

Selective carbonylation of benzene to benzaldehyde using O_2 as the oxidant in the presence of cobalt complex

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Received 15 March 2004; received in revised form 21 May 2004; accepted 21 May 2004

Available online 7 October 2004

Abstract

An efficient strategy on facial, environmentally friendly, economic, selective carbonylation of benzene to give benzaldehyde using O_2 as the oxidant was firstly developed. $Co(OAc)_2/CCl_3COOH$ with the addition of additives such as pyridine was found to be an effective catalyst system for direct catalytic carbonylation of benzene to benzaldehyde with relatively high yield (37.3%) and selectivity (80%) under mild conditions. The influence of various reaction conditions on reaction performance was shown. A possible reaction mechanism was proposed. © 2004 Published by Elsevier B.V.

Keywords: Benzene; Selective carbonylation; Benzaldehyde; Oxygen; Cobalt complex

1. Introduction

Benzene is one of the least reactive aromatic compounds, therefore selective conversion to more useful chemical products would be of great value. One of useful target products for direct catalytic carbonylation of benzene is benzaldehyde. It is difficult to achieve because the selectivity is hard to be controlled. In literature there are two approaches [1] 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 $HF-SbF_5$ [2] and other liquid superacids [3]. The second approach is via oxidative addition of the metal center of the complex, usually with irradiation. $Ir(CO)(Ph_2CH_2PPh_2)$ [4], $RhCl(CO)(PPh_3)_2$ [5] and $RhCl(CO)(PMe_3)_2$ [6] were found to be the efficient catalysts for selective carbonylation of benzene to give benzaldehyde using irradiation.

In our previous study it has been reported [7], that benzaldehyde was obtained through selective carbonylation of benzene under the catalyst system of $Co(OAc)_2/CCl_3COOH/K_2S_2O_8$ /pyridine, with relatively high yield (38.3%) and selectivity (ca. 90%). The catalyst system is characteristic of neither the addition of highly corrosive HF or $HF-SF_5$ nor the use of irradiation. However, previous reports of

the direct catalytic conversion of benzene to benzaldehyde have involved peroxydisulphate ($K_2S_2O_8$) or *t*-BuOOH as the oxidants, but any such process that could be adapted to large-scale applications would have to use O_2 as the oxidant, because it is environmentally friendly and economic. So to achieve this efficient and environmentally benign and economic conversion, the new catalyst system $Co(OAc)_2/CCl_3COOH$ with the addition of additives such as pyridine, iminazole, 2,2'-bipyridine, PPh_3 , and $P(n-Bu)_3$ was developed to achieve the selective carbonylation of benzene to benzaldehyde using O_2 as the oxidizing agent under mild conditions. The carbonylation reaction is shown in Scheme 1.

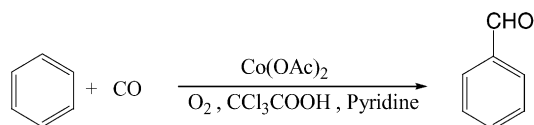
2. Experimental

2.1. Reagents

Benzene (Shanghai Chemical Reagent Company) was dried with 4A molecular sieves, CCl_3COOH was purchased from Shanghai Chemical Reagent Company and used without further purification. Acetate cobalt, PPh_3 , pyridine, 2,2'-bipyridine and iminazole were purchased from Shanghai Chemical Reagent Company and used as received, $P(n-Bu)_3$ was prepared as literature [8]. CO and O_2 was obtained from Shanghai Gas Company and Gas Company of Zhejiang University, respectively, and used without further purification.

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2.2. Analysis

The reaction was monitored by gas chromatography (HP-1102) equipped with a 30 m capillary column (FFAP). The injector and FID detector were set at 210 °C and 230 °C, respectively. The temperature program: started at 100 °C and ended at 190 °C, with a heating rate of 20 °C min⁻¹. The products obtained were purified and identified by GC-MS (HP-5973).

2.3. Reaction procedure

The reaction was conducted in a stainless-steel autoclave (100 mL) equipped with a stirrer, a purging valve and a thermometer. A mixture of benzene, CCl₃COOH, additive and acetic cobalt were fed into the autoclave. Before reaction, air was replaced by purging with a stream of N₂. Then the autoclave was pressurized with CO and O₂ to the desired pressures and heated to a certain temperature (e.g. 130 °C) under stirring. Once the reaction was completed, the reaction mixture was cooled down to room temperature, filtered and analyzed by GC.

