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Cobalt Salts-Catalyzed Carbonylation of Aromatic Halides under Photostimulation

Kiyoshi KUDO,* Tadashi SHIBATA, Tsugunori KASHIMURA,
Sadayuki MORI, and Nobuyuki SUGITA

Institute for Chemical Research, Kyoto University,
Gokanosho, Uji 611

A novel method for the carbonylation of aromatic halides by the cobalt salt catalysts such as $Co(OAc)_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, $Co(OH)_2$, $Co(OH)_3$, CoO, and Co_2O_3 was investigated in an aqueous alkaline solution under photostimulation. These salts were found to have a catalytic activity as high as that of $Co_2(CO)_8$ under mild conditions.

Several methods for cobalt-catalyzed carbonylation of aryl halides to the corresponding acid derivatives have been reported.[1-5] In our previous publications,[6,7] we have reported that cobalt carbonyl($Co_2(CO)_8$)-catalyzed polycarbonylation of polyhalogenated benzenes could be easily achieved under photostimulation. We have also reported that cobalt carbonyl-catalyzed double-carbonylation was observed to occur at ortho position as well. The scope of the application of the carbonylation reaction, however, is still limited and cobalt carbonyl complexes have been used as the sole catalytic precursor. It is of interest to find a pre-catalyst other than zero-valent cobalt carbonyls. Caubere et al. investigated the carbonylation of halides using Co(II) salt under the coexistence of reducing agents such as NaH(termed CoCRACO), and they have found that an active catalyst was essentially $Co(CO)_4^-$.[1] The use of inorganic cobalt salts as pre-catalyst without reducing agents has never been reported for the catalytic carbonylation of halides under ambient conditions.

During our studies we have observed that the cobalt(II) salts; $Co(OAc)_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, $Co(OH)_2$, and CoO, also catalyzed the photostimulated carbonylation of aromatic halides, including much less reactive chlorobenzene, under mild conditions(atmospheric pressure and room temperature). We report here the results of this novel and convenient catalytic system, which shows catalytic activites as high as that of cobalt carbonyl and some different features.

$$\mathrm{ArX} + \mathrm{CO} + 2\mathrm{NaOH} \xrightarrow[\text{aq. NaOH}]{\text{Co-salts}/h\nu\,(350\text{ nm})} \mathrm{ArCOONa} + \mathrm{NaX}$$

Experimental apparatus and procedure are essentially the same as those given in the previous reports,[6-8] except for the use of inorganic salts in place of cobalt carbonyl. Other relevant conditions are specified in Tables.

First, we examined the catalytic properties of various cobalt salts using

Table 1. Cobalt Salts-Catalyzed Cabonylation of *m*-Bromobenzoic Acid a)

Run	Cobalt salt	Temp	Conversion b)	Products(Yield/%) b)	
		°C	%	Isophthalic acid	Benzoic acid
1	$Co(OAc)_2 \cdot 4H_2O$	65	100	97.5	1.0
2	$Co(OAc)_2 \cdot 4H_2O$	30	99.4	96.2	2.0
3	$CoCl_2 \cdot 6H_2O$	65	100	97.0	2.4
4	$CoSO_4 \cdot 7H_2O$	65	100	97.4	1.6
5	$Co(OH)_2$	65	100	97.1	2.4
6	$Co(OH)_3$	65	100	80.3	1.0
7	CoO	65	98.6	98.0	1.5
8	Co_2O_3 c)	65	73.5	68.2	2.1
9	$Co_2(CO)_8$	65	100	92.5	5.7
10	$Co_2(CO)_8$	30	49.7	42.4	1.6

a) Cobalt salt:0.2 mmol($Co_2(CO)_8$:0.1 mmol); *m*-bromobenzoic acid:2.0 mmol; CO:2 atm; reaction time:1 h; aqueous 2.5 mol dm^{-3} NaOH:20 ml. b) Determined by GLC with internal standards, as methyl esters obtained by esterification of acids with diazomethane, and based on the halide used. c) Containing 15%(wt) of CoO.

m-bromobenzoic acid as substrate in aqueous NaOH solution. The results are listed in Table 1, together with the result with cobalt carbonyl(Runs 9 and 10). Among the cobalt salts examined, cobalt(II) salt exhibited higher catalytic activities than cobalt(III) salts(Runs 5 to 8), and almost the same activity as cobalt carbonyl. There was no essential difference in the catalytic activity among cobalt(II) salts used here. The yields of isophthalic acid were usually quantitative and reduction to benzoic acid was not so significant. The reactions were usually carried out at 65 °C, but they also proceeded well enough even at room temperature(Run 2). While, with cobalt carbonyl catalyst, the carbonylation yield at room temperature(Run 10) was lower than those obtained with cobalt salts.

Next, the carbonylation of various aromatic halides to corresponding aromatic acids were investigated using cobalt(II) acetate as catalyst(Table 2). In the cases where the starting halides have no hydrophilic groups, ethanol was found to be the best co-solvent (Medium B). The maximum yield was obtained at the volume ratio of 1/3 of EtOH/H_2O. On the other hand, the use of methanol(Run 12) or alcoholic solution(Run 15) were disadvantageous to the reaction. Except for the ortho substituted halides(Run 21), reduction to benzene derivatives was not substantial. Although the carbonylation of bromides was not appreciably affected by the reaction temperature(Table 1, Runs 1 and 2), the carbonylation rates of chlorides were increased with rising temperature(Runs 22-24). Increase of CO pressure(up to 8 atm) had little influence on the relative yields of carbonylated products. Of the several bases examined(NaOH, KOH, LiOH and CsOH), NaOH was by far the best. The concentration of base was an important variable and the optimum concentration of NaOH was found to be about 2.5 mol dm^{-3}.

