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Effect of Base on Palladium-Black Catalyzed Carbonylation of Iodobenzene

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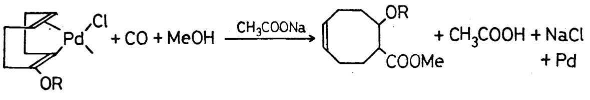
It was found that palladium-black is a highly active catalyst for the carbonylation of iodobenzene with carbon monoxide and methanol in the presence of potassium acetate, triethylamine, or tributylamine to give methyl benzoate. The kinetic study of the carbonylation showed that the oxidative addition of iodobenzene to a palladium(0) complex is rate-determining, and that the bases affect considerably the rate-determining step.

It is known that relatively stable alkoxy-enyl complexes such as **1** are quantitatively carbonylated in the presence of sodium acetate in methanol[1)] and that a complex containing Pd–C sigma-bond reacts extremely rapidly with carbon monoxide in the presence of sodium methoxide in methanol–benzene to give the corresponding ester almost quantitatively.[2)] Maitlis, *et al.* demonstrated that an acyl–Pd bond is much less readily cleaved by acid than by base.[2)] The styrene-palladium complex can be carbonylated with carbon monoxide and alcohol in the presence of tertiary amines to give cinnamate and phenylsuccinate *via* carbomethoxy palladium as an intermediate.[3,4)] Hidai, *et al.* obtained $Pd(CO)(P\phi_3)_3$ and $Pd_3(CO)_3(P\phi_3)_3$ by the reaction of $PdCl_2(P\phi_3)_2$ with carbon monoxide in methanol-amine systems by use of primary or secondary amines, while a carbomethoxy complex, $(P\phi_3)_2PdCl(COOCH_3)$, was isolated by use of tertiary amines.[5)]



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The present work was undertaken to examine whether these stoichiometric reactions in a basic medium is reflected in a palladium-catalyzed carbonylation. Palladium(0) complexes is readily oxidized by aryl iodide and bromide to give σ-arylpalladium(II) complexes.[6,7)] This reaction was successfully utilized for the palladium-black catalyzed phenylation of olefin with iodobenzene in the presence of potassium acetate in methanol.[8)] In a basic medium, palladium-black is also highly active for the carbonylation of iodobenzene. Thus, the effect of bases on the carbonylation was kinetically investigated.

Experimental

Procedure. All the carbonylations were carried out using a Ti–Mn alloy autoclave (100 ml) equipped with a magnetic stirrer. The experimental procedure is illustrated by the carbonylation of iodobenzene with carbon monoxide and methanol to give methyl benzoate. Iodobenzene (40 mmol), methanol (1—30 ml), palladium-black (0.01—1.0 mmol), and a base selected from potassium acetate, triethylamine, and tributylamine were placed in the autoclave. Benzene or toluene (30 ml) was used as the solvent, if necessary. The autoclave was heated up to a desired temperature (60—130 °C) within 20 min, and carbon monoxide (purity 98%) was then introduced up to 5—70 kg/cm². The pressure was kept constant during the reaction by supplying carbon monoxide from a high pressure vessel. After the reaction, the autoclave was rapidly cooled by water, and then carbon monoxide was purged out.

Analysis. Liquid products were quantitatively determined by gas chromatography. A DC-550 columun (3 m) with hydrogen carrier was used at 130 °C for the determination of methyl benzoate, iodobenzene, benzaldehyde, and propiophenone by use of bromobenzene as an internal standard. The amounts of benzal acetophenone and benzanilide were determined using the same columun at 190—230 °C with benzophenone or 1-bromonaphthalene as an internal standard. All the materials were obtained from commercial sources, and utilized without purification.

Results and Discussion

Formation of Methyl Benzoate. As shown in Table 1, the yield of methyl benzoate increased with increase in the amount of potassium acetate. Most of iodobenzene is consumed for the carbonylation when the amount (mmol) of potassium acetate exceeds that of iodobenzene used. Benzoic acid was always found as a product, although its amount was not determined. Accordingly the selectivity based on the amount of iodobenzene consumed is higher than that described in Table 1. The reaction mixtures were always colourless, and most of the catalyst was present in the form of palladium-black. Triethylamine and tributhylamine were also effective, while pyridine was much less

Table 1. Effect of base on yield of methyl benzoate
C_6H_5I 40 mmol, CH_3OH 30 ml, P_{CO} 45 kg/cm² (at r.t.), Temp. 98 °C, Time 90 min.

