

Kinetic Study of the Carboxymethylation of Aryl Iodides catalyzed by Palladium-Triphenylphosphine Complexes

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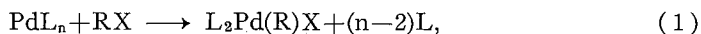
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Carboxymethylation reactions of several para-substituted iodobenzenes catalyzed by palladium-triphenylphosphine compounds were kinetically investigated. Initial rate of reaction (V_0) increased as CO pressure (P_{CO}) was raised but was retarded by application of much higher P_{CO} . Under identical conditions, dependences of V_0 on the initial concentration of aryl iodides ($[ArI]_0$) became smaller as the electron withdrawing properties of para substituents increased, for example under 1 atm of CO, apparent order of V_0 on $[ArI]_0$ was observed to vary successively 1 to 0. Dependences of V_0 on $[ArI]_0$ became larger as P_{CO} was raised. Addition of PPh_3 retarded the reaction rate, but in the presence of large excess PPh_3 , V_0 was of the first order with respect to the concentration of the catalyst ($[Pd]_0$) though the deactivation of the catalyst under higher $[Pd]_0$ was observed when excess PPh_3 was not present. A mechanism including oxidative addition of aryl iodides to Pd(0) complexes and carbonyl insertion reactions of Pd(II)-aryl compounds, was considered and the rate equation was derived to reasonably interpret the above-mentioned observations.

KEY WORDS: Carbonylation/ Carbon monoxide reaction/ Aryl iodide/
Catalytic reaction

INTRODUCTION

Though palladium catalyzed carbonylation reactions of aryl, vinyl, benzyl or other halides¹⁻⁵⁾ are important in synthetic respects, these reactions have also been interested from the standpoint of their reaction mechanisms. These reactions have been considered to be composed of two principal reactions, the oxidative addition of halides to Pd(0) species initially added or formed *in situ* from Pd(II) compounds,



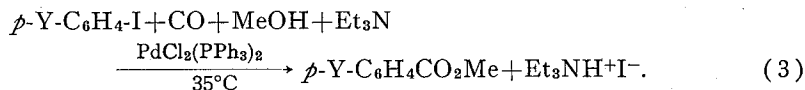
and the subsequent insertion of CO into the resultant palladium-carbon bonds,



Many studies have been made on the intermediate complexes of these reactions⁶⁾, in case of aryl halides for example, detailed mechanisms of the oxidative addition reaction of aryl halides to Pd(0) complexes^{7,8)} and the CO insertion reaction of Pd(II)-aryl compounds^{9,10)} were already clarified. Very interestingly, the effects of para substituents on these reactions were reported to be quite the reverse, namely the acceleration of the former by the electron withdrawing substituents and the retardation of CO insertion by them. We have taken an interest in how these opposite influences are revealed in

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the catalytic reactions. Though some author referred to the substituent effects on this catalytic reaction²⁾, their results are only qualitative ones and include the possibly diffusion-controlled data, and it seems almost impossible to discuss the mechanism in detail. For these reasons, we studied this catalytic reaction kinetically using several para-substituted iodobenzenes as substrates,



RESULTS AND DISCUSSION

Carboxymethylation reactions of aryl iodides were carried out at 35°C under the constant CO pressure (P_{CO}) using $\text{PdCl}_2(\text{PPh}_3)_2$ as a catalyst precursor and triethylamine as a base. Methanol and triethylamine were used in such excess that their concentrations would be invariable throughout the reaction. Benzene was added to dissolve aryl iodides. The ratio of methanol, triethylamine and benzene was 10 : 1 : 10 (vol.). In all cases, no detectable by-product was observed by gas chromatography.

The effect of P_{CO} The effect of P_{CO} on the initial rate (V_0) of the carboxymethylation of methyl *p*-iodobenzoate (MTB) was examined and shown in fig. 1. It was found that relatively lower P_{CO} values brought about maximum rates. Although the retardation effect on the entitled reaction has not been reported yet¹¹⁾, similar inhibition by higher CO concentration are well known in some catalytic reactions of CO, e.g. hydroformylation reaction of olefins¹²⁾ and nickel-catalyzed carboxylation of aryl halides.¹³⁾ In the latter case, this effect was interpreted as follows; the coordinatively unsaturated $\text{Ni}(\text{CO})_3$ equilibrated with $\text{Ni}(\text{CO})_4$ can only undergo the oxidative addition reaction with aryl halides, so the increase of P_{CO} decreases the concentration of reactive $\text{Ni}(\text{CO})_3$ and consequently retards the rate. Similar circumstances must be revealed in the present case. Then, we supposed the formation of **7** under higher P_{CO} and the

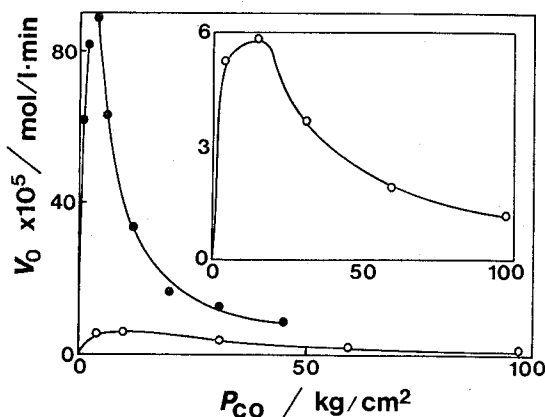
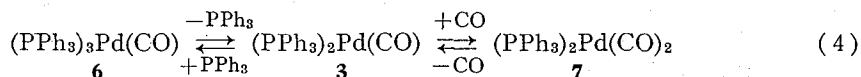


