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<th>Kinetic Study of the Carboxymethylation of Aryl Iodides catalyzed by Palladium-Triphenylphosphine Complexes</th>
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<td>Author(s)</td>
<td>Inamasa, Kenji; Kudo, Kiyoshi; Sugita, Nobuyuki</td>
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Kyoto University
Kinetic Study of the Carboxymethylation of Aryl Iodides catalyzed by Palladium-Triphenylphosphine Complexes

Kenji Inamasa, Kiyoshi Kudo and Nobuyuki Sugita*

Received July 11, 1983

Carboxymethylation reactions of several para-substituted iodobenzenes catalyzed by palladium-triphenylphosphine compounds were kinetically investigated. Initial rate of reaction \( V_o \) increased as CO pressure \( (P_{CO}) \) was raised but was retarded by application of much higher \( P_{CO} \). Under identical conditions, dependences of \( V_o \) on the initial concentration of aryl iodides \([\text{ArI}]_0\) became smaller as the electron withdrawing properties of para substituents increased, for example under 1 atm of CO, apparent order of \( V_o \) on \([\text{ArI}]_0\) was observed to vary successively 1 to 0. Dependences of \( V_o \) on \([\text{ArI}]_0\) became larger as \( P_{CO} \) was raised. Addition of \( \text{PPh}_3 \) retarded the reaction rate, but in the presence of large excess \( \text{PPh}_3 \), \( V_o \) was of the first order with respect to the concentration of the catalyst \([\text{Pd}]_0\) though the deactivation of the catalyst under higher \([\text{Pd}]_0\) was observed when excess \( \text{PPh}_3 \) 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 halides\(^1\text{--}^5\) 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,

\[
PdL_n+RX \rightarrow L_2\text{Pd}(R)X+(n-2)L, \tag{1}
\]

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

\[
L_2\text{Pd}(R)X+CO \rightarrow L_2\text{Pd}(COR)X. \tag{2}
\]

Many studies have been made on the intermediate complexes of these reactions\(^6\), 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...
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.

**RESULTS AND DISCUSSION**

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 yet\(^{11}\), similar inhibition by higher CO concentration are well known in some catalytic reactions of CO, e.g. hydroformylation reaction of olefins\(^{12}\) and nickel-catalyzed carboxylation of aryl halides.\(^{13}\) In the latter case, this effect was interpreted as follows; the coordinatively unsaturated \( \text{Ni(CO)}_a \) equilibrated with \( \text{Ni(CO)}_4 \) can only undergo the oxidative addition reaction with aryl halides, so the increase of \( P_{CO} \) decreases the concentration of reactive \( \text{Ni(CO)}_3 \) 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
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.\(^{14}\)

\[
\begin{align*}
6 & \xrightarrow{-\text{PPh}_3} (\text{PPh}_3)_3\text{Pd(CO)} \\
& \xrightarrow{+\text{CO}} (\text{PPh}_3)_3\text{Pd(CO)} \\
& \xrightarrow{+\text{PPh}_3} (\text{PPh}_3)_2\text{Pd(CO)}_2
\end{align*}
\]

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.

**PPh\(_3\) concentration** The effect of added PPh\(_3\) on \(V_0\) of MIB carboxymethylation was examined under 1 atm\(^{**}\) and 31 kg/cm\(^2\) of CO (fig. 2). In both cases, \(V_0\) were retarded by the addition of PPh\(_3\), but under 31 kg/cm\(^2\) 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)\}

<table>
<thead>
<tr>
<th>Run</th>
<th>ArI</th>
<th>(P_{CO}) kg/cm(^2)</th>
<th>(Y=t/(a t+b)+c)</th>
<th>(10^8) mol/l min</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-1</td>
<td>IBN</td>
<td>5</td>
<td>—</td>
<td>1.88</td>
</tr>
<tr>
<td>N-2</td>
<td>IBN</td>
<td>10</td>
<td>—</td>
<td>3.40</td>
</tr>
<tr>
<td>N-3</td>
<td>IBN</td>
<td>15</td>
<td>—</td>
<td>4.25</td>
</tr>
<tr>
<td>N-4</td>
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<td>6.41</td>
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<td>N-5</td>
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<td>4.18</td>
<td>6.84</td>
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<td>N-6</td>
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<td>4.96</td>
<td>5.77</td>
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</tr>
<tr>
<td>N-7</td>
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<td>6.31</td>
<td>4.54</td>
<td></td>
</tr>
<tr>
<td>N-8</td>
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<td>3.69</td>
<td></td>
</tr>
<tr>
<td>C-1</td>
<td>IBN</td>
<td>5</td>
<td>—</td>
<td>3.45</td>
</tr>
<tr>
<td>C-2</td>
<td>0.0036</td>
<td>4.93</td>
<td>5.79</td>
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<td>C-4</td>
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<td>C-5</td>
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<td>4.79</td>
<td>5.98</td>
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<td>C-6</td>
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<td>5.60</td>
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<td>C-7</td>
<td>0.0061</td>
<td>7.27</td>
<td>3.91</td>
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<tr>
<td>C-8</td>
<td>0.0070</td>
<td>9.40</td>
<td>3.04</td>
<td></td>
</tr>
</tbody>
</table>

