JOURNAL OF CATALYSIS 31, 8-12 (1973)

Palladium-Catalyzed Competitive Reaction of Aromatic Compounds

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Received February 15, 1973

The oxidative coupling of aromatic compounds proceeded catalytically, accompanied by regeneration of Pd(0) to Pd(II) with molecular oxygen. The relative reactivities to benzene and compositions of biaryls gave partial rate factors by the application of a two stage coupling process, showing remarkable polar and steric effects. The reactivity ratios *o/m*, *p/m* differ from those reported in a palladium salt–acetic acid system and a phenyl radical coupling.

Van Helden and Verberg (*1*) have reported the oxidative coupling of aromatic compounds with palladium chloride and sodium acetate in acetic acid medium. Isolating a σ-aryl palladium(I) complex and measuring the kinetic isotope effect (*2*) an intermolecular coupling process has been postulated. Later the system of toluene–mercuric acetate–palladium acetate was investigated and the mechanism was proposed on the basis of isomer distributions of biaryls obtained (*3*). The coupling reported was not catalytic, because palladium black was precipitated during the reaction and thus the yields of biaryls were less than 100% based on palladium. Under oxygen pressure in the absence of acetic acid medium, however, the coupling proceeded catalytically, retaining palladium in solution (*4*). Our preceding paper reported the rate dependence on pressures of oxygen and amounts of palladium acetate and in addition, the remarkable isotope effect on the coupling of benzene and deuterobenzene. A two stage coupling process was postulated for explaining the isotope effect. The present paper deals with isomer distributions of coupling products and the competitive reaction between benzene and substituted benzenes. From these data, the partial rate factors were calculated.

EXPERIMENTAL METHODS

Reagents and analysis of the products were described in the previous paper (*4, 5*).

Competitive coupling between benzene and an aromatic compound. A mixture of benzene (5.85 g, 0.075 mol), the aromatic compound (0.075 mol) listed in Table 1, palladium acetate (33.6 mg, 0.15 mmol) and acetylacetone (15 mg, 0.15 mmol) was placed in a glass vessel (65 ml capacity), which was inserted into an autoclave (100 ml capacity). After pressurized 50 kg/cm^2 of a gaseous mixture of nitrogen and oxygen (1:1) at room temperature, the reaction was carried out at 150°C for 6 hr. Products were analyzed by glc as shown in the previous paper (*4*). In the case of dimethyl phthalate, however, the extent of biphenyl was determined after it was hydrolyzed with 20% solution of alcoholic potassium hydroxide and then extracted with benzene.

RESULTS AND DISCUSSION

1. *Competitive Reaction*

In order to clarify the influence of substituents, the relative reactivity of aromatic compounds was examined by the competitive reaction with benzene. Table 1 shows the yields and compositions of the

TABLE 1

Yield of Competitive Reaction Between Benzene and Aromatic Compounds

Aromatic compound	Molar ratio (%) Biaryl	Aryl-benzene	Bi-phenyl	Products yield (%)[a]
Naphthalene	74	26	0.3	4070
o-Xylene	23	50	27	6040
m-Xylene	9	53	38	2570
p-Xylene	2	51	47	1940
Dimethyl phthalate	13	47	40	5140
Chloro-benzene	0	36	64	210
Toluene	21	50	29	7100

[a] Sum of the percentage yields of biaryl, arylbenzene, and biphenyl based on $Pd(OAc)_2$ used.

coupling products of benzene and aromatic compounds. From the ratio of biaryl to biphenyl, it is seen that naphthalene is more reactive than benzene whereas chloro- or methoxycarbonylbenzene is less. This order is consistent with an electrophilic substitution on aromatic nucleus (*6*). In the case of dimethyl-substituted benzenes, the ratio of biaryl to biphenyl decreases in the order of *o*-xylene > *m*-xylene > *p*-xylene. No coupling of mesitylene was observed (*4*). These facts indicate a profound steric effect in the course of the coupling reaction.