Fig. 1. Effect of P_{CO} on V_0 of MIB carboxymethylation
 $[\text{MIB}]_0 = 2.87 \times 10^{-2} \text{ mol/l}$, $[\text{Pd}]_0 = 5.73 \times 10^{-4} \text{ mol/l}$, temp. 35°C,
 ○: $[L]_0 = 9.53 \times 10^{-3} \text{ mol/l}$, ●: $[L]_0 = 0$.

inertness of both **7** and **6**⁴⁾ to aryl iodides. The formation of **7** under higher P_{CO} was reportedly confirmed by IR measurement at high pressure.¹⁴⁾



The facts, that V_0 were considerably reduced by the application of excess P_{CO} or by the addition of PPh_3 and that excess PPh_3 increased P_{CO} causing the maximum V_0 , indicate the occurrence of the competitive coordinations of CO and PPh_3 as shown by the proposed eq. 4.

Table I shows the pressure effects on the carboxymethylation of *p*-iodonitrobenzene (INB) and *p*-iodobenzonitrile (IBN) in the presence of excess PPh_3 . Similar retardation by CO was observed. The pressure causing the maximum V_0 increased in the order of MIB, IBN, INB. This order parallels the electron withdrawing properties of the *para* substituents.

PPh₃ concentration The effect of added PPh_3 on V_0 of MIB carboxymethylation was examined under 1 atm** and 31 kg/cm² of CO (fig. 2). In both cases, V_0 were retarded by the addition of PPh_3 , but under 31 kg/cm² of CO, less retardation effect

Table I. Effect of P_{CO} on V_0 of the carboxymethylation of *p*-iodonitrobenzene(INB) and *p*-iodobenzonitrile(IBN)¹⁾

Run	ArI	P_{CO} kg/cm ²	$Y = t/(az + b) + c$			V_0 10 ⁵ mol/l min
			a	b	c	
N-1 ²⁾	IBN	5	—	—	—	1.88
N-2 ²⁾		10	—	—	—	3.40
N-3 ²⁾		15	—	—	—	4.25
N-4		31	0.0088	4.47	0	6.41
N-5		59.5	0.0082	4.18	0.4	6.84
N-6		97	0.0093	4.96	0.4	5.77
N-7		124	0.0078	6.31	0.6	4.54
N-8		151	0.0106	7.76	0.2	3.69
C-1 ²⁾	IBN	5	—	—	—	3.45
C-2		10	0.0036	4.93	0	5.79
C-3		20	0.0038	4.28	0.3	6.68
C-4		31	0.0054	4.25	0.6	6.73
C-5		45	0.0046	4.79	1.1	5.98
C-6		59.5	0.0060	5.60	0.9	5.11
C-7		79	0.0061	7.27	1.2	3.91
C-8		97	0.0070	9.40	1.1	3.04

1) $[\text{ArI}]_0 = 2.86 \times 10^{-2}$ mol/l, $[\text{Pd}]_0 = 5.71 \times 10^{-4}$ mol/l, $[\text{L}]_0 = 9.51 \times 10^{-3}$ mol/l, Temp. 35°C, MeOH: Et₃N: PhH = 10 : 1 : 10 (vol.) mixed solvent.

2) Pseudo-zeroth order time-yield curve was obtained and V_0 was calculated directly from it.

** 1 atm = 1.01325×10^5 Pa = 1.033 kg/cm². In this paper, we used the term 1 atm of CO to denote the reaction conducted where P_{CO} plus vapor pressure of solvents equal 1 atm.

Carboxymethylation of aryl iodides

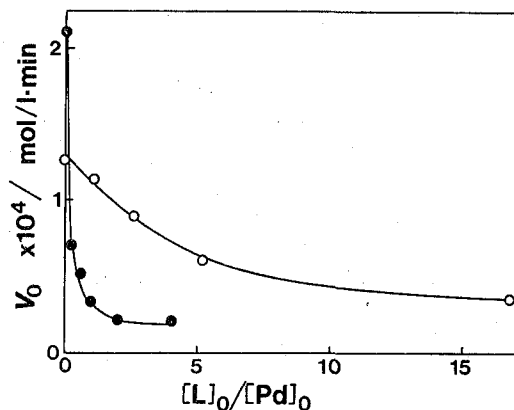


Fig. 2. Effect of added PPh_3 on V_0 of MIB carboxymethylation (Temp. 35°C)
 \circ : $P_{\text{CO}}=31 \text{ kg/cm}^2$, $[\text{MIB}]_0=2.86 \times 10^{-2} \text{ mol/l}$, $[\text{Pd}]_0=5.71 \times 10^{-4} \text{ mol/l}$,
 \bullet : $P_{\text{CO}}=1 \text{ atm}$, $[\text{MIB}]_0=1.43 \times 10^{-2} \text{ mol/l}$, $[\text{Pd}]_0=2.86 \times 10^{-4} \text{ mol/l}$.

was observed. This is considered to indicate the competitive interaction of CO and PPh_3 with Pd species in this system.