1) \([\text{ArI}]_0=2.86 \times 10^{-3}\) mol/l, \([\text{Pd}]_0=5.71 \times 10^{-4}\) mol/l, \([\ell]\_0=9.51 \times 10^{-3}\) mol/l; Temp. 35°C, MeOH: Et\(_3\)N: 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 \times 10^5 Pa = 1.033 kg/cm\(^2\). 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.
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Fig. 2. Effect of added PPh₃ on $V₀$ of MIB carboxymethylation (Temp. 35°C)
○: $P_{CO}=31$ kg/cm², $[MIB]₀=2.86 \times 10^{-2}$ mol/l, $[Pd]₀=5.71 \times 10^{-4}$ mol/l,
●: $P_{CO}=1$ atm, $[MIB]₀=1.43 \times 10^{-2}$ mol/l, $[Pd]₀=2.86 \times 10^{-4}$ mol/l.

was observed. This is considered to indicate the competitive interaction of CO and PPh₃ with Pd species in this system.

Initial concentration of aryl iodides ([ArI]₀) In order to grasp the outline of the substituent effect, reactions under 1 atm of CO were conducted by the use of ₇-iodotoluene (IT), ₇-chloroiodobenzene (CIB), MIB and INB as substrates (fig. 3). When the reactions were initiated by the addition of PdCl₂(PPh₃)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, $V₀$

Fig. 3. Carboxymethylation of Aryl Iodides under 1 atm of CO
[ArI]₀=1.43 \times 10^{-2}$mol/l, $[Pd]₀=2.86 \times 10^{-4}$ 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 show 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 additions and carbonyl insertion 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 IBN 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 stoichiometry of

$$\text{PdCl}_2(\text{PPh}_3)_2 + \text{CO} + 2\text{MeOH} + 2\text{Et}_3\text{N} \rightarrow [\text{Pd}(\text{PPh}_3)_2] + \text{CO(OMe)}_2 + 2\text{Et}_3\text{NH}^+\text{Cl}^-.$$ (5)

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

\[ [\text{Pd}]_0 = 5.73 \times 10^{-4} \text{ mol/l}, P_{\text{CO}} = 31 \text{ kg/cm}^2, \text{Temp. } 35^\circ\text{C}, \]
\[ \bullet : [\text{L}]_0 = 9.52 \times 10^{-3} \text{ mol/l}, \quad \circ : [\text{L}]_0 = 0. \]

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

\[ [\text{Pd}]_0 = 5.73 \times 10^{-4} \text{ mol/l}, P_{\text{CO}} = 31 \text{ kg/cm}^2, \text{Temp. } 35^\circ\text{C}, \]
\[ \bullet : [\text{L}]_0 = 9.52 \times 10^{-3} \text{ mol/l}, \quad \circ : [\text{L}]_0 = 0. \]

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 \( \text{PdCl}_2(\text{PPh}_3)_2 \). The effect of the initial concentration of \( \text{PdCl}_2(\text{PPh}_3)_2 \) ([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 \( \text{Pd}_3(\text{CO})_9(\text{PPh}_3)_3 \) and \( \text{Pd}_3(\text{CO})_9(\text{PPh}_3)_4 \) which exist in equilibrium with mononuclear Pd(0) species.