Pd-black mmol	Base mmol		Conv. %	$C_6H_5COOCH_3$ mmol	Select. %
1.0	AcOK	—	14	0.90	16
1.0	AcOK	15	44	13	73
1.0	AcOK	25	64	19	74
1.0	AcOK	50	77	23	74
1.0	AcOK	60	81	24	75
0.1	AcOK	50	80	29	90
0.25	AcOK	50	79	28	88
0.50	AcOK	50	76	28	91
1.0	Py	50	14	5.6	100
1.0	NEt_3	50	51	17	83
1.0	NBu_3	50	28	10	85

($AcO=CH_3COO$, $Py=C_5H_5N$, $Et=C_2H_5$, $Bu=n\text{-}C_4H_9$)

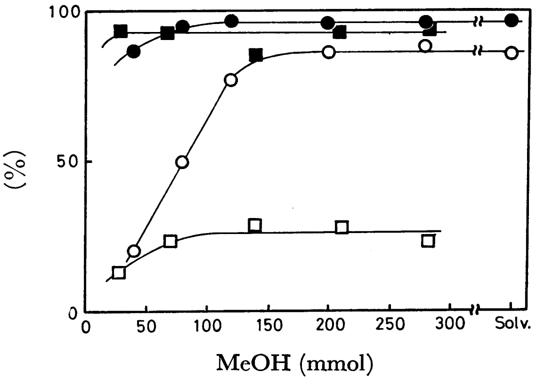

Fig. 1. Effect of amount of methanol.
C_6H_5I 40 mmol, C_6H_6 30 ml, NEt_3 50 mmol, Pd-black 0.5 mmol, P_{co} 20 kg/cm^2 (Const.), Time 90 min.
□ (Conv.), ■ (Select.) at 73 °C, ○ (Conv.), ● (Select.) at 98 °C.

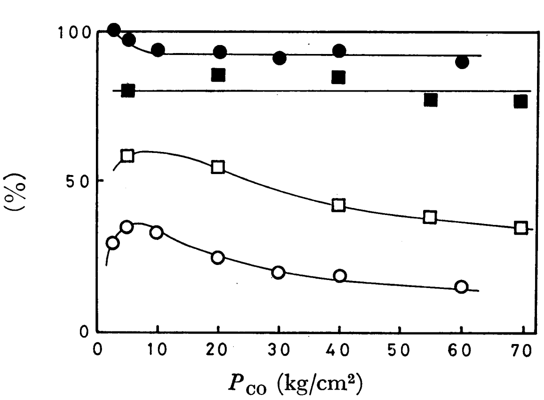

Fig. 2. Effect of the pressure of CO.
○ (Conv.) and ● (Select.) under the condition that C_6H_5I 40 mmol, C_6H_6 30 ml, MeOH 280 mmol, NEt_3 50 mmol, Pd-black 0.5 mmol, and Time 90 min.
□ (Conv.) and ■ (Select.) under the condition that C_6H_5I 40 mmol, MeOH 30 ml, AcOK 50 mmol, Pd-black 0.25 mmol and Time 90 min.

effective giving a reddish reaction mixture, from which a palladium(II) compound, $Pd(C_5H_5N)_2I_2$, was isolated. In any case, neither diphenyl nor anisole was detected in the products. The effect of the amount of palladium-black is also represented in Table 1. Palladium-black is so active that it was difficult to examine the effect of the amount of palladium-black in detail.

The effects of the amount of methanol and the pressure of carbon monoxide on the yield of methyl benzoate using triethylamine ($C_6H_5I/N(C_2H_5)_3=1/1.25$ in mol) and benzene as the solvent, are shown in Figs. 1 and 2 respectively. The yield of methyl benzoate is independent of the amount of methanol when the molar ratio of methanol to iodobenzene is more than 3 (Fig. 1). The carbonylation is slightly retarded under higher pressures of carbon monoxide (Fig. 2). The rate of carbonylation was determined under a constant pressure of carbon monoxide (20 kg/cm^2) in the presence of enough amounts of methanol ($MeOH/C_6H_5I=7/1$ in mol) and triethylamine or tributhylamine (amine/$C_6H_5I=1.25/1$ in mol) as the base. The results are shown in Fig. 3, where C_t is the conversion of iodobenzene. The yield of methyl benzoate significantly depends not only on the base used, but also its amount as described in Table 1. It was confirmed, however, that in the presence of an enough amount of a base ($base/C_6H_5I \geq 1$), the carbonylation rate was almost independent of its amount. Potassium acetate was not used for this kinetic study because of its low solubility in benzene. Admitting that the concentration of an active palladium species is constant during the reaction with an equilibrium apparently established among the enough amount of amine, carbon monoxide, and palladium-black, the rate is proportional to the amount of iodobenzene. The rate constants are obtained from the gradients of these linear plots, and the Arrehenius plot is shown in Fig. 4. Tributhylamine needs higher reaction temperature than triethylamine does, while the apparent activation energy in the former case (14 kcal/mol) is smaller than that in the latter case (25 kcal/mol).