Initial concentration of aryl iodides ($[\text{ArI}]_0$) In order to grasp the outline of the substituent effect, reactions under 1 atm of CO were conducted by the use of *p*-iodotoluene (IT), *p*-chloriodobenzene (CIB), MIB and INB as substrates (fig. 3). When the reactions were initiated by the addition of $\text{PdCl}_2(\text{PPh}_3)_2$, rapid absorption of CO (ca. 1-2 equivalent to Pd) was always observed. After 0.5-1 min. of this absorption, slow and steady up-take of CO was attained and this amount of up-take was proved to be equal to the amount of produced ester. In the case of INB, these CO up-take curves were straight and their tangents were not affected by the initial concentration of INB. Whereas, CO up-take curves for MIB, CIB and IT were not straight and the reaction rates changed with time. Some decomposition of the catalyst to metal were observed, especially in the case of IT carboxymethylation. From time-CO absorption curves, V_0

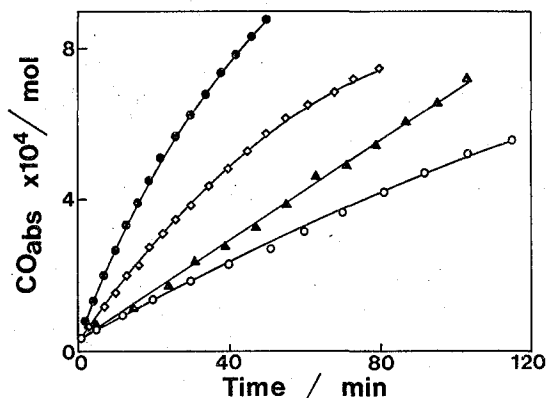


Fig. 3. Carboxymethylation of Aryl Iodides under 1 atm of CO
 $[\text{ArI}]_0=1.43 \times 10^{-2} \text{ mol/l}$, $[\text{Pd}]_0=2.86 \times 10^{-4} \text{ mol/l}$, Temp. 35°C ,
 \circ : IT, \diamond : CIB, \bullet : MIB, \blacktriangle : INB.

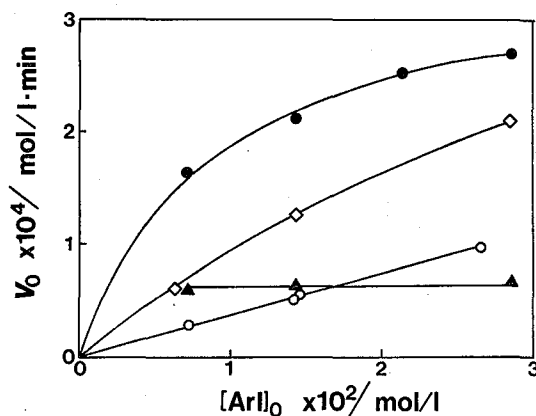
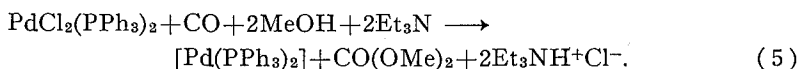


Fig. 4. Effect of $[\text{ArI}]_0$ on V_0 under 1 atm of CO
 $[\text{Pd}]_0 = 2.86 \times 10^{-4}$ mol/l, Temp. 35°C,
 ○: IT, ◇: CIB, ●: MIB, ▲: INB.

were calculated and plotted against $[\text{ArI}]_0$ (fig. 4). The respective apparent orders of V_0 to $[\text{ArI}]_0$ were 0 for INB, 0.3 for MIB, 0.8 for CIB, and 1 for IT, and this shows the tendency for the reaction order to increase with the decrease in the electron-withdrawing properties of the para substituents. In our experimental conditions, the highest V_0 was observed for MIB. Above-mentioned observation carries a significant implication when they are considered in the light of the facts of stoichiometric oxidative addition⁸⁾ and carbonyl insertion¹⁰⁾ reactions (see introduction). When INB possessed of a very strong electron-withdrawing nitro group at the para position was used as substrate, oxidative addition was much faster than CO insertion and the latter reaction became the rate determining step. Hence, the reaction rate is independent of INB concentration. In the presence of electron-donating para-methyl group, however, oxidative addition was rate determining and V_0 was of first order as to the initial concentration of IT. In the case of MIB or CIB, the rates of the two reactions were comparable, and the respective overall rate was expressed in the intermediate order between those of INB and IT regarding the substrate concentration. From the above discussions, the fact of the highest relative rate for MIB can be easily understood. Rapid CO up-take in the first stage of the reaction could be attributed to the generation of Pd(0) species possibly by the stoichiometry¹⁵⁾ of



Then, carboxymethylation of MIB was attempted under 31 kg/cm² of CO (figs. 5 and 6). Apparent order of V_0 to the initial concentration of MIB was 0.8 in the absence of PPh₃ and 0.7 in the presence of excess PPh₃. Table II shows the relation of V_0 , with initial concentrations of IBN and INB, and P_{CO} . Dependences of V_0 on $[\text{ArI}]_0$ became larger as P_{CO} was raised. These effects would be well understood with the following considerations; under higher P_{CO} , the concentrations of Pd(0) species are supposed to increase by the formation of **7** and other Pd(0) species in equilibrium with **7**, and then