(287)
Table II. Effects of the initial concentrations of p-iodonitrobenzene(INB) and p-iodobenzonitrile(IBN) on $V_0$^{13}

<table>
<thead>
<tr>
<th>Run</th>
<th>ArI</th>
<th>$P_{CO}$ (kg/cm²)</th>
<th>[ArI]₀ (10⁻⁵ mol/l)</th>
<th>Y = (ar + b) + c</th>
<th>$V_0$ (10⁻⁴ mol/l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-9</td>
<td>INB</td>
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<td>1.43</td>
<td></td>
<td>3.43</td>
</tr>
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<td>10</td>
<td>2.86</td>
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<td>3.40</td>
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<tr>
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<td>97</td>
<td>5.71</td>
<td>0.0113</td>
<td>11.5</td>
</tr>
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</table>

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.
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**KINETIC EXPRESSION AND REACTION MECHANISM**

Consulting Stille’s proposal, 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. 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 PPh₃. In this condition, the amount of polynuclear Pd(0) can be considered to be negligibly small because the reaction rate is of the first order with regard to [Pd]₀. According to the reports by Heck and co-workers, we assumed the complexes 12 and 13 ligating only one PPh₃ to be excluded and further the concentration of 4 to be negligible in the presence of excess PPh₃. 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 equilibriums among Pd(0) complexes 1, 2, 3, 5, 6 and 7 and applied the steady-state approximation to the formation of Pd(II) species 9, 10 and 11. The material balance for palladium can be expressed as

\[
\]

where \([n]\) represents the concentration of intermediate \(n\). The concentration of free PPh₃([L]) is then expressed as

\[
\]

and is approximately equal to the initial concentration of added PPh₃([L]₀). The initial rate of the ester formation \(V₀\) which is expressed as

![Scheme 1](image-url)

\[
[PdCl₂L₂]+CO+2MeOH+2Et₃N \xrightarrow{\text{fast}} [PdL₃]+CO(OMe)₂+2Et₃NH⁺Cl⁻
\]

where \(\text{fast}\) indicates a reaction that occurs very quickly compared to other steps in the mechanism. The equilibrium constants and rate constants are denoted as \(K\), \(k\), and \(Kₖ\) respectively.
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\[ V_0 = -\frac{d[\text{ester}]}{dt} = k_0[11], \] (8)

is calculated approximately to be

\[ V_0 \approx \left( k_1 + \frac{k_2K_1}{[L]_0} \right)[CO] + \frac{k_3K_1K_2}{[L]_0}[CO]^2 \alpha[CO]^3 + \beta[CO]^2 + \gamma[CO] + \delta. \] (9)

Here, \([CO]\) stands for the concentration of CO dissolved in the solution, and \(\alpha, \beta, \gamma\) and \(\delta\) involve the concentration terms of \([ArI]_0\) and \([L]_0\) as shown below,

\[
\alpha = \frac{K_1K_2K_4}{[L]_0}, \quad \beta = K_1K_2K_5 + \frac{K_1K_2}{[L]_0} + \frac{k_3K_1K_2}{k_0[L]_0}[ArI]_0,
\]

\[
\gamma = 1 + \frac{k_1}{[L]_0} + K_0[L]_0 + \left( \frac{k_1}{[L]_0} + \frac{k_2K_1}{k_0[L]_0} + k_3K_1K_2 \left( \frac{k_{-\delta}}{k_6K_0[L]_0} + \frac{k_{-\delta}k_{-\delta}}{k_0k_6k_9} \right) \right)[ArI]_0,
\]

\[
\delta = \left( k_1 + \frac{k_2K_1}{[L]_0} \right) \left( \frac{k_6}{1} + \frac{k_{-\delta}}{k_6k_9} + \frac{k_{-\delta}L[L]_0}{k_6k_9k_6} + \frac{k_{-\delta}k_{-\delta}[L]_0}{k_6k_9k_9[L]_0} \right)[ArI]_0.
\]

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

\textbf{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 \([CO]\). 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,

\[
k_1 + \frac{k_2K_1}{[L]_0}[CO] \ll \frac{k_3LK_1K_2}{[L]_0}[CO]^2,
\]

\[\alpha[CO]^3 + \beta[CO]^2 \gg \gamma[CO] + \delta.\] (10)

![Fig. 8. Plot of \(V_0^{-1}\) against \(P_{CO}\).](image)

[ArI]_0 = 2.86 \times 10^{-2} \text{mol/l}, [Pd]_0 = 5.71 \times 10^{-4} \text{mol/l},

[L]_0 = 9.52 \times 10^{-2} \text{mol/l}, \text{Temp. 35°C,}

\(\bullet\) : MIB, \(\diamond\) : IBN, \(\triangle\) : INB.

