Selective carbonylation of benzene to benzaldehyde

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An efficient strategy on facial, selective carbonylation of benzene to give benzaldehyde was developed. $Co(OAc)_2/K_2S_2O_8/CCl_3COOH/$pyridine was found to be a novel multi-catalytic system for direct carbonylation of benzene to benzaldehyde under mild conditions, in which the yield of benzaldehyde was up to 38.3% at the present stage.

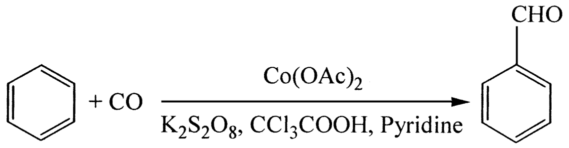
KEY WORDS: benzene carbonylation; benzaldehyde; cobalt complex.

1. Introduction

The transformation of aromatics and saturated hydrocarbons through C–H bond activation constitutes an extremely important field of contemporary chemistry [1]. The direct carboxylation of aromatic compounds is an interesting topic in this area. Carboxylation is the simultaneous or sequential breaking of a C–H bond and insertion of CO to form a –COOH group. In 1990, Fujiwara and co-workers [2] found that the carboxylation of aromatic compounds could take place over Pd-based catalysts in the presence of *t*-BuOOH and allyl chloride (acting as a reoxidizing agent), giving carboxylic acids and phenol in one step. Moreover, they reported that the $Pd(OAc)_2/TFA/K_2S_2O_8$ catalytic system could cause the direct carboxylation of aromatic compounds with CO at room temperature and atmospheric pressure to give the corresponding acids [3]. They suggested the reaction to proceed via an ArPdL σ-complex intermediate by electrophilic substitution. Although high yields of the corresponding acids were obtained, with biphenyl and phenyl as the by-products, all these catalytic systems did not, however, lead to the formation of benzaldehyde using benzene as the starting material.

Clearly the selective carbonylation of benzene is more difficult because the selectivity is more difficult to control. There are few literature reports of this selective carbonylation reaction [4]. To date two strategies have been used for the formylation of benzene to benzaldehyde. The first is typified by electrophilic attack on the C–H bond. This usually occurs in strong acids such as $HF–SbF_5$ [5] and other liquid superacids [6]. It involves the intermediate formation of carbonium ions. The second strategy is through oxidative addition of the metal center of the complex, usually with irradiation. $IrH_3(CO)(Ph_2PCH_2CH_2PPh_2)$ [7], $RhCl(CO)(PPH_3)_2$ [8] and $RhCl(CO)(PMe_3)_2$ [9] were found to be efficient catalysts for selective carbonylation of benzene to afford benzaldehyde using irradiation.

In the present paper we report a novel catalytic system for selective carbonylation of benzene under mild conditions, giving benzaldehyde as the predominant product with relatively high yield and selectivity. The catalytic system is characteristic of neither the addition of highly corrosive HF or $HF–SbF_5$ nor excitation by irradiation. To achieve this remarkably efficient and environmentally friendly conversion, the new catalytic system $Co(OAc)_2/K_2S_2O_8/CCl_3COOH/$pyridine was developed. The reaction is shown in scheme 1.



Scheme 1.

2. Experimental

Typical reaction procedures were as follows. In a 50 ml autoclave 20 ml (0.225 mol) of benzene, 0.002 mol of $Co(OAc)_2$, 0.0037 mol of $K_2S_2O_8$, 0.018 mol of CCl_3COOH and 0.012 mol of pyridine were added. After flushing with CO three times, the autoclave was pressurized with CO to 1.0 MPa, this value being maintained in the reaction process. The reaction lasted for 24 h at 100 °C under stirring. The products were analyzed by GC (HP-1102; column: FFAP $30\,m \times 0.25\,mm \times 0.33\,\mu m$;

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flame ionization detector) and identified using GC-MS (HP-5973).

3. Results and discussion

When benzene under 1.0 MPa pressure of carbon monoxide was stirred for 24 h in the presence of the catalytic system described above, benzaldehyde, chlorobenzene and diphenylmethane were obtained in the yields of 38.3, 2.5 and 2.1%, respectively, with the conversion of benzene of 50.2%. The absence of pyridine results in the formation of benzoic acid and phenol as the main products. This result is fairly similar to that reported by Fujiwara *et al.* [3]. In that case, trifluoroacetic acid was used instead of trichloroacetic acid for direct carboxylation of saturated hydrocarbons by $Co(OAc)_2$ catalyst.

As given in table 1, in the absence of trichloroacetic acid or the replacement by monochloroacetic acid, no significant reaction occurs (only 7.4% phenol obtained). The addition of co-catalyst $Mn(OAc)_2$ or $Cu(OAc)_2$ did not improve the conversion of benzene. However, the pyridine derivative, such as DMAP, decreases the yield of benzaldehyde. When the CO was replaced with atmospheric air, phenol and chlorobenzene became the major products. Therefore, the selective oxygenation of benzene, phenol, benzaldehyde and benzoic acid could be obtained depending on whether or not pyridine and pressurized CO were present in the catalytic system.

The effect of pyridine on the yield of benzaldehyde was investigated and the results are shown in figure 1. At low concentration of pyridine (<0.015 mol), the yield of benzaldehyde increases with increasing pyridine. Meanwhile the by-product, benzoic acid, gradually decreased. When the concentration of pyridine was greater than *ca.* 0.017 mol, there was no obvious effect on the yield of benzaldehyde; however, the presence of chlorobenzene as a by-product was observed.