Carboxymethylation of aryl iodides

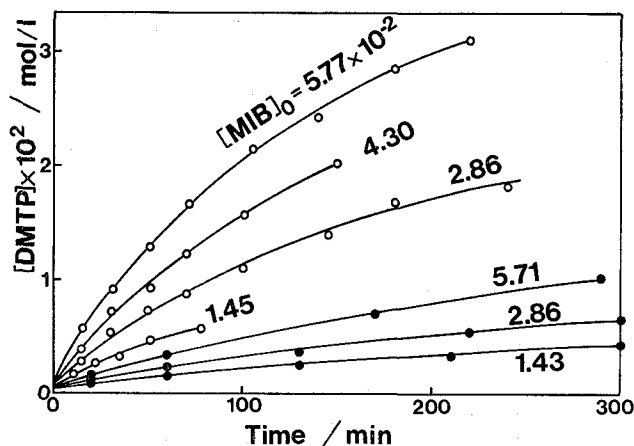


Fig. 5. Time-yield curves of the carboxymethylation of MIB to dimethyl terephthalate (DMTP)

$[Pd]_0 = 5.73 \times 10^{-4}$ mol/l, $P_{CO} = 31$ kg/cm², Temp. 35°C,

● : $[L]_0 = 9.52 \times 10^{-3}$ mol/l, ○ : $[L]_0 = 0$.

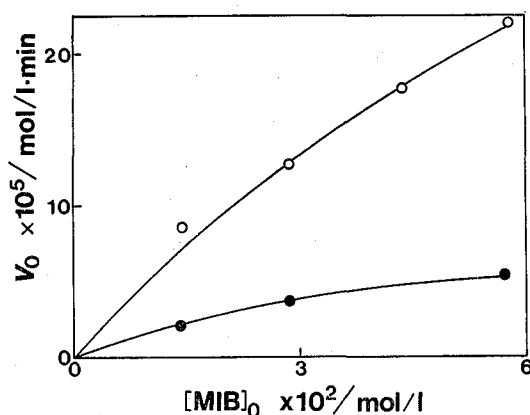


Fig. 6. Effect of the initial concentration of MIB ($[MIB]_0$) on V_0 under compressed CO

$[Pd]_0 = 5.73 \times 10^{-4}$ mol/l, $P_{CO} = 31$ kg/cm², Temp. 35°C,

● : $[L]_0 = 9.52 \times 10^{-3}$ mol/l, ○ : $[L]_0 = 0$.

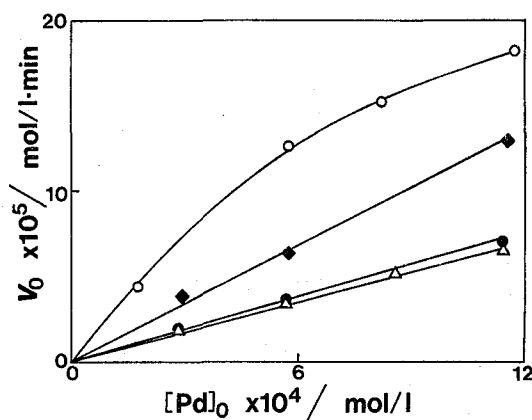
the contribution of oxidative addition reactions of Pd(0) species with aryl iodides to the overall rate are conjectured to increase. These effects will be further discussed in the kinetic section.

Concentration of $PdCl_2(PPh_3)_2$ The effect of the initial concentration of $PdCl_2(PPh_3)_2$ ($[Pd]_0$) on V_0 were examined under compressed CO by using MIB, IBN and INB as substrates. From fig. 7, it can be concluded that in the presence of excess PPh_3 , V_0 was of the first order as to $[Pd]_0$. In no employment of excess PPh_3 , linear relation was not observed and this is considered to indicate the formation of inactive polynuclear Pd(0) species such as $Pd_3(CO)_3(PPh_3)_3$ and $Pd_3(CO)_3(PPh_3)_4$ ^{17,18)} which exist in equilibrium with mononuclear Pd(0) species.

Table II. Effects of the initial concentrations of *p*-iodonitrobenzene(INB) and *p*-iodobenzonitrile(IBN) on V_0 ¹⁾

Run	ArI	P_{CO}	$[ArI]_0$	$Y = t/(at+b)+c$			V_0
		kg/cm ²	10 ² mol/l	a	b	c	10 ⁵ mol/l min
N-9 ²⁾	INB	10	1.43	—	—	—	3.43
N-2 ²⁾		10	2.86	—	—	—	3.40
N-10 ²⁾		10	5.71	—	—	—	3.58
N-11	IBN	31	1.43	0.0073	2.51	0	5.69
N-4		31	2.86	0.0088	4.47	0	6.41
N-12		31	5.71	0.0029	8.41	0	6.79
N-13		124	1.44	0.0085	5.09	1.3	2.83
N-7		124	2.86	0.0078	6.31	0.6	4.54
N-14		124	5.71	0.0107	9.28	0.3	6.17
C-9		31	1.45	0.0058	2.41	1.0	6.01
C-4		31	2.86	0.0054	4.25	0.6	6.37
C-10		31	5.70	0.0049	8.21	0.4	6.96
C-11		79	1.39	0.0062	5.94	2.4	2.34
C-7		79	2.86	0.0061	7.27	1.2	3.95
C-12		79	4.29	0.0071	8.57	0.9	5.01
C-13		79	5.71	0.0187	9.63	0.6	5.94
C-14		97	1.43	0.0074	7.92	2.1	1.80
C-8	97	2.86	0.0070	9.40	1.1	3.04	
C-15	97	5.71	0.0113	11.5	0.5	4.97	