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Carboxymethylation of aryl iodides

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

\[ V_0^{-1} = \frac{1}{[\text{Pd}]_0} \left( \frac{K_4[\text{CO}]}{k_4[\text{ArI}]_0} + \frac{K_5[\text{L}]_0}{k_4[\text{ArI}]_0} + \frac{1}{k_5} + \frac{1}{k_6} \right). \]  

(11)

We made the following examination as to the validity for the experimental facts. The gradient of the plot of \( V_0^{-1} \) vs. \( P_{\text{CO}} \) is expressed as \( K_4/k_4[\text{ArI}]_0[\text{Pd}]_0 \) and if the concentration terms, [ArI]_0 and [Pd]_0 are the same, the gradient would be proportional to \( k_4^{-1} \), 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 \( k_4 \) 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) complexes\(^9\). The values of \( k_4/K_4 \) for INB, IBN and MIB were calculated as 340, 170 and 69 (in mol·kg⁻¹·l⁻¹·min⁻¹·cm⁻²) respectively.

Relation between \( V_0 \), [ArI]_0 and \( P_{\text{CO}} \)

Rearranging eq. 9 with respect to [ArI]_0, the relation of [ArI]_0 and \( V_0 \) is formulated as,

\[ V_0^{-1} = \frac{1}{\varepsilon[\text{Pd}]_0} \left( \frac{\zeta}{[\text{ArI}]_0^{-1} + \eta} \right) \]

(12)

where \( \varepsilon \), \( \zeta \) and \( \eta \) 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 \( P_{\text{CO}} \), [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 \( \zeta/\varepsilon[\text{Pd}]_0 \) of eq. 12, in which \( \zeta \) and \( \varepsilon \) are the functions of the first order and the second order as to [CO] respectively. Therefore, the gradient should increase with an increase in \( P_{\text{CO}} \). Secondly, the intercept of this plot (\( \zeta/\varepsilon[\text{Pd}]_0 \)) in which the numerator and the denom-
ator are both of the second order as to [CO], should converge to $1/k_s[Pd]_9$ 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/cm² and 97 kg/cm² of CO. We obtained $k_s$ values as 0.23 min⁻¹ (MIB at 31 kg/cm² of $P_{CO}$) 0.20 min⁻¹ (IBN at 79 and 97 kg/cm² of $P_{CO}$) and 0.18 min⁻¹ (INB at 124 kg/cm² of $P_{CO}$). No significant differences have been found out among $k_s$ 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 PPh₃ where dissociative route 12→13→14 predominates.

**EXPERIMENTAL**

**Reagents** PdCl₂(PPh₃)₂ was prepared by the conventional method¹⁰. MIB was prepared from its acid with diazomethane as methylating agent and recrystallized twice from methanol. Mehtanol and benzene were dried over molecular sieves 3A. Other materials were all commertially 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 PdCl₂(PPh₃)₂, PPh₃, aryl iodide, methanol, triethylamine and benzene were charged in the autoclave, which was purged with ca. 10 kg/cm² 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. 1 h. 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. 1 ml) 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 deoxigenated 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 Teflon-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 V₀** V₀ 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

\[ Y = \frac{t}{(at + b) + c} \]  

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

and \( V₀ \) 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.

**REFERENCES AND NOSES**

(11) In fig. 2 of ref. 5, the same retardation appeared, but its author did not pay attention to this phenomenon.
(18) \[ \varepsilon = \left( k_1 + \frac{k_2K_1}{[L]_0} \right)[CO] + \frac{k_3K_1K_2}{[L]_0}[CO]^3, \]
\[ \zeta = \frac{k_3K_1K_4}{[L]_0}[CO]^3 + \left( \frac{K_1K_2K_3}{[L]_0} \right)[CO]^2 + \left( 1 + \frac{K_1}{[L]_0} + K_4 [L]_0 \right)[CO], \]
\[ \eta = \frac{k_3K_1K_4}{[L]_0}[CO]^3 + \left( \frac{k_1}{k_2} + \frac{k_3[CO]}{k_2K_1} + k_3K_1K_2 \left( \frac{k_{-6}}{k_{6k_6}}[L]_0 + \frac{k_{-6k_6}}{k_{6k_6}} \right) \right)[CO] \]
\[ + \left( k_1 + \frac{k_2K_1}{[L]_0} \right) \left( \frac{1}{k_2} + \frac{k_{-6}}{k_{6k_6}} + \frac{k_3K_1}{k_{3k_3}} + \frac{k_{-6k_6}}{k_{6k_6}} \right). \]

(294)