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OXIDATIVE COUPLING OF AROMATIC COMPOUNDS WITH AN AQUEOUS PALLADIUM(II) SALT SOLUTION

Riichiro NAKAJIMA and Tadashi HARA
Depertment of Chemical Engineering, Faculty of Engineering,
Doshisha University, Kamikyo-ku, Kyoto, Japan

The oxidative coupling of aromatic compounds was carried out between the organic phase containing an aromatic compound and the aqueous phase containing palladium(II) perchlorate - ferric perchlorate system as the catalyst. The yields of biphenyl and bitolyl per hour based on palladium charged were 350 and 1000 percent, respectively.

Since the oxidative coupling of benzene derivatives by palladium salts in sodium acetate - acetic acid solution was reported by van Helden and his co-workers,[1)] many reports have dealt with this reaction. There has been, however, no report except one by Itatani et al.,[2)] in which palladium salt is used as a catalyst.

Davidson et al.[3)] mentioned that oxygen shows the positive effect to the reaction, but the results were not reported in detail. Recently it has been shown by Itatani et al.[2)] that the palladium-catalyzed reactions proceed in an aromatic compound system under oxygen pressure at 150°C or so. However the reaction does not seem to be so useful since the reaction mixture under the reaction conditions is very explosive. This paper deals with the oxidative coupling of aromatic compounds, which proceeds under the mild conditions. In the present procedure, the palladium metal deposit is oxidized by oxygen or air at the reflux of the aromatic compound and therefore the palladium salt can be used as a catalyst.

The reaction between an aromatic compound phase and an aqueous phase containing palladium salt and a co-catalyst is carried out by passing oxygen through the bubbling tower, 70 cm in length and 20 mm in diameter. The reaction tower is charged with 10 ml of palladium(II) perchlorate - perchloric acid solution(if necessary, the co-catalyst was added to the solution.), 20 ml of benzene or aromatic compound, and 10 ml of acetic anhydride, followed by heating it at the reflux temperature for 6 hours with the passage of oxygen gas.

Table 1. Effect of oxygen

$Pd(ClO_4)_2$	$HClO_4$	reaction time	gas passed[a]	yield of biphenyl[b]
1.117 mmol	1.82 N	6 hr	N_2	7 % [c]
1.117	1.82	6	N_2	14 [c]
1.117	1.82	7	O_2	180
1.117	1.82	8	O_2	224

a) Gas flow rate ; ca. 60 ml/min

b) Based on palladium charged

c) Black polymeric matter was obtained

Table 1 shows the effect of oxygen on the yield of biphenyl. The reaction under nitrogen gave only ten percent yield of biphenyl and a small amount of polymeric matter (dark-brown ∼ black). The similar result was also obtained under the atmosphere of carbon dioxide. The reaction under the atmosphere of oxygen gave over 100 percent yield of biphenyl based on palladium charged, and did not give any polymeric matter. As the palladium deposited during the reaction is oxidized by oxygen, the yield of biphenyl becomes more than 100 percent. The reaction took place scarcely when palladium powder or plate was used as a palladium source, and therefore the yield of biphenyl was very low. The relationship between the reaction time and the yield of biphenyl was shown in Fig. 1. Fig. 2 shows the acid concentration

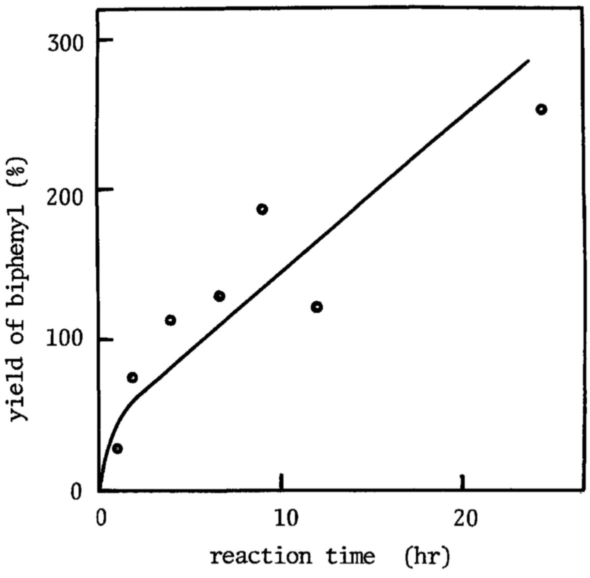

Fig. 1. Relation between the yield of biphenyl and the reaction time

Reaction conditions ; $Pd(ClO_4)_2$: 0.304 mmol, $HClO_4$: 0.54 N, reaction temp. : 68°C, and gas flow rate : 60 ml O_2/min

