62	16
	21.8		2.85	17
	11.1		2.12	22
100 °C	44.5		2.68	22
	22.2		2.42	30
	11.9		2.03	35

a) $PdCl_2$ 1.70×10^{-2} mol l^{-1}, PPh_3 6.70×10^{-2} mol l^{-1}, CHE 0.822 mol l^{-1}, PhH 40—45 ml, P_{co} 44.5 atm, 120 °C, 750 rpm. b) $PdCl_2$ 1.70×10^{-2} mol l^{-1}, CHE 0.822 mol l^{-1}, MeOH 4.12 mol l^{-1}, PhH 40 ml, P_{co} 44.5 atom, 120 °C, 750 rpm. c) $PdCl_2$ 1.70×10^{-2} mol l^{-1}, PPh_3 6.70×10^{-2} mol l^{-1}, MeOH 4.12 mol l^{-1}, PhH 40—43 ml, P_{co} 44.5 atm, 120 °C, 750 rpm. d) PPh_3 6.70×10^{-2} mol l^{-1}, CHE 0.822 mol l^{-1}, MeOH 4.12 mol l^{-1}, PhH 40 ml, P_{co} 44.5 atm, 120 °C, 750 rpm. e) $PdCl_2$ 1.70×10^{-2} mol l^{-1}, PPh_3 6.70×10^{-2} mol l^{-1}, CHE 0.822 mol l^{-1}, MeOH 4.12 mol l^{-1}, 750 rpm.

When the initial concentration of methanol was reduced to half, both X_c and t_0 remained unchanged, indicating that the rate is independent of the concentration of methanol. Variation of the molar ratio of triphenylphosphine to palladium(II) chloride from 3 to 8 had no effect on either X_c or t_0, indicating that the rate is also independent of the molar ratio. A decrease in the initial concentration of cyclohexene had no effect, indicating that the rate is of first order with respect to the concentration of cyclohexene. In contrast, X_c increased as the initial concentration of palladium(II) chloride increased, while t_0 changed irregularly. An increase in the pressure of carbon monoxide caused X_c to increase, while it changed t_0 irregularly at each temperature. The rise in temperature caused an increase in X_c but hardly any in t_0.

Discussion

Reaction Mechanism. Methyl 2-chlorocyclohexanecarboxylate obtained as a by-product was reported[5] to be produced in the carbonylation of cyclohexene–palladium(II) chloride complex, (cyclohexene–Pd-Cl_2)$_2$, in a methanol solution, but the complex, prepared by the method described by Kharasch *et al.*,[10] decomposed even at room temperature in the methanol–benzene solution, giving the precipitate of palladium metal. It thus appears to be absent under the present reaction conditions. The rapid reaction from 3 to 5, which affords methyl 2-chlorocyclohexanecarboxylate and hydride–palladium intermediate **1**, probably proceeds before the catalytic carbonylation proceeds.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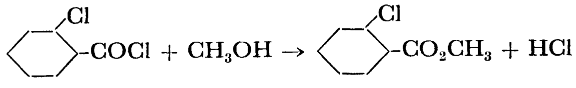
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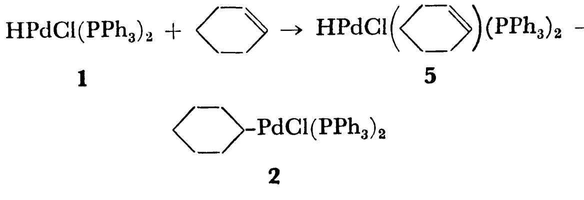
$$Pd + HCl + 2PPh_3 \rightarrow HPdCl(PPh_3)_2 \qquad (5)$$
1