In the system of palladium chloride, sodium acetate, and acetic acid, partial rate factors were obtained from reactivities of substituted benzenes and isomer distributions of biaryls, showing polar and steric effect on the coupling. The process shown in the Eq. (1) has been extensively studied (*2*, *3*), and elucidated to involve a σ-phenyl palladium intermediate.

$$2RH + Pd(OAc)_2 \rightarrow R\text{–}R + Pd + 2HOAc. \quad (1)$$

Under oxygen pressure in the absence of acetic acid medium, however, the coupling proceeded catalytically and promoted by the addition of acetylacetone, gave greatly improved yields of biaryls (*4*). This process is different from the reported one since molecular oxygen played an important role to the coupling, regenerating Pd(0) formed to active Pd(II) species. Really, isomer distributions of biaryls and rate factors are somewhat different from those already reported (*1*, *3*). Our preceding paper discussed isotope effects on the coupling of benzene and deuterated benzene according to a two stage coupling process as shown below;

$$RH + Pd + O_2 \rightarrow R\text{-}Pd\text{-}OOH$$
$$\xrightarrow{RH} R\text{–}R + Pd + HOOH. \quad (2)$$

Similar catalytic reaction was already discussed on the case of cumene autoxidation with an oxygen adduct palladium complex (*7*).

Palladium-catalyzed competitive coupling between benzene (AH) and a substituted benzene (BH) can be presented as follows:

$$AH + Pd + O_2 \xrightarrow{k_1} A\text{–}Pd\text{–}OOH,$$
$$BH + Pd + O_2 \xrightarrow{k_2} B\text{–}Pd\text{–}OOH,$$
$$A\text{–}Pd\text{–}OOH + AH \xrightarrow{k_3} A\text{–}A + Pd + HOOH,$$
$$A\text{–}Pd\text{–}OOH + BH \xrightarrow{k_4} A\text{–}B + Pd + HOOH,$$
$$B\text{–}Pd\text{–}OOH + AH \xrightarrow{k_5} A\text{–}B + Pd + HOOH,$$
$$B\text{–}Pd\text{–}OOH + BH \xrightarrow{k_6} B\text{–}B + Pd + HOOH.$$

In these reaction schemes, applying the stationary state approximation for A–Pd–OOH and B–Pd–OOH, and presuming $k_3/k_5 = k_4/k_6$ and a concentration of AH = BH, the product ratios can be represented as below;

$$\frac{A\text{–}B}{A\text{–}A} = \frac{k_2}{k_1} + \frac{k_4}{k_3},$$
$$\frac{B\text{–}B}{A\text{–}A} = \frac{k_2}{k_1} \times \frac{k_4}{k_3}.$$

Table 2 shows the relative reactivity calculated from the product ratio shown in Table 1. Here, the values of k_2/k_1 and k_4/k_3 are not able to be distinguished by calculation of the product ratios. However, it is reasonable to consider that the reac-

TABLE 2

RELATIVE REACTIVITIES[a] OF AROMATIC COMPOUNDS AGAINST BENZENE

Aromatic compound	k_2/k_1	k_4/k_3
Naphthalene	3.0	84
o-Xylene	0.85	1.00
m-Xylene	0.20	1.20
p-Xylene	0.04	1.04
Dimethyl phthalate	0.73	0.45
Chlorobenzene	0.57	0
Toluene	0.79	0.93

[a] Calculated from the values of Table 1.

TABLE 3

ISOMER DISTRIBUTION OF TETRAMETHYL BIPHENYLTETRACARBOXYLATE[a]

Reaction temp (°C)	Composition (%) 2,3,2′,3′	2,3,3′,4′	3,4,3′,4′	Yield (%)[b]
120	Trace	39	61	1460
150	1	60	39	1610
180	3	68	29	3420
150[c]	1	49	50	4920

[a] Carried out with $Pd(OAc)_2$ (0.15 mmol), dimethyl phthalate (15 ml) and N_2–O_2 (1:1) (50 kg/cm^2) for 4 hr.

[b] Based on $Pd(OAc)_2$ used.

[c] Acetylacetone (0.15 mmol) was added.

tion ratios k_4/k_3 are influenced by polar effect due to the substituent but k_2/k_1 are not, since Pd(0) species seems to have little cationic character while a σ-phenyl palladium(II) can be considered as an intermediate similar to that of the oxypalladation (*3*). As shown in Table 2 there is large difference between k_2/k_1 and k_4/k_3 whereas two kinds of isotope effects (*5*) were not remarkably distinguished in two stage coupling process. In the step of k_4/k_3, higher reactivity of methyl-substituted benzenes and lower reactivity of chloro- and methoxycarbonylbenzenes are parallel to the result of electrophilic substitution. Whereas, k_2/k_1 step shows the steric requirement caused by substituents on benzene, a hydrogen adjacent to methyl group being less reactive for the coupling. In our preceding study of isotope effect (*5*), the coupling of *p*-xylene with benzene and benzene-d_6 has given sole primary isotope effect, whereas, the coupling of benzene and benzene-d_6 gave two kinds of primary isotope effects. This observation is consistent with an extremely small value of k_2/k_1 in the *p*-xylene coupling.