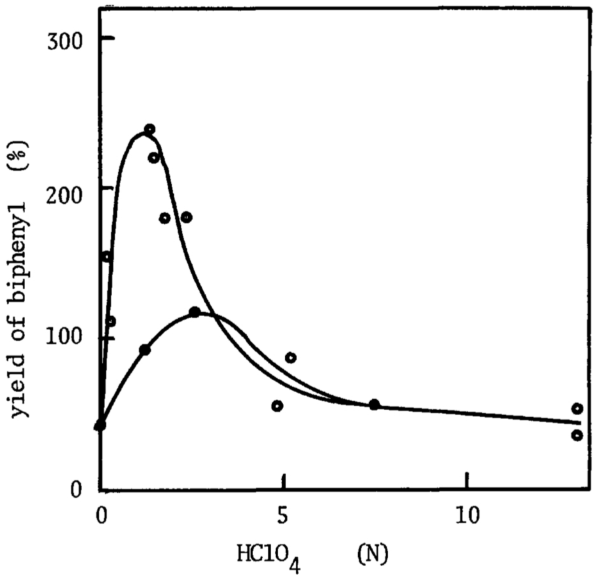

Fig. 2. Effect of concentration of perchloric acid

—●—●— ; $Pd(OAc)_2$ —○—○— ; $Pd(ClO_4)_2$

Reaction conditions ; Pd(II) : 0.304 mmol, reaction temp. : 68°C, gas flow rate : 60 ml O_2/min, and reaction time : 6 hr

Table 2. Effect of co-catalyst

co-catalyst	M/Pd	$HClO_4$	yield of biphenyl^a
–	0^b	0.54 N	130 %
perchlorate			
Na(I)	53.8^b	0.54	140
Co(II)	15.9^b	0.54	278
Fe(III)	93.0^b	0.54	580
Cu(II)	10.4^b	0.54	270
Ag(I)	24.4^b	1.55	227
Zn(II)	15.8^c	1.51	109
Mn(II)	13.5^c	2.24	137
acetate			
Na(I)	81.0^b	0.54	140
Co(II)	40.0^b	0.54	101
Fe(III)	10.2^b	0.54	140
Cu(II)	16.7^b	0.54	trace
sulfate			
Cu(II)	26.7^b	0.54	79
chloride			
Cu(II)	12.5^b	0.54	trace

a) Based on palladium charged
b) $Pd(ClO_4)_2$: 0.304 mmol
c) $Pd(ClO_4)_2$: 0.378 mmol
Reaction conditions ; gas flow rate : 60 ml O_2/min, reaction temp. : 68°C, and reaction time : 6hr

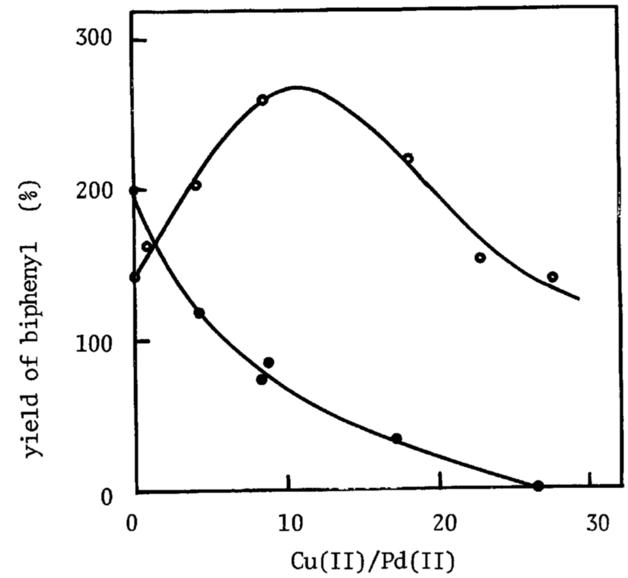

Fig. 3. Effect of copper acetate and copper perchlorate

—●——●— ; copper acetate
$Pd(ClO_4)_2$: 0.568 mmol, $HClO_4$: 2.45 N
—○——○— ; copper perchlorate
$Pd(ClO_4)_2$: 0.304 mmol, $HClO_4$: 0.54 N
other conditions ; same as in Table 2

dependence upon biphenyl yield, which is the highest at about 1.5 N perchloric acid. As seen from Fig. 2, the results suggest that both acetate and perchlorate have transformed into the same species in the course of the reaction, and the reactive species might be formed by the perchlorate faster than by the acetate. No biphenyl was obtained with the palladium salts such as chloride, sulfate, nitrate, etc.