Reactions 3 and 4 have been reported[5] to proceed smoothly even at room temperature. Reaction 5 is also known[11] and complex **1** was prepared[12] from palladium(0) complex and hydrogen chloride. Insertion of the coordinated cyclohexene into the hydrogen-palladium bond in intermediate **1** would give cyclohexyl–palladium intermediate **2** (Reaction 6), which is the converted into cyclohexylcarbonyl–palladium intermediate **3** by the insertion of carbon monoxide (Reaction 7).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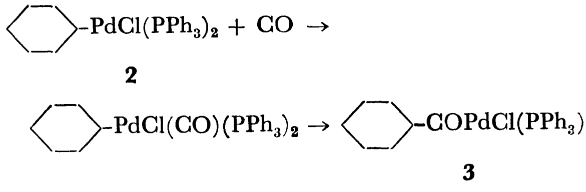
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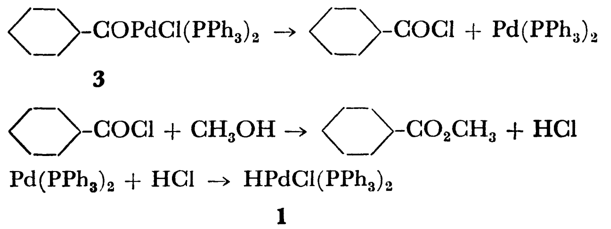
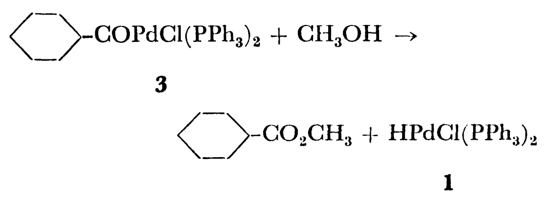
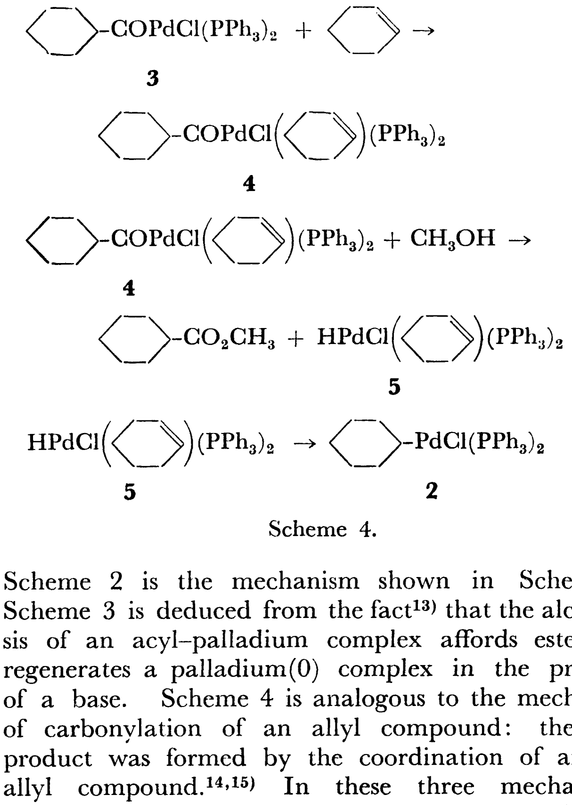
Reactions 6 and 7 have the same mechanisms as in Scheme 1. The following three mechanisms (Schemes 2, 3, and 4) can be inferred as the final process which affords methyl cyclohexanecarboxylate and regenerates the catalyst from intermediate **3**.

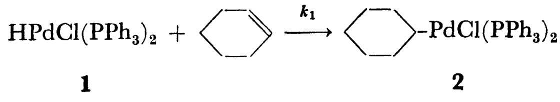

Scheme 2.


Scheme 3.


Scheme 4.

Scheme 2 is the mechanism shown in Scheme 1. Scheme 3 is deduced from the fact[13] that the alcoholysis of an acyl–palladium complex affords ester and regenerates a palladium(0) complex in the presence of a base. Scheme 4 is analogous to the mechanism of carbonylation of an allyl compound: the final product was formed by the coordination of another allyl compound.[14,15] In these three mechanisms, Scheme 4 seems to be the most probable mechanism to explain the kinetic result in which the rate of carbonylation is proportional to the concentration of cyclohexene.