- 1) $[Pd]_0 = 5.71 \times 10^{-4}$ mol/l, $[L]_0 = 9.52 \times 10^{-2}$ mol/l, Temp. 35°C, MeOH: Et₃N: PhH = 10 : 1 : 10 (vol.) mixed solvent.
- 2) Pseudo-zeroth order time-yield curve was obtained and V_0 was calculated directly from it.

Fig. 7. Effect of the initial concentration of catalyst ($[Pd]_0$) on V_0 (Temp. 35°C)

- : $[MIB]_0 = 2.86 \times 10^{-2}$ mol/l, $[L]_0 = 0$, $P_{CO} = 31$ kg/cm²,
- : $[MIB]_0 = 2.86 \times 10^{-2}$ mol/l, $[L]_0 = 9.52 \times 10^{-3}$ mol/l, $P_{CO} = 31$ kg/cm²,
- ◆ : $[IBN]_0 = 2.86 \times 10^{-2}$ mol/l, $[L]_0 = 9.52 \times 10^{-3}$ mol/l, $P_{CO} = 31$ kg/cm²,
- △ : $[INB]_0 = 2.86 \times 10^{-2}$ mol/l, $[L]_0 = 9.52 \times 10^{-3}$ mol/l, $P_{CO} = 10$ kg/cm².

KINETIC EXPRESSION AND REACTION MECHANISM

Consulting Stille's proposal⁶), we propose the mechanism (scheme 1) in order to explain our experimental facts. The reverse reactions of oxidative addition were all ignored because the reductive elimination seems to be unimportant at least in the stoichiometric reactions of aryl halides.⁹⁾ This scheme is so complicated that it is almost impossible to obtain the complete rate equation. So, we confined our aim to obtaining the rate equation on condition of a large excess presence of PPh_3 . In this condition, the amount of polynuclear $\text{Pd}(0)$ can be considered to be negligibly small because the reaction rate is of the first order with regard to $[\text{Pd}]_0$. According to the reports by Heck and co-workers^{9,10)} we assumed the complexes **12** and **13** ligating only one PPh_3 to be excluded and further the concentration of **4** to be negligible in the presence of excess PPh_3 . The steps for methanol or triethylamine to react with palladium complexes must be very fast because of a large excess addition of methanol and triethylamine. Here we assumed the equilibria among $\text{Pd}(0)$ complexes **1**, **2**, **3**, **5**, **6** and **7** and applied the steady-state approximation to the formation of $\text{Pd}(\text{II})$ species **9**, **10** and **11**. The material balance for palladium can be expressed as

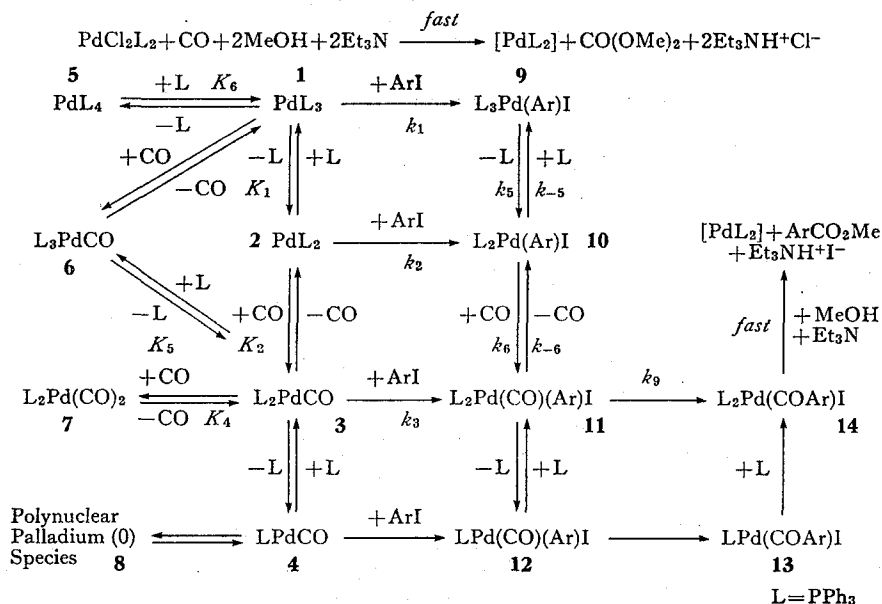
$$[\mathbf{1}] + [\mathbf{2}] + [\mathbf{3}] + [\mathbf{5}] + [\mathbf{6}] + [\mathbf{7}] + [\mathbf{9}] + [\mathbf{10}] + [\mathbf{11}] \doteq [\text{Pd}]_0, \quad (6)$$

where $[\mathbf{n}]$ represents the concentration of intermediate **n**. The concentration of free $\text{PPh}_3([\text{L}])$ is then expressed as

$$[\text{L}] \doteq [\text{L}]_0 - [\mathbf{1}] - [\mathbf{6}] - 2[\mathbf{5}] \doteq [\text{L}]_0, \quad (7)$$

and is approximately equal to the initial concentration of added $\text{PPh}_3([\text{L}]_0)$. The initial rate of the ester formation V_0 which is expressed as

