

Palladium(II)-catalyzed carboxylation of benzene and other aromatic compounds with carbon monoxide under very mild conditions

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Abstract

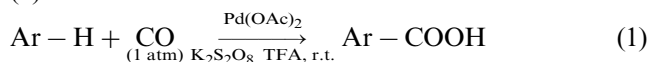
Aromatic compounds such as benzene, toluene, chlorobenzene, anisole, and naphthalene were carboxylated by palladium(II) acetate catalyst with carbon monoxide in the presence of potassium peroxodisulfate in trifluoroacetic acid (TFA) at room temperature under atmospheric pressure. The aromatic carboxylic acids were formed in good yields; for example, the carboxylation of benzene with carbon monoxide proceeds quantitatively under the optimal conditions. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

C–H bond activation by transition metal complexes has been of great interest for a few decades [1–3]. In 1967, we reported the Pd-catalyzed reaction of olefins with aromatic compounds to give aromatic-substituted olefins via thermal activation of both aromatic and olefinic C–H bonds [4]. This coupling reaction proceeds via an ArPdL σ -complex intermediate derived from direct activation of an aromatic C–H bond by Pd(II). It was found that the ArPdL σ -complex formed in situ from the direct aromatic C–H bond activation reacted with CO, CO₂ [5–7] and O₂ [8] to give carboxylic acids and phenol in one step, respectively. For example, various aromatic acids could be prepared from aromatic compounds and CO by Pd-based catalysts in the presence of *t*-BuOOH at over 75°C [6]. We also succeeded in the direct carboxylation reaction of alkanes

with CO by the Pd(OAc)₂/Cu(OAc)₂ and Yb(OAc)₃/Mn(OAc)₂ based catalysts [7,9,10]. However, all of these reactions require elevated temperature and CO pressure. Recently, we found that the Pd(OAc)₂/TFA/K₂S₂O₈ system could cause the direct carboxylation of aromatic compounds with CO under very mild conditions such as room temperature and atmospheric pressure to give the acids in high yields as depicted in Eq. (1).



Preliminary communication of this work has appeared [11]. Here, we report the details of this reaction of aromatic compounds with CO by Pd(OAc)₂ catalyst in TFA solvent.

2. Results and discussion

2.1. Effect of oxidizing agents

The Pd(OAc)₂/trifluoroacetic acid (TFA)/oxidizing agent system was selected to study for the carboxyla-

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Table 1
Effect of oxidizing agents on carboxylation of benzene with CO^a

Entry	Oxidizing agent	Yield of benzoic acid (%) ^b
1	None	23
2	K ₂ S ₂ O ₈	570
3	<i>t</i> -BuOOH	Trace
4	Oxone ^c	— ^d

^a Pd(OAc)₂ (0.5 mmol), benzene (5 ml), oxidizing agent (5 mmol), TFA (5 ml), CO (1 atm), r.t., 20 h.

^b Isolated yield based on Pd.

^c 2KHSO₅·KHSO₄·K₂SO₄.

^d Complex reaction occurred.

tion reactions of aromatic compounds with CO (1 atm) at room temperature.

First, the effect of oxidizing agents was investigated to make the reaction catalytic with respect to Pd(II) (Table 1). From the data in Table 1, it is seen that the yield of benzoic acid was only 23% based on Pd(OAc)₂ and palladium black precipitated during the reaction without any oxidizing agents added (entry 1). However, when *t*-BuOOH or Oxone was added in the reaction, almost no product was obtained (entries 3 and 4). The good result was obtained with potassium peroxodisulfate (K₂S₂O₈) (entry 2), showing that K₂S₂O₈ is an appropriate oxidizing agent which can oxidize Pd(0) to Pd(II) effectively under very mild conditions such as room temperature and atmospheric pressure.

2.2. Effect of the amounts of K₂S₂O₈

Then, the effect of the amounts of K₂S₂O₈ on the yield was investigated (Fig. 1). Fig. 1 shows that the yields of the reactions with 5 mmol K₂S₂O₈ and with 2.5 mmol K₂S₂O₈ are not apparently different within the first 20 h of these reactions; however, after 20 h, the use of 5 mmol K₂S₂O₈ gives higher yield than 2.5 mmol K₂S₂O₈ does. It seems that about 2.5 mmol K₂S₂O₈ has been consumed for both oxidation of Pd(0) to Pd(II)