Thus, the following mechanism is assumed on the basis of the reaction path described above.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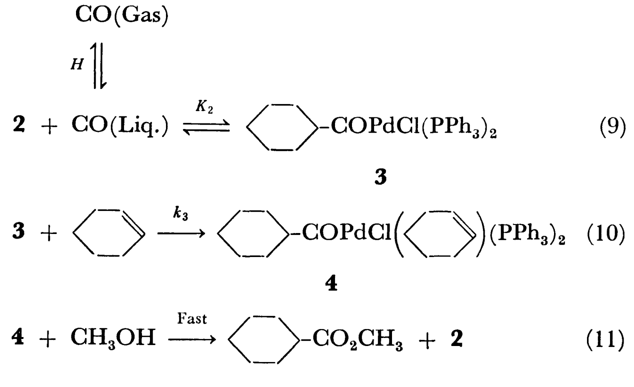

In this mechanism, k_1 and k_3 are the rate constants of Reactions 8 and 10 respectively, and K_2 and H the equilibrium constant of Reaction 9 and Henry's constant of carbon monoxide respectively. The non-catalyzed reaction from 3 to 5, which affords intermediate **1**, is assumed to proceed rapidly. The rate of Reaction 11 is also assumed to proceed rapidly, since the rate of carbonylation was independent of the concentration of methanol.

Rate Equation. The rate equation expressing the production of methyl cyclohexanecarboxylate is derived as follows.

The material balances for palladium species and cyclohexene can be given by,

$$C_1 + C_2 + C_3 \fallingdotseq (\mathrm{PdCl_2})_0 \tag{12}$$

$$(\mathrm{CHE}) + (\mathrm{MCC}) \fallingdotseq (\mathrm{CHE})_0 \tag{13}$$

where C_n is the concentration of intermediate n, and $(\mathrm{PdCl_2})_0$ and (CHE) are the concentrations of palladium(II) chloride charged and remaining cyclohexene, respectively. The equilibrium constant K_2 can be given by,

$$K_2 = \frac{C_3}{C_2HP} \tag{14}$$

where P is the pressure of carbon monoxide. The rate of decreasing concentration of intermediate **1** can be expressed from Reaction 8 as

$$-\frac{\mathrm{d}C_1}{\mathrm{d}t} = k_1C_1(\mathrm{CHE}) \tag{15}$$

where (CHE) should be nearly equal to $(\mathrm{CHE})_0$, since Reaction 8 proceeds as an elementary process of non-catalyzed reaction before the catalytic cycle from Reaction 9 to Reaction 11 proceeds. Thus, Eq. 15 can be written as

$$C_1 = (\mathrm{PdCl_2})_0\mathrm{e}^{-k_1(\mathrm{CHE})_0t} \tag{16}$$

By using Eqs. 12, 14, and 16, the rate of producing methyl cyclohexanecarboxylate is given as follows.

$$\frac{\mathrm{d(MCC)}}{\mathrm{d}t} = k_3C_3(\mathrm{CHE})$$

$$= \frac{k_3K_2HP(\mathrm{PdCl_2})_0(\mathrm{CHE})}{1+K_2HP}\{1-\mathrm{e}^{-k_1(\mathrm{CHE})_0t}\} \tag{17}$$

By substituting Eq. 13 into Eq. 17, the following equation is derived.

$$\ln\frac{(\mathrm{CHE})_0}{(\mathrm{CHE})_0-(\mathrm{MCC})}$$

$$= \frac{k_3K_2HP(\mathrm{PdCl_2})_0}{1+K_2HP}\left\{t - \frac{1-\mathrm{e}^{-k_1(\mathrm{CHE})_0t}}{k_1(\mathrm{CHE})_0}\right\} \tag{18}$$