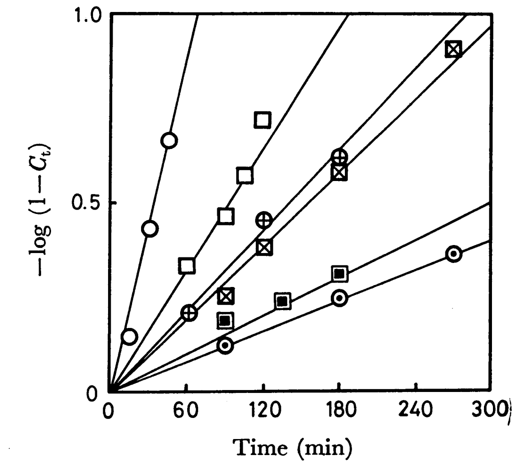

Fig. 3. Plot of $-\log(1-C_t)$ against time in the presence of NEt_3 or NBu_3.
C_6H_5I 40 mmol, C_6H_6 30 ml, Amine 50 mmol, MeOH 280 mmol, Pd-black 0.5 mmol, P_{co} 20 kg/cm^2.
NEt_3; ○ (98 °C), ⊕ (82 °C), and ⊙ (73 °C).
NBu_3; □ (137 °C), ⊠ (122 °C), and ▣ (110 °C).

In the arylation of olefin with iodobenzene catalyzed by palladium-black, it was considered that the palla-

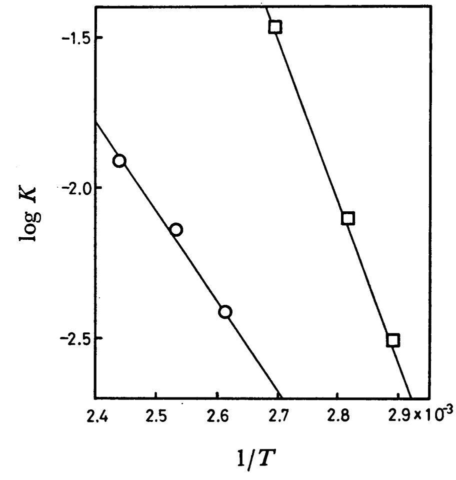

Fig. 4. The Arrhenius plot.
□ NEt_3 25 kcal/mol. ○ NBu_3 14 kcal/mol.

Table 2. Formation of benzoyl derivatives
C_6H_5I 40 mmol, NEt_3 50 mmol, Pd-black 0.5 mmol, $C_6H_5CH_3$ 30 ml.

Reactant	p_{CO} (Kg/cm^2)	Temp. (°C)	Time (hr)	Conv. (%)	Prod. (mmol)		Select.$^{d)}$ (%)
$C_6H_5NH_2$ 50 mmol	20$^{a)}$	98	1	36	$C_6H_5CONHC_6H_5$	14	100
$C_6H_5NH_2$ 50 mmol	20$^{a)}$	98	2	66	$C_6H_5CONHC_6H_5$	25	96
$C_6H_5NH_2$ 50 mmol	20$^{a)}$	98	3	71	$C_6H_5CONHC_6H_5$	27	94
H_2 60 kg/cm$^{2b)}$	60$^{b)}$	150	4.5	49	C_6H_5CHO	16	82
$C_2H_4$$^{c)}$ 30 kg/cm$^{2b)}$	30$^{b)}$	160	3	77	$C_6H_5COC_2H_5$	12	39

a) The pressure was kept constant during the reaction. b) At the room temperature. c) NBu_3 was used as the base. d) Based on the amount of C_6H_5I consumed.

dium-black supplied an active palladium complex of low oxidation state during the reaction, and that the arylation proceeded *via* σ-arylpalladium intermediate.[8] Four processes were proposed as essential for the arylation of olefin. The kinetics of carbonylation of iodobenzene with carbon monoxide and methanol can also be understood by the following scheme similar to that of the arylation. The fact that the rate of carbonylation is proportional to the amount of iodobenzene as shown in Fig. 3, indicates the oxidative addition of iodobenzene to the palladium complex 2, where n is probably 4 as seen in $Pd(CO)(P\phi_3)_3$ and $Pd(P\phi_3)_4$, to be rate-determining. The acylpalladium intermediate 4 must be formed rapidly, because of no increase in the yield of methyl benzoate with increasing the pressure of carbon monoxide as shown in Fig. 2. This is consistent with the fact that neither diphenyl nor anisole was detected in the product. Methyl benzoate must be also formed rapidly by the attack of methanol to the acylpalladium 4, because the yield of methyl benzoate is almost independent of the amount of methanol as shown in Fig. 1. This is consistent with the result of stoichiometric reaction that acylpalladium sigma-bond is readily cleaved in a basic medium.[1,2] No detection of palladium(II) compound in the products obtained on using potassium acetate, triethylamine, or tributylamine as the base, suggests that the equilibrium of the reaction (4) is much inclined to the right.