The acetate, sulfate, and chloride as a co-catalyst did not show the positive effect on the yield of biphenyl, but the perchlorates did the positive effect on the yield(Table 2). Therefore the present system seemed to be considerably different from the conventional acetic acid - acetate system, in which both acetate and chloride showed the positive effect on the yield of biphenyl. The effects of anions were understood by the formation of the palladium-chloro complex, which is insoluble in benzene layer, and by the high solubility of the acetate to an aqueous phase. The perchlorates such as iron(III), cobalt(II), copper(II), and silver(I) oxidized the palladium metal in the presence of oxygen. There were maxima in the positive effects of cobalt(II) and copper(II) perchlorate within the concentration shown in Table 2. The effects of copper perchlorate and acetate were compared each other in Fig. 3.$^{4)}$ The yield of biphenyl decreased by the addition of

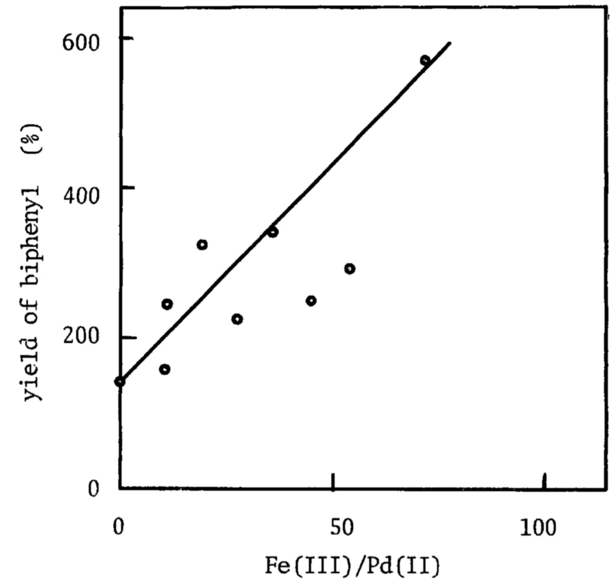

Fig. 4. Effect of ferric perchlorate

Reaction conditions ; same as in Table 2 except the oxygen gas flow rate, 120 ml/min

copper acetate, but it showed a maximum by copper perchlorate. This is understood by the formation of copper acetate and its inhibitory effect on the coupling reaction. Ferric acetate did not show the positive effect on the yield, but ferric perchlorate did (Table 2). The relation between the yield of biphenyl and the amount of ferric perchlorate was shown in Fig. 4. This relation changed by the concentration of the perchloric acid, and the yield of biphenyl was higher in 4.11 N perchloric acid solution(Table 3) than in 0.54 N(Fig. 4). As seen from Table 3, the yield of biphenyl in a definite period did not change even at twice the reaction time. This means that the activity of the catalyst is almost uniform throughout the reaction. The present reaction proceeds even at the room temperature, and it was applied to the other aromatic compounds(Table 4). The main dimers from toluene and o-xylene were the products coupled at the meta and para positions, the yield of 3,4,3',4'-tetramethylbiphenyl being about 65 mole percent of products in the case of o-xylene.

Table 3. Oxidative coupling of benzene in the palladium-ferric perchlorate system

$Pd(ClO_4)_2$	Fe(III)/Pd(II)	$HClO_4$	reaction time	yield of biphenyl
0.0508 mmol	195	3.89 N	14.5 + 1.75^a hr	5660 %
0.0508	195	3.89	6	2140
0.1016	65	4.11	6	1370

a) The reaction was carried out at room temperature

Table 4. Oxidative coupling of aromatic compound

monomer	benzene	toluene	chlorobenzene	o-xylene	m-xylene	p-xylene
yield of dimer	700 %	6424 %	338 %	3000 %	867 %	3500 %

Reaction conditions ; $Pd(ClO_4)_2$: 0.0508 mmol, $Fe(ClO_4)_3$: 6.576 mmol, $HClO_4$: 2.98 N, and reflux temperature

1) R. van Helden, G. Verberg, and B. Balder, U. S. 3145237(1964).

2) H. Itatani and H. Yoshimoto, Chem. Ind.(London), 1971,674.

3) J. M. Davidson and C. Triggs, J. Chem. Soc.(A), 1968,1324.

4) The change in the concentration of perchloric acid did not change the type of effect.

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