

# Direct synthesis of diphenyl carbonate by oxidative carbonylation of phenol using Pd–Cu based redox catalyst system

Meenakshi Goyal<sup>a,b</sup>, Ritsuko Nagahata<sup>a,b</sup>, Jun-ichi Sugiyama<sup>a,b</sup>, Michihiko Asai<sup>a,b</sup>, Mitsuru Ueda<sup>a,b,c</sup>, Kazuhiko Takeuchi<sup>a,b,\*</sup>

<sup>a</sup> Joint Research Centre for Precision Polymerization-Tsukuba, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

<sup>b</sup> National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

<sup>c</sup> Graduate School of Engineering, Yamagata University, Yonezawa, Yamagata 992-0038, Japan

Received 14 November 1997; accepted 11 March 1998

## Abstract

A catalyst system was designed for direct synthesis of diphenyl carbonate by oxidative carbonylation of phenol. Besides Pd carbonylation catalyst, inorganic and organic redox cocatalysts were included in the catalyst system for in situ regeneration of active Pd species. Copper(II) acetate was used as inorganic redox cocatalyst and hydroquinone was found to give good results as organic redox cocatalyst. Efficiency of various bases, effect of a drying agent, and optimum reaction conditions for achieving high catalytic activity were also investigated in detail. Using suitable components of catalyst system and under optimum reaction conditions, a Pd turnover number of 250 could be obtained. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Oxidative carbonylation; Diphenyl carbonate; Catalyst; Redox cocatalyst; Turnover number

## 1. Introduction

Oxidative carbonylation of alcohols and phenols to corresponding dialkyl or diaryl carbonates is a redox reaction and it can be catalyzed by group VIII B metal compounds with Pd catalysts being the most successful. Although synthesis of dialkyl carbonates by this method with a variety of metal catalysts is well known and well documented [1–7], literature regarding analogous reaction for phosgene free synthesis

of diaryl carbonate is still limited mainly by patents [8–12]. Evidently the reason lies in lower basicity and ease of oxidation of phenol. In 1981, Hallgren et al. [13] reported that diphenyl carbonate (DPC) can be prepared by oxidative carbonylation of phenol using catalytic quantities of palladium, a tertiary amine, and oxidation cocatalyst at room temperature and under atmospheric pressure, but the yield of DPC per palladium, i.e., Pd turnover number was only 100 thus the catalyst activity was not satisfactory. In a recent paper Moiseev et al. [14] have reported that giant palladium-561 clusters were

\* Corresponding author.

effective in the catalysis of oxidative carbonylation of phenol to DPC in conjugation with reductive carbonylation and reduction of nitrobenzene under CO pressure.

The patented literature [8–12] describes DPC synthesis by oxidative carbonylation of phenol with CO and O<sub>2</sub> under high pressure, using a catalyst system comprised of a Pd carbonylation catalyst, a base, and a combination of metallic redox cocatalyst (selected from Mn, Co, Cu, Fe, Ce etc.) and organic redox cocatalyst (selected from various quinones, ketones, terpyridine etc.) for in situ regeneration of active Pd species. Usage of a desiccating agent for removal of water produced in the reaction is also prescribed in few patents [8].

In the present work we studied oxidative carbonylation of phenol using various group VIII B metals as carbonylation catalyst with copper(II) acetate [Cu(OAc)<sub>2</sub>] as inorganic redox cocatalyst. Efficiency of many quinone type compounds and other organic redox cocatalysts was tested and in order to realise the enhanced catalytic activity, reaction conditions were also optimised.

## 2. Experimental

### 2.1. Materials

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<sub>2</sub> before use. Palladium carbonyl chloride and [Pd(CO)Cl] and palladium carbonyl bromide [Pd(CO)Br] were prepared according to the method reported in literature [15].

### 2.2. Synthesis

Palladium(II) chloride (PdCl<sub>2</sub>) 2.2 mg (0.012 mmol), anhydrous Cu(OAc)<sub>2</sub> 13.6 mg (0.075 mmol), tetrabutylammonium bromide 120 mg (0.375 mmol), hydroquinone 41 mg (0.375

mmol), and 1 g 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 the drying, 0.78 g (8.33 mmol) phenol and 5 ml dichloromethane were added followed by charging 60 kg/cm<sup>2</sup> CO and 3 kg/cm<sup>2</sup> O<sub>2</sub>, 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.