2.4. Typical example

The typical procedure of selective carbonylation of benzene to benzaldehyde by using O₂ as the oxidant was as follows: a mixture of benzene (0.225 mol), Co(OAc)₂ (2.24 mmol), CCl₃COOH (24 mmol) and pyridine (25 mmol) was added in a 100 mL autoclave. Then the mixture was heated to 130 °C under 12 kg cm⁻² of carbon monoxide and 4 kg cm⁻² of oxygen for 26 h by stirring. The mixture was filtered and the products were analyzed by GC (HP-1102; capillary column: FFAP 30 m × 0.25 mm × 0.33 μm; flame ionization detector) and identified by using GC-MS (HP-5973).

3. Results and discussion

3.1. Additive effect

Two types of additives, N-containing (e.g. pyridine, 2,2'-bipyridine, iminazole) and P-containing (e.g. PPh₃ and P(*n*-Bu)₃) compounds were used in this study. The effects of additives on reaction performance were presented in Table 1. It can be seen therein that by using pyridine as the additive the yield (37.3%) and selectivity (ca. 80%) of benzaldehyde were achieved, which reached the same level as

Table 1
Additive effect on reaction performance

Entry	Additive	Yield (%)			
		Benzaldehyde	Phenol	Chlorobenzene	Benzoic acid
1	Pyridine	37.3	4.08	2.11	4.08
2	Iminazole	12.3	Trace	1.86	Trace
3	2,2'-bipyridine	10.8	Trace	1.03	Trace
4	PPh ₃	1.24	2.53	0.85	12.8
5	P(<i>n</i> -Bu) ₃	11.2	0.41	1.90	1.20

Reaction conditions: benzene (0.225 mol), Co(OAc)₂ (2.24 mmol), CCl₃COOH (24 mmol), additive (25 mmol), P_{CO}: 12 kg cm⁻², P_{O₂}: 4 kg cm⁻², 130 °C, 26 h.

using K₂S₂O₈ as the oxidant [7]; while using iminazole and 2,2'-bipyridine as the additives the yields of benzaldehyde were decreased to 12.3% and 10.8%, respectively. However, it is interesting to note that both phenol and benzoic acid were observed with trace level. This observation implies that oxidative reaction of benzene to phenol and benzoic acid is suppressed in this case. The presence of pyridine may alter the coordinative environment of cobalt species with the formation of N-Co bond in the complex to modify catalytic activity. However in the case of iminazole and 2,2'-bipyridine a chelating configuration with cobalt species may be formed via double nitrogen atoms to affecting the reactivity. On the other hand, when PPh₃ was used as the additive the main product was benzoic acid, indicating the alternation in reaction selectivity. By using P(*n*-Bu)₃ as the additive, however, the reaction selectivity was changed back to benzaldehyde as the main product with 11.2% yield. These results probably related to stereoscopic effect of the additives.

3.2. Influence of the amount of pyridine

In concerning influence of the amounts of pyridine on reaction performance the experimental results were shown in Fig. 1. It can be seen from therein that with the increase in the

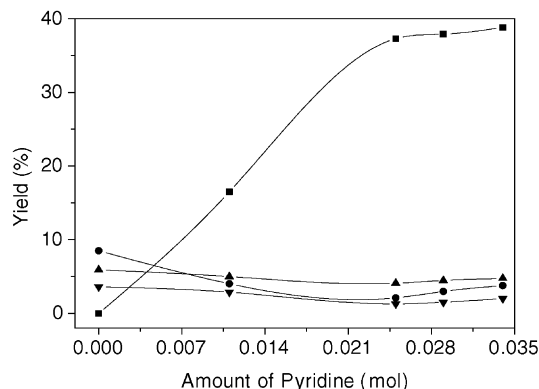


Fig. 1. Effect of the amount of pyridine on reaction performance. Reaction conditions: benzene (0.225 mol), Co(OAc)₂ (2.24 mmol), CCl₃COOH (24 mmol), P_{CO}: 12 kg cm⁻², P_{O₂}: 4 kg cm⁻², 130 °C, 26 h, (■) yield of benzaldehyde, (●) yield of chlorobenzene, (▼) yield of phenol, (▲) yield of benzoic acid.