Scheme 1



$$V_0 = \frac{d[\text{ester}]}{dt} \doteq k_9[\mathbf{11}], \quad (8)$$

is calculated approximately to be

$$V_0 \doteq \left\{ \left(k_1 + \frac{k_2 K_1}{[L]_0} \right) [\text{CO}] + \frac{k_3 K_1 K_2}{[L]_0} [\text{CO}]^2 \right\} \frac{[\text{Pd}]_0 [\text{ArI}]_0}{\alpha [\text{CO}]^3 + \beta [\text{CO}]^2 + \gamma [\text{CO}] + \delta}. \quad (9)$$

Here, $[\text{CO}]$ stands for the concentration of CO dissolved in the solution, and α , β , γ and δ involve the concentration terms of $[\text{ArI}]_0$ and $[L]_0$ as shown below,

$$\begin{aligned} \alpha &= \frac{K_1 K_2 K_4}{[L]_0}, & \beta &= K_1 K_2 K_5 + \frac{K_1 K_2}{[L]_0} + \frac{k_3 K_1 K_2}{k_9 [L]_0} [\text{ArI}]_0, \\ \gamma &= 1 + \frac{k_1}{[L]_0} + K_6 [L]_0 + \left\{ \frac{k_1}{k_5} + \frac{k_1}{k_9} + \frac{k_2 K_1}{k_9 [L]_0} + k_3 K_1 K_2 \left(\frac{k_{-6}}{k_6 k_9 [L]_0} + \frac{k_{-5} k_{-6}}{k_5 k_6 k_9} \right) \right\} [\text{ArI}]_0, \\ \delta &= \left(k_1 + \frac{k_2 K_1}{[L]_0} \right) \left(\frac{k_6}{1} + \frac{k_{-6}}{k_6 k_9} + \frac{k_{-5} [L]_0}{k_5 k_6} + \frac{k_{-5} k_{-6} [L]_0}{k_5 k_6 k_9} \right) [\text{ArI}]_0. \end{aligned}$$

Requirement by eq. 9 is the proportionality between V_0 and $[\text{Pd}]_0$ and this is in agreement with the experimental fact as mentioned before.

P_{CO} dependence The dependence of V_0 on P_{CO} , that is, the acceleration of the rate at the lower pressure and the retardation at the higher pressure, can be easily explained by eq. 9, because the denominator of eq. 9 is of the second order and the numerator of the third order with respect to $[\text{CO}]$. As eq. 9 is of much complicated form and it is almost impossible to obtain more information than above, further approximation must be made to compare the observations with the scheme. From fig. 8 which shows the plots of V_0^{-1} vs. P_{CO} in the presence of excess PPh_3 under the relatively higher P_{CO} , linear relationships are seen. From this, the following relations of inequality can be valid for the denominator and numerator of eq. 9 when P_{CO} is higher,

$$\begin{aligned} k_1 + \frac{k_2 K_1}{[L]_0} [\text{CO}] &\ll \frac{k_3 K_1 K_2}{[L]_0} [\text{CO}]^2, \\ \alpha [\text{CO}]^3 + \beta [\text{CO}]^2 &\gg \gamma [\text{CO}] + \delta. \end{aligned} \quad (10)$$

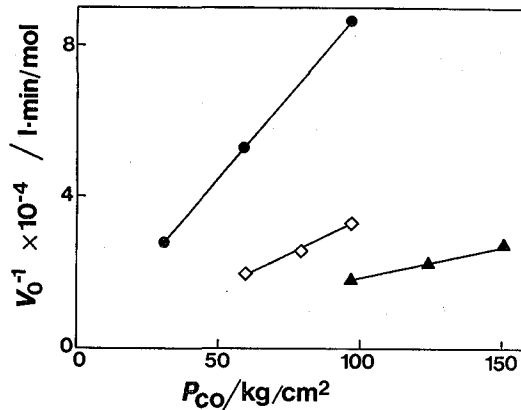


Fig. 8. Plot of V_0^{-1} against P_{CO}
 $[\text{ArI}]_0 = 2.86 \times 10^{-2} \text{ mol/l}$, $[\text{Pd}]_0 = 5.71 \times 10^{-4} \text{ mol/l}$,
 $[L]_0 = 9.52 \times 10^{-3} \text{ mol/l}$, Temp. 35°C ,
 ●: MIB, ◇: IBN, △: INB.