$$\underset{\mathbf{2}}{PdL_n} + C_6H_5I \longrightarrow \underset{\mathbf{3}}{C_6H_5PdIL_{n-2}} + 2L \qquad (1)$$

$$C_6H_5PdIL_{n-2} + CO \longrightarrow \underset{\mathbf{4}}{C_6H_5COPdIL_{n-2}} \qquad (2)$$

$$C_6H_5COPdIL_{n-2} + CH_3OH \longrightarrow C_6H_5COOCH_3 + \underset{\mathbf{5}}{HPdIL_{n-2}} \qquad (3)$$

$$HPdIL_{n-2} + 2L + \text{base} \longrightarrow PdL_n + (\text{H-base})^+\,I^- \qquad (4)$$

(L = CO, base, or solvent)

It is worthy of notice that the rate of carbonylation depends significantly on the base used. The difference in the rate and the apparent activation energy shown in Fig. 4 demonstrates that the amines work as ligand to control the concentration of palladium complex **2** and its reactivity for the oxidative addition of iodobenzene. This difference can be explained by assuming that less crowded triethylamine coordinates to the complex **2** more tightly than tributhylamine. That is, triethylamine will keep the concentration of complex **2** higher than tributhylamine during the course of carbonylation, resulting in increasing the rate of reaction (1). Triethylamine, however, needs higher activation energy, since the oxidative addition of iodobenzene to the complex **2** must be accompanied by dissociation of the ligand (amine, CO, and solvent) coordinate to the complex **2**. Pyridine is less effective. It probably stabilizes the intermediate **3**, **4**, or **5**, and retards the regeneration of the active complex **2**.

The other possible scheme, *via* carbomethoxy palladium intermediate, is worthy of metnion here, since carbomethoxy palladium was suggested as an intermediate in the carbonylation of olefin or acetylene.[3,4] Neither of carbomethoxy nor the other palladium(II) complexes, however, were detected in the carbonylation products of iodobenzene. Hidai, *et al.* reported that the stoichiometric reaction of carbomethoxy palladium, $(P\phi_3)_2PdCl(COOCH_3)$, with methyl iodide at 90 °C or with benzyl bromide at 140 °C gave quantitatively methyl acetate or methyl phenylacetate respectively,[5] while the reaction with iodobenzene gave no methyl benzoate even at higher temperature.[9] These facts positively eliminate the scheme *via* carbomethoxy palladium intermediate in the carbonylation of iodobenzene catalyzed by palladium-black.*

Formation of Benzoyl Derivatives. The carbonylation of iodobenzene with carbon monoxide and aniline or hydrogen was examined in benzene or toluene. As summarized in Table 2, the carbonylation in aniline-benzene gives benzanilide selectively. The rate is almost proportional to the amount of iodobenzene. The carbonylation with carbon monoxide and hydrogen also gives benzaldehyde selectively, although it needs an enforced reaction condition. In the absence of carbon monoxide, iodobenzene was hydrogenated quantitatively to benzene under the condition specified in

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* Yoshida *et al.* independently reported on the carbonylation of C_6H_5I with CO and methanol catalyzed by $PdCl_2$–Py system (*Nippon Kagaku Kaishi*, **1974**, 1386), where Py seemed to be most effective as the base, and they postulated kinetically the scheme *via* carbomethoxy palladium(II) intermediate. The present carbonylation using palladium-black, however, was strongly retarded by the addition of Py as shown in Table 1, and the catalyst was mostly converted into $Pd(Py)_2I_2$ after the carbonylation. This fact also eliminates the carbomethoxy palladium(II) intermediate.

Table 2, while only a trace amount of benzene was detected in the carbonylation product. The carbonylation with carbon monoxide and ethylene gives a considerable amount of propiophenone and a polymer, contrary to our expectation that acrylophenone would be formed. The sources of hydrogen to give propiophenone remains unclarified. The carbonylation with styrene gives a small amount of benzal acetophenone as determined by retention time of gas chromatograph. The arylation of ethylene or styrene was observed only in the absence of carbon monoxide. The formation of these benzoyl derivatives can also be explained by an acylpalladium intermediate.

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