### 2.3. Characterization

The reaction products were identified and quantified by gas chromatography on a GC-9A chromatograph of Shimadzu (Silicon SE-30 column).

## 3. Results and discussion

### 3.1. Efficiency of various group VIII B metal complexes as carbonylation catalysts

PdCl<sub>2</sub>, palladium(II) bromide (PdBr<sub>2</sub>), Pd(CO)Cl, Pd(CO)Br, bis-(benzonitrile) palladium(II) chloride [Pd(PhCNCl)<sub>2</sub>], and palladium(III) acetylacetonate [Pd(acac)<sub>2</sub>] were tested for their efficiency as carbonylation catalyst. Under present reaction conditions all of the Pd(I) complexes and Pd(II) complexes were found to be equally effective Pd sources with no significant difference in DPC yields (50 to 60% in 24 h, Table 1). Besides various Pd complexes, rhodium(II) acetate, rhodium(III) nitrate, tetrarhodium dodecacarbonyl, rhodium(III) acetylacetonate, rhodium carbonyl chloride, iridium(III) chloride, iridium(IV) chloride, iridium(III) acetylacetonate, platinum(II) acetylacetonate, platinum(II) chloride, bis-(benzonitrile) platinum(II) chloride, and platinum(II) iodide were also tested but none of them resulted in formation of DPC suggesting that they can not catalyse oxidative carbonylation of phenol.

Table 1  
Study of various Pd complexes as carbonylation catalyst

Run	Catalyst	DPC yield <sup>a</sup> (%)	Pd turnover number
1	PdCl <sub>2</sub>	51.2	170
2	PdBr <sub>2</sub>	46	153
3	Pd(CO)Cl	53	176
4	Pd(CO)Br	60	200
5	Pd(PhCNCl) <sub>2</sub>	50	166
6	Pd(acac) <sub>3</sub>	50	166

Phenol 8.33 mmol, Pd catalyst 0.0125 mmol, Cu(OAc)<sub>2</sub> 0.075 mmol, tetrabutylammonium bromide 0.375 mmol, hydroquinone 0.375 mmol, CH<sub>2</sub>Cl<sub>2</sub> 5 ml, 4A molecular sieves 5 g, CO 60 kg/cm<sup>2</sup>, O<sub>2</sub> 3 kg/cm<sup>2</sup>, temp. 100°C, time 24 h.

<sup>a</sup>Yield based on phenol.

### 3.2. Study of redox cocatalysts

Although Pd is capable of carrying out DPC synthesis without any cocatalysts, stoichiometric amount of Pd is required [16]. To convert this process into catalytic process, in situ reoxidation of the palladium metal to regenerate active Pd species is required. Direct reaction of Pd metal with gaseous oxygen has been reported to be a slow process, requiring a catalyst to achieve rapid oxidation. Nakata et al. [17] reported that for the carboxylation of gaseous alkanes with CO, combination of palladium(II) acetate [Pd(OAc)<sub>2</sub>] and Cu(OAc)<sub>2</sub> gives the best results and Pd(OAc)<sub>2</sub> alone gives inferior yield. This behaviour is attributed to the fact

that when Pd and Cu salts coexist in presence of an oxidising agent, Cu(II) is reduced to univalent and zero-valent Pd (Pd black) is oxidised to divalent [18].

In the present work, Cu(OAc)<sub>2</sub> was added as oxidation cocatalyst but it was found that with O<sub>2</sub> as oxidising agent, Cu(OAc)<sub>2</sub> alone could not effectively reoxidise Pd metal and after 3 h yield of DPC per palladium (i.e., Pd turnover number) was only 20 (Table 2 run 1). In the process of reoxidising the Pd metal to active Pd species Cu(II) gets reduced to Cu(I). For good catalytic activity of Cu(OAc)<sub>2</sub>, this reduced Cu(I) should be effectively reoxidised to Cu(II). However, in the system under investigation Cu turnover number was only 3.3. Thus it can be inferred that O<sub>2</sub> alone is not a good oxidising agent for reoxidising Cu(I) to Cu(II) and another oxidation cocatalyst is needed to facilitate reoxidation of Cu(I).