2. Isomer Distribution and Partial Rate Factor

The coupling of *ortho*-disubstituted benzenes gives the mixture of 2,3,2′,3′-, 2,3,3′,4′-, and 3,4,3′,4′-tetrasubstituted biphenyls. In the case of dimethyl phthalate, the ratio of 2,3,3′,4′- to 3,4,3′,4′-isomers varies with the reaction temperature as shown in Table 3. Interestingly, by the addition of equimolar of acetylacetone to palladium acetate, the yield of the coupling products and also the ratio of 3,4,3′4′- to 2,3,3′,4′-isomers increase. Table 4 shows the compositions of biaryls obtained at 150°C. The coupling reactions of *o*-xylene and dimethyl phthalate gave predominantly *p*-substituted biaryls over *o*-substituted biaryls whereas naphthalene prefers the substitution at 1-position. A similar result (*8*) has been reported in the nitration of naphthalene where the partial rate factor of the 1-position is greatly larger than that of 2-position. Dimethyl

TABLE 4

ISOMER DISTRIBUTION OF PRODUCTS OBTAINED BY COMPETITIVE REACTION BETWEEN BENZENE AND AROMATIC COMPOUNDS

Aromatic compound	Compositions (%) of Biaryls *o,o′*	*o,p′*	*p,p′*	Arylbenzenes *o*	*p*	*o*[a]	*p*[a]
o-Xylene	1	24	75	14	86	15	85
Dimethyl-phthalate	2	60	38	36	64	39	61
Naphthalene	43	50	7	86	14	84	16

[a] Calculated from partial rate factors in Fig. 1. *o*-Arylbenzene/*p*-arylbenzene = $(k_o + k_o')/(k_p + k_p')$.

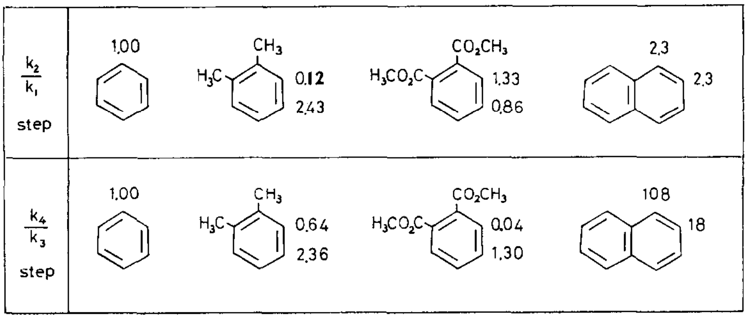

FIG. 1. Partial rate factors of disubstituted benzenes; the relative reactivity to benzene was represented as the sum of the reactivities on both *o*- and *p*-positions; $k_2/k_1 = 2k_o + 2k_p$, $k_4/k_3 = 2k_{o'} + 2k_{p'}$.

phthalate gave larger amounts of *ortho*-substituted biaryls than *o*-xylene did. Probably carbonyl group plays somewhat complicated role on the reaction as is seen in the palladium-catalyzed acetoxylation of olefins.

In Fig. 1, partial rate factors of disubstituted benzenes for the coupling were calculated from relative reactivities (Table 2) and isomer distributions of biaryls (Table 4). Larger differences of the reactivity ratio *o/p* were observed at the second stage coupling compared to the first one. Table 4 shows the isomer ratios of arylbenzenes which are in good agreement with the values calculated from the partial rate factor. In the case of toluene, the partial rate factors (Fig. 2) were presumed to agree with the observed values shown in Table 5. The reactivity ratio *m/p* is larger than that observed in electrophilic aromatic substitution such as oxypalladation (*9*) and mercuration (*10*). In homolytic substitution of toluene with phenyl radical (*11*) was found mainly the formation of *ortho*-substituted biphenyl. Therefore, it is unlikely that a classical electrophilic substitution or phenyl radical

FIG. 2. Partial rate factors of toluene.

TABLE 5
ISOMER DISTRIBUTION OF PRODUCTS OBTAINED BY COMPETITIVE REACTION BETWEEN BENZENE AND TOLUENE

	Compositions (%) of								
	Dimethylbiphenyl						Methylbiphenyl		
	2,2′	2,3′	2,4′	3,3′	3,4′	4,4′	2	3	4
Obsd[a]	2	13	10	28 ±	35 ±	12 ±	15	50	35
Calcd	2	12	10	26	37	13	14	51	35

[a] ± means that inaccuracy can not be avoided since the components were not completely separated in glc.

intermediate is applied on the coupling catalyzed with palladium which was regenerated by molecular oxygen.

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