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Preliminary communication

PALLADIUM-CATALYZED CARBOXYLATION OF AROMATIC COMPOUNDS WITH CARBON DIOXIDE

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Summary

Carbon dioxide has been found to react with aromatic compounds such as benzene, anisole, furane, and thiophene to give aromatic acids in modest yields with palladium(II) salts as catalysts. The addition of t-BuOOH increases the yield.

We have previously reported that carboxylation of aromatic compounds with carbon monoxide (CO) occurs under formation of aromatic acids via direct activation of an aromatic C—H bond by palladium(II) salts [1]. This reaction was made catalytic with palladium(II) and using t-butyl hydroperoxide (t-BuOOH) as a reoxidizing agent [2]. In this connection, a study has been carried out using carbon dioxide (CO_2) instead of CO as part of a program aimed at exploring the carboxylation reaction in which CO_2 and a reactive intermediate, Ar—Pd—X, derived from aromatic hydrocarbons and palladium(II) salts [3], are employed.

Effective synthetic utilization of CO_2 is of great importance [4]; however, relatively few reports are available on the reactions of CO_2 with organic substances in the presence of transition metal compounds [5]. We now report the palladium-catalyzed (method B) or palladium-promoted (method A) reactions of CO_2 with aromatic compounds such as benzene, anisole, chlorobenzene, furane, and thiophene, giving aromatic acids.

$$\mathrm{ArH} + \mathrm{CO_2} \xrightarrow{\text{Pd salt}} \mathrm{ArCOOH}$$

(Ar = phenyl, chlorophenyl, anisyl, furyl, thienyl)

The reactions of aromatic compounds with CO_2 giving aromatic acids were performed by two different methods, A and B. Method A: in a 200-ml autoclave was placed a 50-ml centrifuge tube containing a palladium(II) salt (1 mmol) and the aromatic compound (20 ml). The autoclave was closed, flushed with CO_2, and pressurized to 30 atm. The mixture was heated at 150° C with stirring for 20 h. The resulting mixture was added to a saturated sodium bicarbonate solution. The water layer was acidified with concentrated HCl and the organic products were extracted with ether. The ethereal layer was dried and after evaporation of the solvent, the products were analyzed and identified as carboxylic acids by GC, NMR, and IR. Considerable amounts of picric acid, nitrobenzene, and biphenyl were also detected from the aromatic layer in the case of the reaction with $Pd(NO_3)_2$ and benzene. Method B was carried out using the aromatic compounds (16 ml), t-BuOOH (8 mmol), acetic acid (4 ml), and carbon dioxide (1 atm pressure) with $Pd(OAc)_2$ (0.2 mmol) at 70° C with stirring for 3 days in a 50-ml centrifuge tube [2].

The results are listed in Table 1, and deserve some comments. Reactions of anisole with CO_2 (entries 1, 7 and 10) give rise to methoxybenzoic acids and in the case of the reaction with $Pd(NO_3)_2$ (entry 7), *o*-, *m*-, and *p*-isomers are formed in the ratio 21/11/68, showing *ortho*, *para* orientation. Reactions of thiophene and furane with CO_2 (entries 2 and 3) give thiophen-2-carboxylic acid and furan-2-carboxylic acid, respectively. These results indicate that the reaction is electrophilic. Reaction of benzene with $Pd(NO_3)_2$ gives benzoic acid together with biphenyl, nitrobenzene, and picric acid (entry 5). In this reaction, the addition of $Fe(NO_3)_3$ (100 mol. equiv. of $Pd(OAc)_2$) increases the yield of benzoic acid from 2 to 66% (entry 6). The use of t-BuOOH as a reoxidizing agent increases greatly the yield of aromatic acids, and the reac-

TABLE 1

CARBOXYLATION OF AROMATIC COMPOUNDS WITH CARBON DIOXIDE

Entry	Pd salt	Aromatics	Method	Carboxylic acid yield (%) [a]	
1	$Pd(OAc)_2$	Anisole	A	Methoxybenzoic acid	13
2	$Pd(OAc)_2$	Thiophene	A	Thiophen-2-carboxylic acid	6
3	$Pd(OAc)_2$	Furane	A	Furan-2-carboxylic acid	trace
4	$Pd(OAc)_2$	Benzene	A [b]	Benzoic acid	13 [c]
5	$Pd(NO_3)_2$ [d]	Benzene	A	Benzoic acid	2 [e]
6	$Pd(NO_3)_2$ [d]	Benzene	A [f]	Benzoic acid	66 [g]
7	$Pd(NO_3)_2$ [d]	Anisole	A	Methoxybenzoic acid	6 [h]
8	$Pd(OAc)_2$	Benzene	B	Benzoic acid	127 [i]
9	$Pd(OAc)_2$	Benzene	B [j]	Benzoic acid	98 [k]
10	$Pd(OAc)_2$	Anisole	B	Methoxybenzoic acid	125
11	$Pd(OAc)_2$	Chlorobenzene	B	Chlorobenzoic acid	40

[a] Yields were determined by GC and are based on Pd salts. [b] AcOH (5 ml) was added. [c] Biphenyl (45%) was also formed. [d] Palladium(II) nitrate hydrate was used. [e] Picric acid (2%), nitrobenzene (7%), and biphenyl (12%) were also formed. [f] $Fe(NO_3)_3 \circ 9H_2O$ (100 mmol) was added. [g] Biphenyl (8%), nitrobenzene (417%), and picric acid (ca. 60%) were also formed. [h] Esterification with CH_2N_2 and GC analysis using a 50-m capillary column revealed that the ratio of *ortho*, *meta*, and *para* is 21/11/68. [i] Biphenyl (107%) and a small amount of phenol were also formed. [j] $Pd(OAc)_2$ (0.1 mmol), t-BuOOH (28 mmol), and allyl chloride (0.6 mmol) were used. [k] Biphenyl (60%) and a small amount of phenol were also formed.

tion can be made catalytic with respect to palladium(II) (entries 8 and 10)*.

There is one possibility that carboxylic acids are given via the reaction with CO which is formed by the reaction of CO_2 with palladium(II) salts. In fact by method A (entry 1), 0.03% of CO was detected by GC in the recovered CO_2 gas when the reaction was completed. However, calculation revealed that this amount of CO was not enough to produce as much as 13% of the methoxybenzoic acid from CO and anisole**. Therefore, it is shown that CO_2 reacts with aromatic compounds under formation of aromatic acids. Furthermore, no CO was detected in the recovered CO_2 gas after the reaction of method B.

The mechanism of the carboxylation of aromatic compounds with CO_2 appears to be closely related to that of the reaction with CO [1,5]. Probably a Pd-carboxylate complex, ArC(O)O—Pd—X, is formed from a homogeneous solution of palladium(II) salts and aromatic compounds via an aromatic σ-palladium complex, Ar—Pd—X [3], followed by coordination and subsequent insertion of CO_2 [5].

This communication is the first example of the carboxylation of aromatic compounds with CO_2 by activation of both CO_2 and aromatic C—H bonds by transition metal complexes.

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*In method B which employed t-BuOOH, no CO_2 pressure was used to avoid explosion. The $Pd(OAc)_2$ / t-BuOOH system itself has been found to cause carboxylation of benzene to give benzoic acid in a considerable yield [2].

**By using the equation $n = (PV/RT)(CO(\%)/100)$, the amount of CO formed was estimated as 0.066 mmol which theoretically gives a 6.6% yield. This value is lower than the experimental yield of anisic acid (13%).