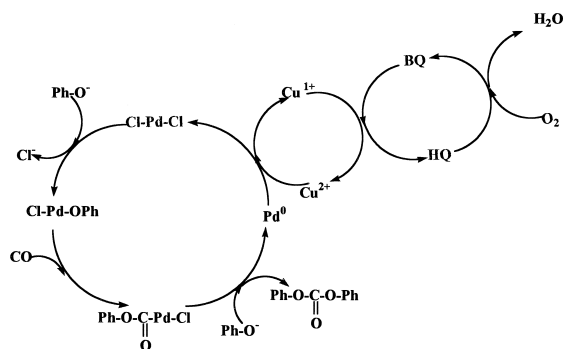
Further studies demonstrated that usage of hydroquinone, an organic redox cocatalyst, in addition to Cu(OAc)<sub>2</sub>, increased the DPC yield per palladium to 81 (Table 2 run 2). However, hydroquinone alone, in the absence of Cu(OAc)<sub>2</sub> was not very effective for regeneration of Pd metal and DPC yield per palladium was less than stoichiometric amount of hydroquinone used (Table 2 run 3). These results suggest that besides helping directly in Pd reoxidation, hy-

Table 2  
Effect of organic redox cocatalysts on DPC yield

Run	Inorganic catalyst	Organic catalyst	DPC yield <sup>a</sup> (%)	Pd turnover number
1	Cu(OAc) <sub>2</sub>	–	6	20
2	Cu(OAc) <sub>2</sub>	Hydroquinone	24.4	81
3	–	Hydroquinone	6	20
4	Cu(OAc) <sub>2</sub>	Benzoquinone	25.4	84
5	Cu(OAc) <sub>2</sub>	Anthraquinone	6.2	12
6	Cu(OAc) <sub>2</sub>	Naphthaquinone	11.8	39
7	Cu(OAc) <sub>2</sub>	Pyridine	4.2	14
8	Cu(OAc) <sub>2</sub>	Terpyridine	4.6	15
9	Cu(OAc) <sub>2</sub>	Quinoline	5.7	19
10	Cu(OAc) <sub>2</sub>	Isoquinoline	5.3	18

Phenol 8.33 mmol, PdCl<sub>2</sub> 0.0125 mmol, Cu(OAc)<sub>2</sub> 0.075 mmol, tetrabutylammonium bromide 0.375 mmol, organic redox cocatalyst 0.375 mmol, CH<sub>2</sub>Cl<sub>2</sub> 5 ml, 4A molecular sieves 5 g, CO 60 kg/cm<sup>2</sup>, O<sub>2</sub> 3 kg/cm<sup>2</sup>, temp. 100°C, time 3 h.

<sup>a</sup>Yield based on phenol.



Scheme 1.

droquinone is mainly assisting in reoxidation of Cu(I) which in turn is helping in the regeneration of active Pd species. The reaction scheme proposed on the basis of this observation is shown in Scheme 1.

In order to further confirm the role of organic redox cocatalyst, reaction was performed in the absence of  $O_2$  and with or without  $Cu(OAc)_2$  with excess benzoquinone (7.39 mmol, rest of the recipe same as given in experimental section) as the sole oxidant. In the reaction without  $O_2$  and  $Cu(OAc)_2$ , Pd turnover number was found to be 12 whereas in the reaction with  $Cu(OAc)_2$  but no  $O_2$ , Pd turnover number was 22 with Cu turnover number as 4. This observation confirms that organic redox cocatalyst is

not only playing a role in reoxidation of Pd but also in the regeneration of active Cu species.

Besides hydroquinone, performance of other organic redox catalysts like benzoquinone, anthraquinone, naphthaquinone, isoquinoline, quinoline, and terpyridine was also investigated. Hydroquinone and benzoquinone were found to give the best results in terms of DPC yield (Table 2). This behaviour may presumably be due to ease of oxidation and less steric hindrance in these two quinones.