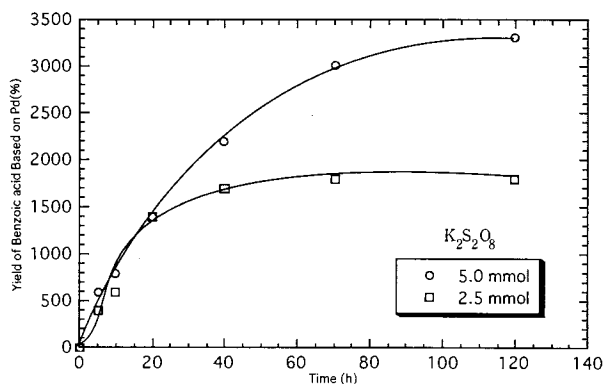


Fig. 1. Effect of amounts of K₂S₂O₈ on the yield of benzoic acid based on Pd. Reaction conditions: Pd(OAc)₂, 0.1 mmol; benzene, 56 mmol; CO 1 atm; TFA, 5 ml; r.t.

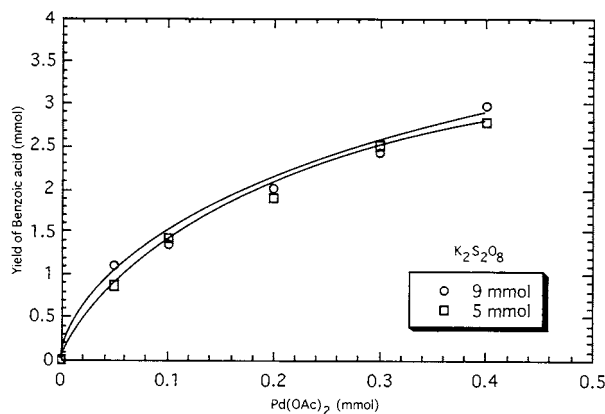


Fig. 2. Effect of amounts of Pd(OAc)₂ on the yield of benzoic acid. Reaction conditions: benzene, 56 mmol; CO, 1 atm; TFA, 5 ml; r.t.; 20 h.

and thermal self-decomposition in the first 20 h of the reaction, and the final yield is dependent of the amount of oxidizing agent added. The final yields are 3300 and 1800% based on Pd in the presence of 5 mmol and 2.5 mmol K₂S₂O₈, respectively.

2.3. Effect of the amounts of Pd(OAc)₂

Pd(OAc)₂ is the catalyst to activate the aromatic C–H bonds in these reactions. The effect of the amounts of Pd(OAc)₂ on the product yield was investigated (Fig. 2). No product is obtained without Pd(OAc)₂ in these reactions. With increasing amounts of Pd(OAc)₂, the product yield increases independent of the amounts of K₂S₂O₈ in the first 20 h of these reactions as shown in Fig. 2. Then, the time-course of the reaction was investigated using 0.1, 0.2, and 0.5 mmol Pd(OAc)₂, and the results are shown in Fig. 3. From the figure, one can see that the increase of the amounts of Pd(OAc)₂ just accelerates the rate of the reactions, and the final product yield is independent of the amounts of Pd(OAc)₂ added. The final yield is about 3.3 mmol in these cases.

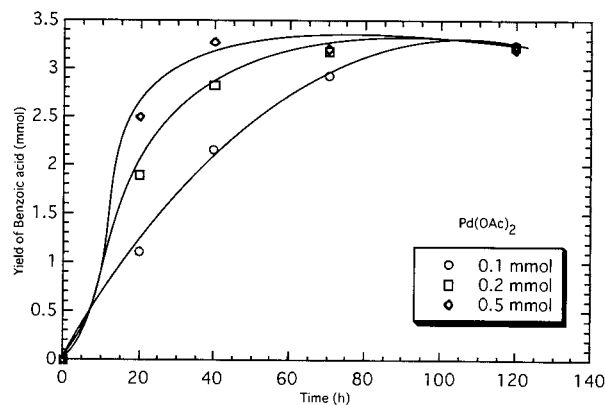


Fig. 3. Time-course of the reaction. Reaction conditions: benzene, 56 mmol; CO, 1 atm; K₂S₂O₈ 5 mmol; TFA, 5 ml; r.t.

Table 2
Effect of amounts of TFA and benzene on carboxylation of benzene with CO^a

Entry	Benzene (mmol)	K ₂ S ₂ O ₈ (mmol)	TFA (ml)	Benzene conversion (%)	Yield of benzoic acid (%) ^b
1	56	5	5	2.5	1400
2	28	5	5	5.6	1571
3	10	5	5	17	1700
4	1	2.5	5	48	480
5	1	2.5	2.5	89	890
6	1	2.5	1	100	1000

^a Pd(OAc)₂ (0.1 mmol), CO (1 atm), r.t., 20 h.