Thus, the reciprocal of eq. 9 is reduced to eq. 11 by the use of eq. 10,

$$V_0^{-1} = \frac{1}{[Pd]_0} \left(\frac{K_4[CO]}{k_3[ArI]_0} + \frac{K_5[L]_0}{k_3[ArI]_0} + \frac{1}{k_3[ArI]_0} + \frac{1}{k_9} \right). \quad (11)$$

We made the following examination as to the validity for the experimental facts. The gradient of the plot of V_0^{-1} vs. P_{CO} is expressed as $K_4/k_3[ArI]_0[Pd]_0$ and if the concentration terms, $[ArI]_0$ and $[Pd]_0$ are the same, the gradient would be proportional to k_3^{-1} , the velocity constant of oxidative addition, as the equilibrium constant of Pd(0) carbonyls, K_4 , is not affected by the changes of aryl iodides. The gradients of these plots increased in the order of INB, IBN, MIB as shown in fig. 8, indicating that k_3 becomes larger as the electron-withdrawing properties of para substituents increase. This tendency is in accordance with the facts observed in the studies of the stoichiometric oxidative addition reaction of aryl halides to Pd(0) complexes⁹. The values of k_3/K_4 for INB, IBN and MIB were calculated as 340, 170 and 69 (in mol·kg/l·min·cm²) respectively.

Relation between V_0 , $[ArI]_0$ and P_{CO} Rearranging eq. 9 with respect to $[ArI]_0$, the relation of $[ArI]_0$ and V_0 is formulated as,

$$V_0^{-1} = \frac{1}{\epsilon[Pd]_0} \left(\frac{\zeta}{[ArI]_0} + \eta \right) \quad (12)$$

where ϵ , ζ and η ¹⁰ comprise concentration terms of $[CO]$ and $[L]_0$. According to eq. 12, the linear relationship should be expected between V_0^{-1} and $[ArI]_0^{-1}$. As shown in figs. 9 and 10, this was proved to be valid for each of six examined cases at the fixed conditions of P_{CO} , $[L]_0$ and $[Pd]_0$. Next is the consideration of the gradient and the intercept. Firstly, the gradient of each straight line should correspond to $\zeta/\epsilon[Pd]_0$ of eq. 12, in which ζ and ϵ are the functions of the first order and the second order as to $[CO]$ respectively. Therefore, the gradient should increase with an increase in P_{CO} . Secondly, the intercept of this plot ($\zeta/\epsilon[Pd]_0$) in which the numerator and the denomin-

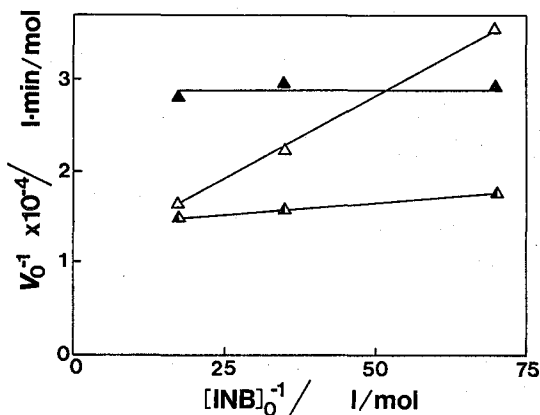


Fig. 9. Plot of V_0^{-1} against $[INB]_0^{-1}$
 $[Pd]_0 = 5.71 \times 10^{-4}$ mol/l, $[L]_0 = 9.52 \times 10^{-2}$ mol/l, Temp. 35°C,
 \blacktriangle : $P_{CO} = 10$ kg/cm², \triangle : $P_{CO} = 31$ kg/cm², \triangle : $P_{CO} = 124$ kg/cm².

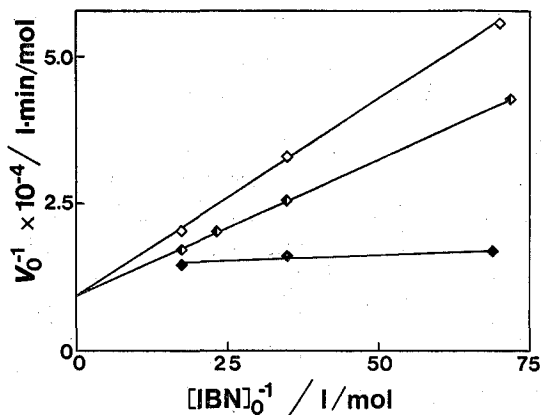


Fig. 10. Plot of V_0^{-1} against $[\text{IBN}]_0^{-1}$
 $[\text{Pd}]_0 = 5.71 \times 10^{-4} \text{ mol/l}$, $[\text{L}]_0 = 9.52 \times 10^{-3} \text{ mol/l}$, Temp. 35°C ,
 \blacklozenge : $P_{\text{CO}} = 31 \text{ kg/cm}^2$, \blacklozenge : $P_{\text{CO}} = 79 \text{ kg/cm}^2$, \diamond : $P_{\text{CO}} = 97 \text{ kg/cm}^2$.

ator are both of the second order as to $[\text{CO}]$, should converge to $1/k_9[\text{Pd}]_0$ where eq. 10 holds. Experimental facts were all in agreement with these two requirements as typically shown in fig 10, where the gradients increased as P_{CO} was raised and the intercepts were equal under 79 kg/cm^2 and 97 kg/cm^2 of CO. We obtained k_9 values as 0.23 min^{-1} (MIB at 31 kg/cm^2 of P_{CO}) 0.20 min^{-1} (IBN at 79 and 97 kg/cm^2 of P_{CO}) and 0.18 min^{-1} (INB at 124 kg/cm^2 of P_{CO}). No significant differences have been found out among k_9 values of three Pd(II)-aryl complexes, though large differences of the reaction rates were reported¹⁰) in stoichiometric CO insertion of the same Pd(II) complexes. But direct comparison is impossible because the data obtained in a stoichiometric reaction were measured in the absence of excess PPh_3 where dissociative route $12 \rightarrow 13 \rightarrow 14$ predominates.