The detailed mechanism involving the selective formation of benzaldehyde remains unclear. As suggested by Fujiwara *et al.* [10], $Co(OAc)_2$ is readily oxidized to high-valence species, for instance $Co_{ox}(III)$ species and analogues [11], in the presence of molecular oxygen, especially in a strong oxidant (e.g. $K_2S_2O_8$). The homolytic decomposition of the O–O bond of cobalt(III) species gives the Co(III)–$O^\bullet$ radical. The latter then attacks the C–H bond of benzene to form the $Ar^\bullet$ radical and subsequently traps CO to afford an acyl radical ($ArCO^\bullet$). This is a typical free-radical reaction [12]. On the other hand, $Ar^\bullet$ also may react with $Cl^\bullet$, which is supplied by CCl_3COOH [13], resulting in the formation

Table 1
$Co(OAc)_2/K_2S_2O_8/CCl_3COOH$/pyridine-catalyzed selective carbonylation of benzene with carbon monoxide

Catalyst	Product	Yield [a] (%)
$Co(OAc)_2 + K_2S_2O_8 + CCl_3COOH$	Phenol	8.5
	Chlorobenzene	5.7
	Benzoic acid	3.8
$CoCl_2 + K_2S_2O_8 + CCl_3COOH$ [b]	Phenol	12.6
$Co(OAc)_2 + K_2S_2O_8 + CCl_3COOH + \text{pyridine}$	Benzaldehyde	38.3
	Chlorobenzene	2.5
	Diphenylmethane	2.1
$Co(OAc)_2 + Cu(OAc)_2 + K_2S_2O_8 + CCl_3COOH + \text{pyridine}$ [c]	Benzaldehyde	36.4
	Chlorobenzene	1.9
	Diphenylmethane	2.8
$Co(OAc)_2 + Mn(OAc)_2 + K_2S_2O_8 + CCl_3COOH + \text{pyridine}$ [d]	Benzaldehyde	39.1
	Chlorobenzene	2.3
	Diphenylmethane	2.2
$Co(OAc)_2 + K_2S_2O_8 + CCl_3COOH + \text{DMAP}$ [e]	Phenol	19.6
	Chlorobenzene	5.1
$K_2S_2O_8 + CCl_3COOH + \text{pyridine}$	No product	0
$Co(OAc)_2 + CCl_3COOH + \text{pyridine}$	No product	0
$Co(OAc)_2 + K_2S_2O_8 + CCl_3COOH + PPH_3$ [f]	Phenol	10.3
	Chlorobenzene	1.7
$Co(OAc)_2 + K_2S_2O_8 + CH_2ClCOOH + \text{pyridine}$ [g]	Phenol	7.4

[a] Calculated based on benzene.
[b] 0.002 mol of $CoCl_2$ was added.
[c] 0.001 mol of $Cu(OAc)_2$ was added.
[d] 0.001 mol of $Mn(OAc)_2$ was added.
[e] 0.001 mol of dimethylaminopyridine (DMAP) was added.
[f] 0.002 mol of PPH_3 was added.
[g] 0.018 mol of $CH_2ClCOOH$ was used.

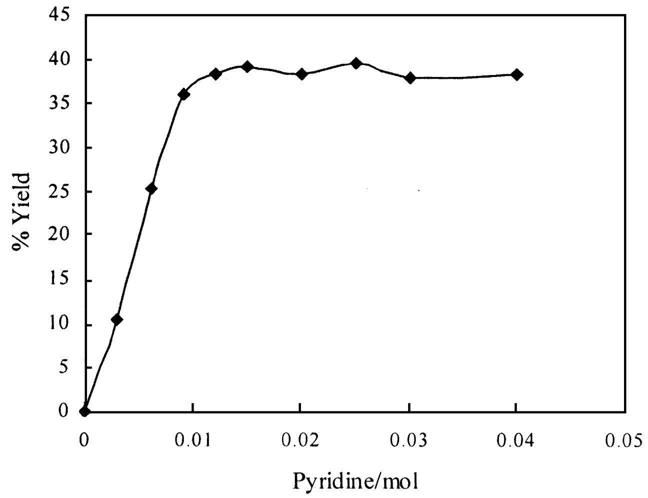

Figure 1. Influence of the concentration of pyridine on the yield of benzaldehyde. Reaction conditions: 0.225 mol of benzene, 0.002 mol of $Co(OAc)_2$, 0.0037 mol of $K_2S_2O_8$, 0.018 mol of CCl_3COOH, $P_{co} = 1.0$ MPa, $T = 100\,^{\circ}C$, $t = 24$ h.

of a chlorinated by-product: chlorobenzene. The experimental results reveal that about 30% trichloroacetic acid is converted to dichloroacetic acid. The function of pyridine may be attributed to the alternation of the coordination environment of cobalt species and thereby alters the selectivity of the reaction. It is worth noting that the formation of acyl radical ($ArCO^{\bullet}$) and chlorobenzene is probably competitive, depending on the absence or presence of pyridine.

In summary, the selective carbonylation of benzene to benzaldehyde has been achieved for the first time using the $Co(OAc)_2/K_2S_2O_8/CCl_3COOH$/pyridine catalytic system.

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