amount of pyridine from null to 0.025 mol, the yield of benzaldehyde obviously increased, the yield of chlorobenzene slightly decreased; while the yields of phenol and benzoic acid were kept at the same values. However, when pyridine was absent, almost no benzaldehyde was observed, implying that the presence of pyridine in the catalyst system plays a crucial role. Its function may be attributed to alter electronic property of cobalt complex by coordination. When the amount of pyridine was up to 0.025 mol, the yield of benzaldehyde was almost constant, (ca. 38%). But the amount of pyridine was continuously increased to 0.034 mol, the yields of chlorobenzene, phenol and benzoic acid were slightly increased. Therefore the optimum amount of pyridine was 0.025 mol in this case.

3.3. Influence of the pressure and CO/O₂ ratio

The CO pressure and CO/O₂ ratio showed significant influence on the carbonylation performance as given in Table 2. It can be seen from Table 2 that when the pressures of CO were varied from 8 to 40 kg cm⁻², while P_{O₂} was kept at constant (4 kg cm⁻²), the yields of benzaldehyde were obviously increased from 20.5% to 39.2%. When the O₂ pressure was slightly increased from 4 kg cm⁻² to 6 kg cm⁻², CO pressure remained at 12 kg cm⁻² (see entries 2 and 4), the yields of benzoic acid and phenol were slightly increased; meanwhile the yield of benzaldehyde was lowered. Therefore the optimum pressure and the ratio of CO/O₂ was 12 to 4 kg cm⁻². However there was only chlorobenzene as the product when O₂ was absent. Therefore oxygen seems to play a crucial role to form active species of cobalt catalyst, even the stoichiometry of this carbonylation reaction (Scheme 1) does not require O₂. The formation of chlorobenzene is possibly due to CCl₃COOH solvent, which is the donor of Cl[•]. For comparison two additional experiments were studied as given in entries 8 and 9 of Table 2. In both experiments, Co(OAc)₂/CCl₃COOH/K₂S₂O₈ was used as the catalyst system, but in the experiment (entry 9) pyridine was used as the additive, while in the other experiment (entry 8)

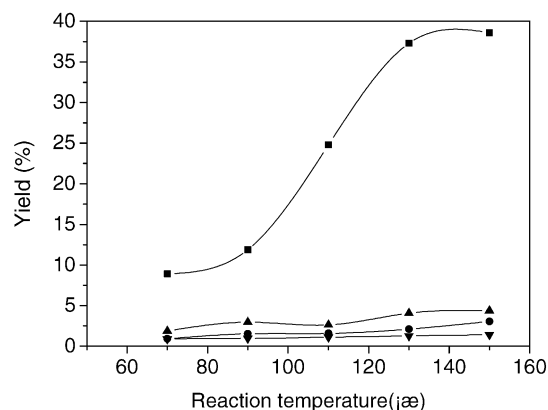


Fig. 2. Influence of reaction temperature on the yields of reaction. Reaction conditions: benzene (0.225 mol), Co(OAc)₂ (2.24 mmol), CCl₃COOH (24 mmol), Pyridine (25 mmol), P_{CO}: 12 kg cm⁻², P_{O₂}: 4 kg cm⁻², 26 h (■) yield of benzaldehyde, (●) yield of chlorobenzene, (▼) yield of phenol, (▲) yield of benzoic acid.

pyridine was absent. It can be seen clearly that benzoic acid was the main product, and phenol and chlorobenzene were the main by-products in entry 8. However, benzaldehyde was the main product, and chlorobenzene was the only by-product in entry 9. It indicated that the presence of pyridine in the catalyst system obviously altered the selectivity of this carbonylation reaction.

3.4. Influence of reaction temperature

The influence of reaction temperature on reaction performance was examined as presented in Fig. 2. From therein one can see that as increasing temperature from 70 °C to 150 °C, the yield of benzaldehyde was enhanced from 8.1% up to 38.6%. Meanwhile the yields of by-products of phenol, chlorobenzene and benzoic acid were slightly increased. When elevating the reaction temperature up to 150 °C, the yield of benzaldehyde almost kept at constant value (ca. 38%). Therefore the optimum reaction temperature is 130 °C at which the yield of benzaldehyde with 37.3% was achieved.