^b Isolated yield based on Pd.

2.4. Effect of the amounts of TFA and benzene

Then, the effect of the amounts of TFA and benzene on the product yield was investigated (Table 2). From the results in the table, one can see that the benzene conversion always increases with decreasing amounts of benzene (entries 1–4). Also, the conversion increases with decreasing amounts of TFA (entries 4–6). The carboxylation of benzene proceeds quantitatively when 1 mmol of benzene, 2.5 mmol of K₂S₂O₈, and 1 ml of TFA were employed in the presence of 10 mol% of Pd(OAc)₂ catalyst (entry 6).

2.5. Carboxylations of arenes with CO

The results of carboxylation of various arenes with CO by using Pd(OAc)₂ at room temperature and under atmospheric pressure are listed in Table 3. It is found that the reaction proceeds with *ortho-para* orientation if an electron-releasing group is attached to the benzene ring (entries 2 and 4) and that naphthalene gives α -naphthoic acid as a main product. The yields of these products (800 ~ 3300% based on Pd(II)) are much higher than those obtained (48–1240% based on Pd(II))

Table 3
Carboxylation of arenes with CO by Pd(OAc)₂^a

Entry	Substrate	Product	Yield (%) ^b	Ratio
1	benzene	benzoic acid	1420	–
2	toluene	toluic acids	800 ^c	26:6:67 ^d
3	chlorobenzene	chlorobenzoic acids	1700	19:27:54 ^e
4	anisole	anisic acids	1200	33:0:67 ^d
5	naphthalene	naphthoic acids	3300	66:34 ^f

^a Pd(OAc)₂ (0.1 mmol), arene (56 mmol), CO (1 atm), K₂S₂O₈ (5 mmol), TFA (5 ml), r.t., 20 h.

^b Isolated yield based on Pd.

^c Bitolyl type coupling products formed in considerable amounts.

^d *o:m:p*, isomer ratio determined by ¹³C-NMR.

^e *o:m:p*, isomer ratio determined by GLC analysis of the methyl esters.

^f α : β isomer ratio determined by GLC analysis.

in the Pd(OAc)₂/*t*-BuOOH/allyl halides system at elevated temperature and CO pressure [6]. This result indicates that the Pd(OAc)₂/TFA/K₂S₂O₈ system is much effective to activate the aromatic C–H bonds in the carboxylation reactions of aromatic compounds with CO under very mild conditions.

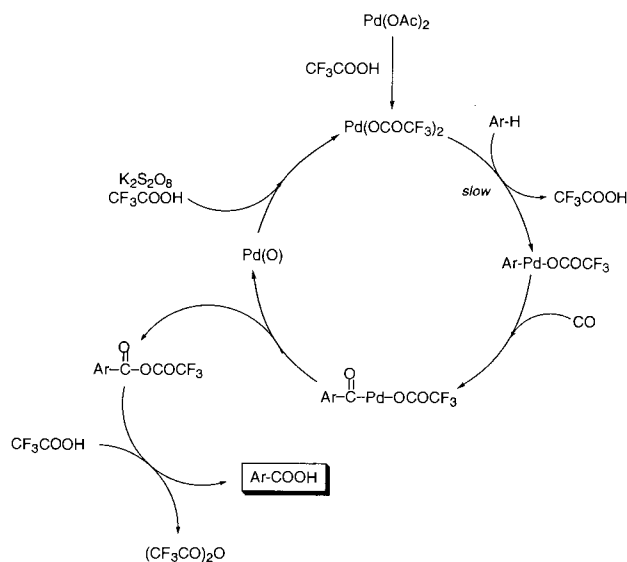
2.6. Mechanism

That the reaction proceeds with *ortho-para* orientation when an electron releasing group is attached to the benzene ring and that naphthalene gives α -naphthoic acid as a main product suggest that the reaction proceeds via electrophilic attack of cationic Pd(II) [6].

Competitive reaction of benzene and chlorobenzene with CO gave benzoic and chlorobenzoic acids in 580 and 60% yields, respectively. Similarly, the reactivities of other aromatic compounds were investigated by competitive reactions. From the result, the relative reactivity was found to be in the order of anisole > toluene > benzene > chlorobenzene. This result also indicates that the reaction is electrophilic.