Thus, the relationship between time and the concentration of methyl cyclohexanecarboxylate is given by

$$(\mathrm{MCC}) = (\mathrm{CHE})_0(1-\mathrm{e}^{-Z}) \tag{19}$$

where

$$Z = \frac{k_3K_2HP(\mathrm{PdCl_2})_0}{1+K_2HP}\left\{t - \frac{1-\mathrm{e}^{-k_1(\mathrm{CHE})_0t}}{k_1(\mathrm{CHE})_0}\right\}$$

Analysis of Kinetic Data. Equation 18 is compared with the kinetic results represented by the empirical formula which gives the relationship between time and X after 30—60 min. The following correlations are obtained by comparison between Eq. 18 and the empirical formula $X=X_c(t-t_0)$.

$$X_c = \frac{k_3K_2HP(\mathrm{PdCl_2})_0}{1+K_2HP} \tag{20}$$

$$t_0 = \frac{1-\mathrm{e}^{-k_1(\mathrm{CHE})_0t}}{k_1(\mathrm{CHE})_0} \tag{21}$$

X_c should be independent of $(\mathrm{CHE})_0$. This is actually the case (Table 2). X_c should be of the

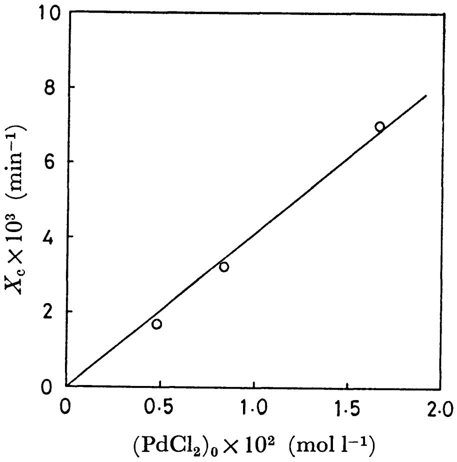

Fig. 4. Relation between $(\mathrm{PdCl_2})_0$ and X_c. Conditions were shown in Table 2.

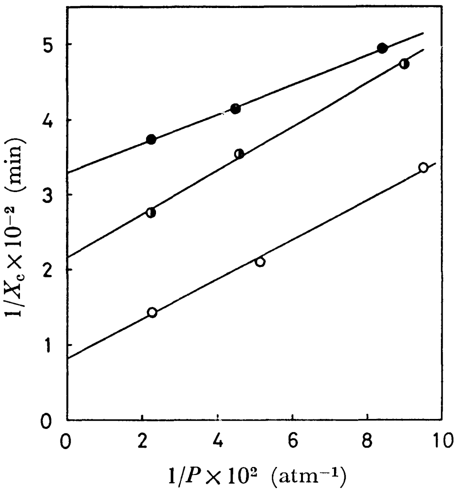

Fig. 5. Relation between $1/P$ and $1/X_c$. Temp: ○ 120, ◑ 108, ● 100 °C. Other conditions were shown in Table 2.

first order with respect to $(\mathrm{PdCl_2})_0$. The kinetic result is in line with the correlation as shown in Fig. 4. If Eq. 20 is written as Eq. 22, the reciprocal of X_c should increase linearly with increasing reciprocal of P.

$$\frac{1}{X_c} = \frac{1}{k_3K_2H(\mathrm{PdCl_2})_0}\cdot\frac{1}{P} + \frac{1}{k_3(\mathrm{PdCl_2})_0} \tag{22}$$

The kinetic result is satisfied with the correlation of Eq. 22 as shown in Fig. 5. On the other hand, the observed values of t_0 is independent of $(\mathrm{CHE})_0$, changing irregularly with the change in $(\mathrm{PdCl_2})_0$, P and temperature (Table 2). The irregularity of observed value of t_0 is related to the assumption that t_0 is constant in the empirical formula, since t_0 is in fact a function containing time as seen in Eq. 21. However, t_0 can be regarded to be constant except for the induction period of 30—60 min, since $\exp\{-k_1(\mathrm{CHE})_0t\}$ in Eq. 21 approaches zero with the elapse of time.