Table 2
Influence of the CO pressure and CO/O₂ ratio on the reactivity

Entry	P _{CO} (kg cm ⁻²)	P _{O₂} (kg cm ⁻²)	Yield (%)			
			Benzaldehyde	Phenol	Chlorobenzene	Benzoic acid
1	15	Null	Null	Null	6.73	null
2	12	4	37.3	4.08	2.11	4.08
3	8	4	20.5	2.35	1.96	3.69
4	12	6	33.5	4.67	1.86	4.96
5	15	4	38.0	3.67	1.89	1.11
6	26	4	38.6	2.74	1.78	1.03
7	40	4	39.2	2.69	1.82	0.73
8 ^a	10	Null	Null	8.8	4.7	16.7
9 ^b	10	Null	36.4	Null	2.5	Null

Reaction conditions: benzene (0.225 mol), Co(OAc)₂ (2.24 mmol), CCl₃COOH (24 mmol), pyridine (25 mmol), 130 °C, 26 h.

^a Reaction conditions: benzene (0.225 mol), Co(OAc)₂ (2.00 mmol), CCl₃COOH (18 mmol), K₂S₂O₈ (3.7 mmol), 100 °C, 26 h.

^b Reaction conditions: benzene (0.225 mol), Co(OAc)₂ (2.02 mmol), CCl₃COOH (18 mmol), K₂S₂O₈ (3.7 mmol), pyridine (25 mmol), 100 °C, 26 h.

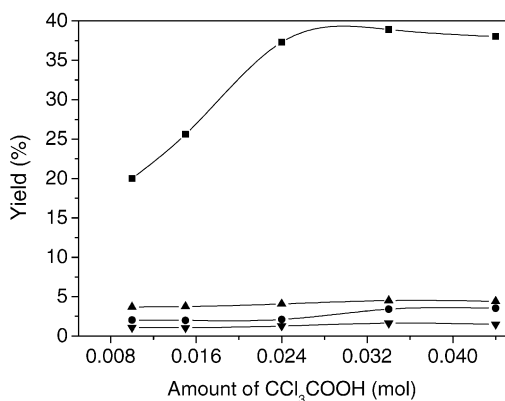


Fig. 3. Effect of the amount of CCl_3COOH on reaction performance. Reaction conditions: benzene (0.225 mol), $\text{Co}(\text{OAc})_2$ (2.24 mmol), pyridine (25 mmol), $P_{\text{CO}}: 12 \text{ kg cm}^{-2}$, $P_{\text{O}_2}: 4 \text{ kg cm}^{-2}$, 130°C , 26 h (■) yield of benzaldehyde, (●) yield of chlorobenzene, (▼) yield of phenol, (▲) yield of benzoic acid.

3.5. Influence of the amount of CCl_3COOH

In the present catalyst system CCl_3COOH as the solvent affords a strong polar media, however, trichloroacetic acid is also an effective Cl^\bullet donor [7] which leads to forming the chlorinated product, chlorobenzene. The influence of the amount of CCl_3COOH on the reaction performance was tested as shown in Fig. 3. It shows that with the increase in CCl_3COOH amount from 0.01 mol to 0.045 mol, the yield of benzaldehyde was enhanced from 20.1% to 38.5%, but the yield of chlorobenzene accordingly increased from 1.5% to 6.3%. With 0.035 mol of CCl_3COOH , the yield of benzaldehyde was nearly constant, ca. 38.8%. Therefore the suitable amount of CCl_3COOH was 0.035 mol in this case.

3.6. Influence of amounts of $\text{Co}(\text{OAc})_2$

The plots of the amounts of $\text{Co}(\text{OAc})_2$ vs the yields of benzaldehyde and by-products were shown in Fig. 4. It can be seen from Fig. 4 that with the increase in $\text{Co}(\text{OAc})_2$ dosage from 0.1 mmol to 3.25 mmol, the yield of benzaldehyde increased dramatically up to 38%, however the yields of the by-products were increased sequentially. When the amount of $\text{Co}(\text{OAc})_2$ was up to 2.24 mmol, the yield of benzaldehyde was nearly constant, ca. 38%. It means that the appropriate amounts of $\text{Co}(\text{OAc})_2$ was 2.24 mmol.