Isotope effect for this carboxylation reaction was also studied by using *d*₆-benzene. The competitive reaction of C₆H₆ and C₆D₆ with CO afforded the mixture of benzoic acid and *d*₅-benzoic acid. The *k*_H/*k*_D ratio was found to be 6.1 by GC-MS analysis of the products. This result indicates that the C–H bond activation of arenes is the rate-determining step of this reaction.

The possible reaction mechanism is shown in Scheme 1. First, Pd⁺(OCOCF₃) is formed by the reaction of Pd(OAc)₂ and TFA. Then, electrophilic attack of an electropositive Pd⁺(OCOCF₃) species on the benzene ring produces an arylpalladium species which undergoes insertion of CO to give an aroylpalladium(II). The subsequent reductive eliminations give Pd(0) and the acid anhydride which reacts with TFA to form Ar-COOH and (CF₃CO)₂O. Pd(0) is reoxidized by K₂S₂O₈ to Pd(II) and thus the catalytic cycle is completed. The reason why the present reaction proceeds under milder conditions than those of the usual Pd(OAc)₂/AcOH system [6] could be attributed to the formation of more electropositive Pd⁺(OCOCF₃) species by use of TFA



Scheme 1. The possible mechanism of Pd(II)-catalyzed carboxylation of aromatic compound with CO.

compared with $\text{Pd}^+(\text{OCOCH}_3)$ which is formed under the usual conditions.

3. Conclusions

Benzene and other aromatic compounds can react with CO to produce aromatic acids by using $\text{Pd}(\text{OAc})_2$ catalysts in the presence of TFA and $\text{K}_2\text{S}_2\text{O}_8$ at room temperature under atmospheric pressure. The reaction is electrophilic and proceeds with *ortho*–*para* orientation when an electron-donating group such as CH_3 or CH_3O is attached to the benzene ring. This method is convenient and useful to synthesize the aromatic acids in a single step via direct C–H bond activation under mild conditions such as room temperature and atmospheric pressure.

4. Experimental

4.1. Materials and methods

$\text{Pd}(\text{OAc})_2$ was prepared by the procedure of Wilkinson and coworkers [12]. All the other starting materials and solvents were reagent grade and purified before use.

NMR spectra were obtained on a JOEL JNM-270 spectrometer; chemical shifts were expressed in parts per million downfield from tetramethylsilane. GC analyses were performed on a Shimadzu GC-14A system with a $3\text{ m} \times 3.2\text{ mm}$ i.d. glass column of OV-17 (2%) on 60 mesh Chromosorb W. Mass spectra were obtained on a Shimadzu GC-MS QP1000 spectrometer

equipped with a $1\text{ m} \times 3.2\text{ mm}$ i.d. glass column of OV-17 (2%) on 60 mesh Chromosorb W.

4.2. General procedure for carboxylation of arenes with CO

In a 50-ml round-bottomed flask equipped with a magnetic stirring bar, arene (56 mmol), $\text{Pd}(\text{OAc})_2$ (0.1 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol) and TFA (5 ml) were placed. The mixture was stirred at room temperature for 20 h under atmospheric pressure of CO (balloon). After addition of ether (50 ml), the mixture was treated with 2 M KOH solution (50 ml \times 3). To the aqueous layer was added concentrated HCl (30 ml) and the products were extracted with ether (50 ml \times 3). The combined ethereal layer was dried over MgSO_4 and filtered. After evaporation of the solvent, the products were isolated by SiO_2 (1 g) short column chromatography.

4.3. Analysis of isomer ratio of substituted benzoic acids and naphthoic acids

The product mixture (200 mg) was dissolved in ether (20 ml) and esterified by diazomethane evolved from *p*-toluenesulfonyl-*N*-methyl-*N*-nitrosoamide until the solution turned yellow. The resulting ester was analyzed by GLC or NMR. Isomer ratios of chlorobenzoic acids and naphthoic acids were determined by GLC and others were analyzed by NMR. Results are listed in Table 3.

4.3.1. *o*-Toulic acid

$^1\text{H-NMR}$ (CDCl_3 , 270.05 MHz) δ 2.65 (3H, s, CH_3), 7.00–8.00 (4H, m, Ph), 11.79 (1H, s, COOH); $^{13}\text{C-NMR}$ (CDCl_3 , 67.80 MHz) δ 22.7, 128.6, 131.6, 131.9, 132.9, 134.3, 144.3, 172.8.