Determination of Constants. The values of k_3 and K_2H can be determined from the linear plots in Fig. 5 by means of Eq. 22. If $\exp\{-k_1(\mathrm{CHE})_0t\}$ is zero, Eq. 21 can be written as

$$t_0 = \frac{1}{k_1(\mathrm{CHE})_0} \tag{23}$$

and the value of k_1 can be estimated from the observed value of t_0. The constants obtained are summarized in Table 3. Their temperature coefficients determined from their Arrhenius plots were obtained as follows: $H=1.26$, $K_2=-18$, and $k_3=22$ kcal mol^{-1}. The value of k_1 was estimated only at 120 °C from the average of t_0 in all the data at 120 °C. From the value of k_1 obtained, $\exp\{-k_1(\mathrm{CHE})_0t\}$ is 0.165 at 60 min when $(\mathrm{CHE})_0$ is 0.822 mol l^{-1}. This indicates that t_0 can be regarded to be constant at and after 60 min.

Table 3. Rate and equilibrium constants

Temp (°C)	H (mol l^{-1} atm^{-1})	K_2 (mol l^{-1})	k_1 (mol^{-1} l min^{-1})	k_3 (mol^{-1} l min^{-1})
120	1.26×10^{-2}	2.5	3.5×10^{-2}	0.75
108	1.21×10^{-2} a)	6.3		0.28
100	1.14×10^{-2}	12		0.18

a) At 110 °C.

Calculated Time-Yield Curve. Equation 18 is compared with the observed values in Fig. 2. By using the constants given in Table 3, theoretical time *vs.* yield curve was calculated by means of Eq. 19. The calculated curves (Fig. 2) are in line with the observed values including the values within 30—60 min. Other calculated curves were also consistent with the observed values over the range of the kinetic experiments at 120 °C.

The proposed mechanism sufficiently satisfies the kinetic results, but the mechanism by way of a methoxycarbonyl intermediate mentioned before does not explain them.

Experimental

Materials. Commercial palladium(II) chloride, triphenylphosphine, methyl cyclohexanecarboxylate, methyl 2-chlorocyclohexanecarboxylate, and cyclohexyl chloride were used without further purification. Cyclohexene, methanol, benzene, and mesitylene were distilled by the usual methods. Carbon monoxide was prepared by decomposing formic acid in hot sulfuric acid, *ca.* 98% purity.

Procedure. Reactions were carried out in a glass-tube placed in a stainless-steel autoclave (*ca.* 200 cm^3) equipped with a Teflon stirrer and a Teflon sampling line.

Palladium(II) chloride(0.2—1 mmol), triphenylphosphine(3—8 mmol), cyclohexene(1—5 ml), methanol(5—10 ml), benzene(40—45 ml) and mesitylene(5 ml) were placed in the autoclave, which was then purged with nitrogen three or four times. The autoclave was heated up to 100—120 °C within 60 min and then maintained over 20 min at the desired temperature. Immediately after carbon monoxide had been pressured to 11—45 atm, stirring (600—1000 rpm) was started, this time being taken as zero time. Stirring was stopped from time to time and a sample (*ca.* 1 ml) was withdrawn through the sampling line into a trap chilled in an ice-bath within 30 s. In order to keep the pressure constant, carbon monoxide was supplied from a reservoir from time to time.

The solubility of carbon monoxide in the reaction medium was measured on the assumption that the solubility in the reaction medium is equal to that in the reaction solution without palladium(II) chloride and triphenylphosphine.

Analysis of Products. The products were identified by comparison of their retention times in gas chromatography with those of authentic samples. A PEG column (2 m, 3 mmø) with a nitrogen carrier was used at 180 °C for the determination of amounts of methyl cyclohexanecarboxylate and cyclohexene with mesitylene as an internal standard.

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