4. Possible reaction mechanism

From experimental results, we consider that two types of possible reaction mechanisms may be suggested. One is radical reaction mechanism as proposed by Asadullah et al. [9]. In the radical mechanism, the formation of $\text{C}_6\text{H}_5^\bullet$ is regarded as the key step. Then $\text{C}_6\text{H}_5^\bullet$ is easily captured by CO and O_2 , and finally lead to the formation of phenol and benzoic acid. However we thought it could not ex-

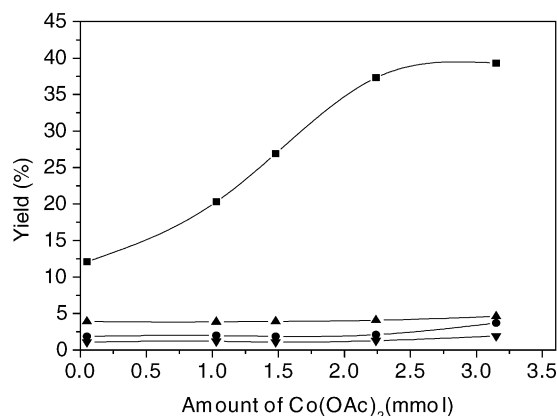
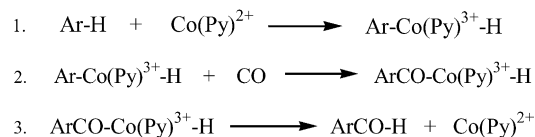


Fig. 4. Effect of the amount of $\text{Co}(\text{OAc})_2$ on catalytic activities. Reaction conditions: benzene (0.225 mol), CCl_3COOH (24 mmol), pyridine (25 mmol), $P_{\text{CO}}: 12 \text{ kg cm}^{-2}$, $P_{\text{O}_2}: 4 \text{ kg cm}^{-2}$, 130°C , 26 h (■) yield of benzaldehyde, (●) yield of chlorobenzene, (▼) yield of phenol, (▲) yield of benzoic acid.



Scheme 2.

plain the formation of benzaldehyde as the main product with $\text{Co}(\text{OAc})_2/\text{CCl}_3\text{COOH}/\text{pyridine}$ as the catalyst system. Because according to radical mechanism benzaldehyde is formed as the intermediate, and then quickly be oxidized to benzoic acid by oxygen. In the present study, by using O_2 as the oxidant instead of $\text{K}_2\text{S}_2\text{O}_8$, the formation of by-products, phenol and benzoic acid, were obviously suppressed by the addition of N-containing additives as presented in entries 1–3 of Table 1. Therefore we proposed the other possible mechanism: oxidative addition, as shown in Scheme 2. At the first step in the presence of oxygen the activation of C–H bond of benzene by $\text{Co}(\text{Py})^{2+}$ to form $\text{Ar-Co}(\text{Py})^{3+}\text{-H}$ complex, the oxidation state of cobalt, then with the insertion of CO (step 2), finally benzaldehyde was produced by reductive elimination as the step 3. While using PPh_3 as the additive in $\text{Co}(\text{OAc})_2/\text{CCl}_3\text{COOH}$ system as presented in entry 4 of Table 1, the radical mechanism seems to be involved. Benzoic acid turned out to be the main product. It implied that the nature of the additive could alter the selectivity of benzene carbonylation reaction. Further studies on the reaction mechanisms are required.

5. Conclusions

For the first time, selective carbonylation of benzene to benzaldehyde by using O_2 as the oxidant under mild conditions in the catalyst system of $\text{Co}(\text{OAc})_2/\text{CCl}_3\text{COOH}/\text{pyridine}$ has been achieved. In the present study the

optimum reaction conditions were as follows: the amounts of $\text{Co}(\text{OAc})_2$, CCl_3COOH and pyridine (as the additive) should be 2.24 mmol, 0.024 mol and 0.025 mol, respectively, and the optimum CO/O_2 ratio was $12 \text{ kg cm}^{-2}/4 \text{ kg cm}^{-2}$. A possible reaction mechanism of oxidative addition was proposed.

Acknowledgements

We are grateful for the financial support of the National Natural Science Foundation of China (No. 20273059).

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