EXPERIMENTAL

Reagents $\text{PdCl}_2(\text{PPh}_3)_2$ was prepared by the conventional method²⁰). MIB was prepared from its acid with diazomethane as methylating agent and recrystallized twice from methanol. Methanol and benzene were dried over molecular sieves 3A. Other materials were all commercially obtained and used without further purifications. CO was obtained by decomposing formic acid in hot sulfuric acid and compressed by a compressor (purity above 98%) or purchased from a supplier (purity 99.9%)

Procedure of kinetic measurement under compressed CO Reactions were carried out in a glass-lining stainless-steel autoclave (ca. 250 ml) equipped with a Teflon sampling line and a Teflon stirrer. The desired amounts of $\text{PdCl}_2(\text{PPh}_3)_2$, PPh_3 , aryl iodide, methanol, triethylamine and benzene were charged in the autoclave, which was purged with ca. 10 kg/cm^2 of nitrogen for 3 or 4 times. Then, the autoclave was placed in a water bath, maintained at 35°C slowly stirring magnetically for ca. 1h. before reaction. Immediately after CO had been introduced up to the desired pressure, stirring (ca. 1200–1500 rpm) was started and this time was marked as zero time. At a certain

interval of time, a sample (ca. 1ml) was withdrawn through the sampling line into the trap chilled with dry ice-methanol bath within 30 sec. CO was supplied from time to time in order to keep pressure constant.

Procedure of kinetic measurement under 1 atm of CO The reaction vessel placed with the desired amounts of aryl iodides and PPh₃ was purged with CO (purity 99.9%) for 3 times and to it was added the deoxygenated mixture of methanol, triethylamine and benzene. Water thermostated at 35°C, was circulated through the jacket of the reaction vessel and the reaction mixture was stirred magnetically till it reached to the reaction temperature (ca. 1h.). Carboxymethylation reaction was initiated by dropping the Tefron-cup containing PdCl₂(PPh₃)₂ to the reaction mixture and the amount of reacted CO was measured by gas burette. All the reaction runs were conducted under the condition where stirring speed did not affect the reaction rate.

Analysis of products Products were identified by comparison of their retention times with those of authentic samples in gas chromatograph. A PEG 20 M on Celite 545 (2m) or an apiezon grase L on Neosorb NC (1 or 2m) was used for the determination of aryl iodides and para-substituted methyl benzoates with hexamethylbenzene, pentamethylbenzene or durene as an internal standard. Material balances were completely satisfied and no by-produce could be detected.

Determination of V_0 V_0 under 1 atm of CO was determined directly from a time-CO absorption curve. Under compressed CO, we expressed the time-yield curve by the experimental equation

$$Y = t / (at + b) + c$$

(Y; yield of ester, t ; time, **a**, **b**, **c**; constant),

and V_0 was determined to be $1/b$, the differential coefficient of this equation at $t=0$. At the first stage of reactions, rapid reaction was observed particularly under higher P_{CO} as seen in fig. 5. This arises possibly from the rapidness of the reaction rate under lower P_{CO} , because 1-2 min. were needed till the physical dissolution of CO ceased. The constant **c** corresponds to this rapid reaction. But **c** was not so large (see tables 1 and 2) and we assumed the rapid reaction at the first stage did not affect the stationary reaction rate.

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$$\begin{aligned} \varepsilon &= \left(k_1 + \frac{k_2 K_1}{[L]_0} \right) [CO] + \frac{k_3 K_1 K_2}{[L]_0} [CO]^2, \\ \zeta &= \frac{K_1 K_2 K_4}{[L]_0} [CO]^3 + \left(K_1 K_2 K_5 + \frac{K_1 K_2}{[L]_0} \right) [CO]^2 + \left(1 + \frac{K_1}{[L]_0} + K_6 [L]_0 \right) [CO], \\ \eta &= \frac{k_3 K_1 K_2}{k_9 [L]_0} [CO]^2 + \left\{ \frac{k_1}{k_5} + \frac{k_1}{k_9} + \frac{k_9 [L]_0}{k_2 K_1} + k_3 K_1 K_2 \left(\frac{k_{-6}}{k_6 k_9 [L]_0} + \frac{k_{-5} k_{-6}}{k_5 k_6 k_9} \right) \right\} [CO] \\ &\quad + \left(k_1 + \frac{k_2 K_1}{[L]_0} \right) \left(\frac{1}{k_6} + \frac{k_{-6}}{k_6 k_9} + \frac{k_{-5} [L]_0}{k_5 k_6} + \frac{k_{-5} k_{-6} [L]_0}{k_5 k_6 k_9} \right). \end{aligned}$$
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