Effect of inorganic redox cocatalyst on Pd-catalyzed oxidative carbonylation of phenol for direct synthesis of diphenyl carbonate

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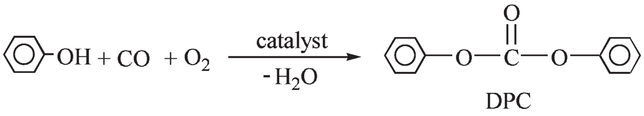
A catalyst system for direct synthesis of diphenyl carbonate by oxidative carbonylation of phenol was investigated with special emphasis on the inorganic redox cocatalyst component. Besides the inorganic redox cocatalyst, the catalyst system was composed of a Pd carbonylation catalyst, an organic redox cocatalyst, a base and a drying agent. $Ce(OAc)_3 \cdot H_2O$ was found to be the most efficient inorganic redox cocatalyst giving DPC in 76% yield with a Pd turnover number of 250 and without producing any major side products.

Keywords: diphenyl carbonate, Redox cocatalyst, phenol, oxidative carbonylation

1. Introduction

Synthesis of dialkyl carbonates by oxidative carbonylation of corresponding alcohols with a variety of metal catalysts is a well known redox reaction [1–3]. Analogous reactions to prepare diaryl carbonates seem to be fairly promising but the literature concerning the catalysts for such reactions is still limited mainly to patents [4–9].



In 1981 Hallgren et al. [10] reported diphenyl carbonate (DPC) synthesis by oxidative carbonylation of phenol using a catalytic amount of palladium, a tertiary amine and oxidation cocatalyst for regeneration of active Pd species, at room temperature and under atmospheric pressure. However, the Pd turnover number was only 100 and the catalyst activity was not satisfactory.

The patented literature describes DPC synthesis by oxidative carbonylation of phenol with CO and O_2 under high pressure, using a catalyst system composed of a Pd carbonylation catalyst, a combination of a metallic and an organic redox cocatalyst, and a base [4–9]. Use of a drying agent for removal of water produced during the reaction is also reported in a few patents [4]. Direct reaction of Pd with gaseous oxygen to regenerate active Pd species has reported be a slow reaction, thus an oxidation cocatalyst is essential to achieve rapid reoxidation of Pd metal. Typically copper salts have been employed as oxidation cocatalysts in a variety of palladium-catalyzed transformations [11]. In a separate publication we reported diphenyl carbonate synthesis by oxidative carbonylation of phenol using a $PdCl_2$–$Cu(OAc)_2$–hydroquinone–tetrabutylammonium bromide based catalyst system [12]. Though a very high yield (76%) of DPC could be achieved successfully with this system, it has a disadavantage of producing *o*-phenylene carbonate as a major side product. In this paper, we wish to report the role of inorganic and organic redox cocatalysts in DPC and *o*-PC formation and how *o*-PC formation can be prevented.

2. Experimental

Phenol was purified by vacuum distillation prior to use. Dichloromethane was distilled and stored over molecular sieves. All other reagents were used as received. Molecular sieves were activated at 350 °C for 10 h under N_2 before use.

A typical reaction procedure was as follows: palladium(II) chloride ($PdCl_2$) 2.2 mg (0.012 mmol), anhydrous $Cu(OAc)_2$ 13.6 mg (0.075 mmol), tetrabutyl ammonium bromide 120 mg (0.375 mmol), hydroquinone 41 mg (0.375 mmol), and 1 g of activated 3A molecular sieves were charged to a 50 ml stainless steel autoclave and dried at 70 °C for 2 h under vacuum before the reaction. After drying, 0.78 g (8.33 mmol) of phenol and 5 ml of dichloromethane were added followed by charging 60 kg/cm^2 of CO and 3 kg/cm^2 of O_2, and the autoclave was placed in an oil bath preheated to 100 °C. After the desired reaction time, reaction was quenched immediately by cooling the autoclave in a water bath. The reaction products were identified and quantified by gas chromatography using a Shimadzu GC-9A chromatograph (Silicon SE-30 column).

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Table 1
Study of various metal complexes as inorganic redox cocatalysts.[a]

Run	Inorg. redox cocat.	DPC yield[b] (%)
1	$Cu(OAc)_2$	24.4
2	$Ce(OAc)_3 \cdot H_2O$	22
3	$Mn(OAc)_2 \cdot 4H_2O$	12
4	$Mn(acac)_3$	5
5	$Co(acac)_2$	10
6	$Co(acac)_3$	7
7	CrO_3	7.5
8	MoO_3	6.8
9	OsO_4	6.1
10	RuO_3	5.9
11	$H_3PMo_{12}O_{40}$	2.2
12	$AuCl_3$	2
13	$FeCl_3$	1

[a] Phenol 8.33 mmol, $PdCl_2$ 0.0125 mmol, inorganic redox cocatalyst 0.075 mmol, tetrabutylammonium bromide 0.375 mmol, hydroquinone 0.375 mmol, CH_2Cl_2 5 ml, molecular sieves 1 g, CO 60 kg/cm^2, O_2 3 kg/cm^2, temp. 100 °C, time 3 h.
[b] Yield based on phenol.

3. Results and discussion

In a recent publication [12], we reported the usage of the $PdCl_2$–$Cu(OAc)_2$–hydroquinone–tetrabutylammonium bromide catalyst system for oxidative carbonylation of phenol to DPC. A very high yield of DPC (76%) could be obtained under optimum reaction conditions. A combination of an organic redox cocatalyst (hydroquinone) and an inorganic redox cocatalyst [$Cu(OAc)_2$] was found to be effective for *in situ* regeneration of active Pd species. Detailed investigations suggested that hydroquinone mainly assists in reoxidation of Cu(I) to Cu(II), which in turn is helping in regeneration of active Pd species.