4.3.2. *m*-Toulic acid

$^1\text{H-NMR}$ (CDCl_3 , 270.05 MHz) δ 2.42 (3H, s, CH_3), 7.32–7.94 (4H, m, Ph), 11.10 (1H, s, COOH); $^{13}\text{C-NMR}$ (CDCl_3 , 67.80 MHz) δ 21.1, 127.3, 128.3, 128.7, 130.7, 134.6, 138.2, 173.7.

4.3.3. *p*-Toulic acid

$^1\text{H-NMR}$ (CDCl_3 , 270.05 MHz) δ 2.43 (3H, s, CH_3), 7.30 (2H, d, $J = 7.9$ Hz, Ar), 7.98 (2H, d, $J = 7.9$ Hz, Ar), 11.10 (1H, s, COOH); $^{13}\text{C-NMR}$ (CDCl_3 , 67.80 MHz) δ 21.7, 126.5, 129.2, 130.2, 144.6, 172.7.

4.3.4. *m*-Anisic acid

$^1\text{H-NMR}$ (CDCl_3 , 270.05 MHz) δ 4.05 (3H, s, OCH_3), 7.03–8.53 (4H, m, Ar), 12.00 (1H, s, COOH); $^{13}\text{C-NMR}$ (CDCl_3 , 67.80 MHz) δ 56.4, 112.9, 116.2, 121.5, 132.7, 134.7, 161.4, 172.6.

4.3.5. *p*-Anisic acid

¹H-NMR (CDCl₃, 270.05 MHz) δ 3.82 (3H, s, CH₃), 6.97 (2H, d, *J* = 8.5 Hz, Ar), 7.94 (2H, d, *J* = 8.5 Hz, Ar), 12.00 (1H, s, COOH); ¹³C-NMR (CDCl₃, 67.80 MHz) δ 55.5, 114.2, 123.3, 132.1, 164.1, 172.6.

4.4. Competitive reactions

The competitive reaction of benzene and chlorobenzene with CO was carried out at room temperature for 20 h under 1 atm CO (balloon), charging benzene, chlorobenzene (28 mmol, each), Pd(OAc)₂ (0.1 mmol), K₂S₂O₈ (5 mmol) and TFA (5 ml) in a 50-ml round-bottomed flask equipped with a magnetic stirring bar. After work-up as described in Section 4.2, the ratio of products was analyzed by HPLC (octadecylsilane on silica gel, 60°C; eluent, MeOH:H₂O = 65:35, 0.5 ml min⁻¹) by using absorbance at 254 nm. Similarly, competitive reactions of other aromatic compounds with CO were performed.

The isotope experiment was performed similarly at room temperature under 1 atm of CO (balloon) for 20 h, charging benzene, *d*₆-benzene (28 mmol, each),

Pd(OAc)₂ (0.1 mmol), K₂S₂O₈ (5 mmol) and TFA (5 ml). The ratio of products was determined by GC-MS analysis.

References

- [1] C.L. Hill, Activation and Functionalization of Alkenes, Wiley Interscience, New York, 1989.
- [2] R.H. Crabtree, Chem. Rev. 95 (1995) 987.
- [3] A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879.
- [4] I. Moritani, Y. Fujiwara, Tetrahedron Lett. (1967) 1119.
- [5] H. Sugimoto, I. Kawata, H. Taniguchi, Y. Fujiwara, J. Organomet. Chem. 266 (1984) C44.
- [6] T. Jintoku, Y. Fujiwara, I. Kawata, T. Kawauchi, H. Taniguchi, J. Organomet. Chem. 385 (1990) 297.
- [7] Y. Fujiwara, K. Takaki, Y. Taniguchi, Synlett. (1996) 591.
- [8] T. Jintoku, H. Taniguchi, Y. Fujiwara, Chem. Lett. (1985) 1865.
- [9] K. Nakata, Y. Yamaoka, T. Miyata, Y. Taniguchi, K. Takaki, Y. Fujiwara, J. Organomet. Chem. 473 (1994) 329.
- [10] M. Asadullah, Y. Taniguchi, K. Kitamura, Y. Fujiwara, Appl. Organomet. Chem. 12 (1998) 277.
- [11] Y. Taniguchi, Y. Yamaoka, K. Nakata, K. Takaki, Y. Fujiwara, Chem. Lett. (1995) 345.
- [12] T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer, G. Wilkinson, J. Chem. Soc. (1965) 3632.