Interestingly, the carbonylation reaction proceeded not only for halides

Table 2. Cobalt(II) Acetate-Catalyzed Carbonylation of Aromatic Halides[a)]

Run	Halides	Reaction medium[c)]	Temp °C	Time h	Conv.[b)] %	Products[b)] (Yield/%)
11	Chlorobenzene	B	30	20	78.5	Benzoic acid(49.3)
12	Chlorobenzene	C	30	20	40.0	Benzoic acid(11.8)
13	Bromobenzene	B	30	1	100	Benzoic acid(98.7)
14	Bromobenzene	D	65	2.5	12.5	Benzoic acid(4.1)
15	*m*-Bromobenzoic acid	E	65	1	95.5	Isophthalic acid(72.6) Benzoic acid(21.3)
16	*p*-Dibromobenzene	B	30	4	100	Terephthalic acid(97.1)
17	*p*-Dichlorobenzene	B	30	20	83.7	Terephthalic acid(66.6) *p*-Chlorobenzoic acid (6.5)
18	1,3,5-Trichlorobenzene	B	65	18	100	Trimesic acid(76.4) Isophthalic acid(21.3)
19	1-Bromonaphthalene	B	65	4	100	1-Naphthoic acid(99.3)
20	2-Bromothiophene	B	30	20	100	2-Thiophene carboxylic acid(96.9)
21	*o*-Chlorobenzoic acid	A	65	22	42.8	Phthalic acid(13.5) Benzoic acid(26.4)
22	*m*-Chlorobenzoic acid	A	30	15	79.8	Isophthalic acid(71.8)
23	*m*-Chlorobenzoic acid	A	65	2.5	64.8	Isophthalic acid(60.0)
24	*m*-Chlorobenzoic acid	A	80	2.5	91.5	Isophthalic acid(81.6)
25	*m*-Bromophenol	A	65	2.5	84.5	*m*-Hydroxy benzoic acid (39.2), Phenol(1.0)
26	*m*-Chlorophenol	A	65	2.5	29.0	*m*-Hydroxy benzoic acid (3.5), Phenol(2.4)

a) $Co(OAc)_2 \cdot 4H_2O$:0.2 mmol; Halide:2.0 mmol; CO:2 atm. b) See footnote of Table 1. c) Medium A: aq. 2.5 mol dm^{-3} NaOH(20 ml); medium B:aq. 3.3 mol dm^{-3} NaOH(15 ml)/EtOH(5 ml); medium C: aq. 3.3 mol dm^{-3} NaOH(15 ml)/MeOH(5 ml); medium D:aq. 2.5 mol dm^{-3} NaOH(15 ml)/C_6H_6(5 ml)/$Bu_4N^+Br^-$(0.3 mmol); medium E:1.3 mol dm^{-3} MeONa/MeOH(20 ml).

bearing an electron-withdrawing group(Runs 16-18 and 22-24) but also for a simple chloride such as chlorobenzene(Run 11), which has been so far reported to be unreactive.3) On the other hand, the halides bearing an electron-releasing group were less reactive(Runs 25 and 26). As far as the leaving groups are concerned, bromides were much more reactive than the corresponding chlorides, in agreement with the general trend.

This catalyst system was successfully extended to the carbonylation of polynuclear aromatic halides and heteroaromatic halides under the same conditions (Runs 19 and 20).

In contrast with the cobalt carbonyl system, the cobalt salt-catalyzed carbonylation did not proceed easily under the phase transfer catalyst(PTC) conditions(C_6H_6/aq. NaOH/$Bu_4N^+Br^-$/$Co(OAc)_2$)(Run 14).

It should be noted that the IR spectrum of the benzene phase showed only an absorption at 1895 cm^{-1} arising from the cobalt carbonyl anion, $Co(CO)_4^-$, and no other carbonyl absorptions were observed after 20 hours irradiation of cobalt(II) acetate in PTC conditions at 65 °C under CO. This fact suggests that under the conditions employed for carbonylation, cobalt(II) acetate is converted partly to $Co(CO)_4^-$ by the reductive carbonylation. However, as shown in Table 2 the rate of carbonylation under PTC conditions, in which $Co(CO)_4^-$ has been assumed as a catalytic species,[9)] was remarkably slower than that in the one-phase process even for the reactive bromobenzene. Thus, the concentration of $Co(CO)_4^-$ generated during the reaction should be very low.

These results suggest that the cobalt salts are photochemically reduced to an active low-valent species and this non-carbonyl cobalt species rather than the $Co(CO)_4^-$ play an important role in the reaction under the system employed.

These reactions did not occur without irradiation even at higher temperature (80 °C), and no reaction proceeded at all when the light was turned off. Consequently, the reaction is photoinitiated and photocatalytic, and not merely photoassisted. But the reaction mechanism and the actual active species are still obscure.

In conclusion, the photostimulated carbonylation of aromatic halides including chlorobenzene were conveniently achieved by cobalt salts, which are cheap and also easily handled. This provides a new route of generation of active cobalt species in the photocarbonylation reaction without the use of cobalt carbonyl complexes and reducing reagents. Work is in progress, and detailed discussion of these processes will be presented later.

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