Further investigations revealed that substantial anhydrous conditions were essential for oxidative carbonylation of phenol, thus molecular sieves were used as drying agent for removing the water produced during the reaction. 24 h reaction in the presence of 1 g, 3A molecular sieves resulted in 76% DPC yield as compared to 23% obtained without molecular sieves.

However, with this catalyst system, under optimum reaction conditions, *o*-PC was produced as a side product in as high yield as 5%. Tyrosinases (dinuclear copper containing monoxygenases) and their chemical mimics such as copper(II) amine complexes are reported to catalyze selective ortho-hydroxylation of phenols by molecular dioxygen into ortho-quinones (phenolase activity) and the oxidation of ortho-diphenols into ortho-quinones (catecholase activity) [13,14]. Therefore, it can be assumed that during oxidative carbonylation of phenol with a Pd–Cu based redox catalyst system, Cu is catalysing copper catecholate formation which in turn is being converted to *o*-phenylene carbonate in the presence of CO with the help of the Pd carbonylation catalyst.

In a continuation of this study, an effort was made to prevent the formation of *o*-PC, by testing various other metal complexes for their efficiency as inorganic redox cocatalysts and the results are given in table 1. Results indicate that among the various metal complexes tested the efficiency of $Ce(OAc)_3 \cdot H_2O$ was comparable to that of $Cu(OAc)_2$ in terms of DPC yield. In addition, usage of $Ce(OAc)_3 \cdot H_2O$ eliminated *o*-PC formation completely making it a better catalyst than $Cu(OAc)_2$ (table 2). Besides acetate, various other cerium complexes were also tested for their efficiency as redox cocatalyst. Results given in table 2 indicate that $Ce(OAc)_3 \cdot H_2O$ gave the highest DPC yield (76%) with a Pd turnover number of 250. Furthermore, unlike $Cu(OAc)_2$, those cerium complexes which gave good DPC yield (53–76%) did not favor *o*-PC formation. On the other hand, cocatalysts like $Ce(VO)_4$ and $Ce(WO_4)_3$ which could not catalyse DPC synthesis efficiently, led to *o*-PC formation in a yield of 1 to 4.8% (table 2, run 8–13).

Table 2
Comparison of the efficiency of various cerium complexes with $Cu(OAc)_2$ as inorganic redox cocatalysts.[a]

Run	Inorg. redox cocat.	DPC yield[b] (%)	*o*-PC yield[b] (%)
1	–	15.4	2.6
2	$Cu(OAc)_2$	76	5
3	$Ce(OAc)_3 \cdot H_2O$	76	–
4	$Ce(i\text{PrCp})_3$	71.7	–
5	$Ce(Cp)_3$	66.3	–
6	$Ce(TMHD)_4$	58.9	–
7	Ce (stearte)$_3$	53.1	–
8	$Ce(trop)_4$	35.8	1.78
9	$Ce_2(WO_4)_3$	8.8	1.0
10	$CeBr_3$	7.84	1.42
11	$Ce(OH)_4$	7.8	1.5
12	Ce(tfacac)	6.53	0.7
13	$Ce(VO)_4$	4.1	4.8

[a] Phenol 8.33 mmol, $PdCl_2$ 0.0125 mmol, inorganic redox catalyst 0.075 mmol, tetrabutylammonium bromide 0.375 mmol, hydroquinone 0.375 mmol, CH_2Cl_2 5 ml, molecular sieves 1 g, CO 60 kg/cm^2, O_2 3 kg/cm^2, temp. 100 °C, time 24 h.
[b] Yield based on phenol.

In order to check whether *o*-PC can be formed in the absence of an inorganic redox cocatalyst, an experiment was carried out with $PdCl_2$ as the sole metal catalyst. Results revealed the formation of *o*-PC in 2.6% yield along with 15.4% DPC in 24 h (table 2, run 1). *o*-PC formation in the absence of an inorganic redox cocatalyst or in the presence of inefficient inorganic redox cocatalysts (table 2, run 8–13) suggests that under the reaction conditions unfavorable for DPC formation, oxidation of phenol to *o*-benzoquinone (precursor of *o*-PC) is in competition with its oxidative carbonylation to DPC. Whereas, in the presence of efficient inorganic redox cocatalysts like $Ce(OAc)_3$, $Ce(i\text{PrCp})_3$ (trisisopropylcyclopentadienylcerium), $Ce(Cp)_3$(triscyclopentadienylcerium), $Ce(TMHD)_4$ [tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)cerium] and Ce(III) stearate, oxidative carbonylation is favored over oxidation of phenol.

4. Conclusions

Direct synthesis of DPC in a yield of 76% could be carried out by catalyst-assisted oxidative carbonylation of phenol. The effect of inorganic redox cocatalyst was investigated in detail. Among the various metal complexes studied, $Cu(OAc)_2$ and $Ce(OAc)_3 \cdot H_2O$ were found to be the most efficient in terms of DPC yield. However, $Cu(OAc)_2$ led to formation of *o*-PC as a side product in 5% yield along with 76% DPC, under optimum reaction conditions. $Ce(OAc)_3 \cdot H_2O$ gave DPC in a yield comparable to that obtained with $Cu(OAc)_2$, without any *o*-PC formation.

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