### 3.3. Effect of various bases

A base with high basicity and low nucleophilicity is required for substantial ionization of phenol to phenoxide ion. Among the various bases tested in present investigation, only tetrabutylammonium bromide and tetrabutylphosphonium bromide were found to be effective resulting in DPC yields of 24.4 and 15.6%, respectively (Table 3). Bis(triphenylphosphoranylidene) ammonium acetate resulted in 6.6% DPC yield, while with tetrabutylammonium chloride, tetrabutylammonium iodide, and 1,2,2,6,6-pentamethyl piperidine, DPC yield was in the range of 1–3 to 6%. All other bases studied were found to be completely ineffective as no DPC was formed. The difference in the efficiency of

Table 3  
Effect of various bases on DPC yield

Run	Base	DPC Yield(%) <sup>a</sup>	Pd turnover number
1	tetrabutylammonium bromide	24.4	81
2	tetrabutylammonium chloride	3.6	12
3	tetrabutylammonium iodide	1.2	4
4	tetrabutylammonium acetate	—	—
5	tetrabutylphosphonium bromide	15.6	52
6	Bis(triphenylphosphoranylidene) ammonium chloride	—	—
7	Bis(triphenylphosphoranylidene) ammonium acetate	6.6	22
8	1,2,2,6,6 pentamethyl piperidine	1.3	4
9	<i>N</i> -ethyl diisopropyl amine	—	—
10	CsI	—	—
11	CsBr	—	—
12	Cs(OAc) <sub>2</sub>	—	—

Phenol 8.33 mmol,  $PdCl_2$  0.0125 mmol,  $Cu(OAc)_2$  0.075 mmol, base 0.375 mmol, hydroquinone 0.375 mmol,  $CH_2Cl_2$  5 ml, 4A molecular sieves 5 g, CO 60 kg/cm<sup>2</sup>,  $O_2$  3 kg/cm<sup>2</sup>, temp. 100°C, time 3 h.

<sup>a</sup>Yield based on phenol.

the bases studied can be attributed to the difference in their basicity, nucleophilicity, and stability towards reaction conditions.

### 3.4. Effect of dehydrating agent

In order to remove the water produced during the reaction, activated 4A molecular sieves were added to the reaction mixture. As can be seen from the results (Figs. 1 and 2), substantial anhydrous conditions are essential for achieving high efficiency of Pd catalyst with improved yield of DPC. On adding 0.3 g 4A molecular sieves to the reaction mixture, DPC yield increased to 40% in 3 h from 23% obtained without molecular sieves (Fig. 1). However, on increasing the amount of molecular sieves to 1 g no significant improvement in DPC yield was observed and further increase up to 5 g, led to a decrease in DPC yield. Decrease in DPC yield on increasing the molecular sieves amount beyond 1 g indicates that excess molecular sieves might be assisting in some side reactions or reverse reaction.

On replacing 4A molecular sieves with 1 g of 3A molecular sieves, 24 h reaction resulted in

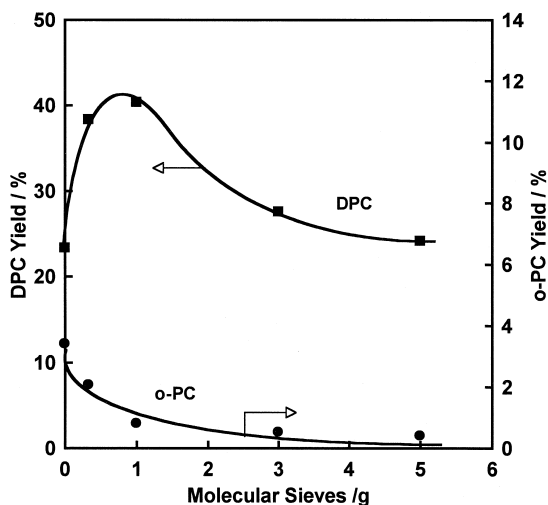


Fig. 1. Effect of amount of 4A molecular sieves on DPC and *o*-PC yields (phenol 8.33 mmol, PdCl<sub>2</sub> 0.0125 mmol, Cu(OAc)<sub>2</sub> 0.075 mmol, tetrabutylammonium bromide 0.375 mmol, hydroquinone 0.375 mmol, CH<sub>2</sub>Cl<sub>2</sub> 5 ml, CO 60 kg/cm<sup>2</sup>, O<sub>2</sub> 3 kg/cm<sup>2</sup>, temp. 100°C, time 3 h).

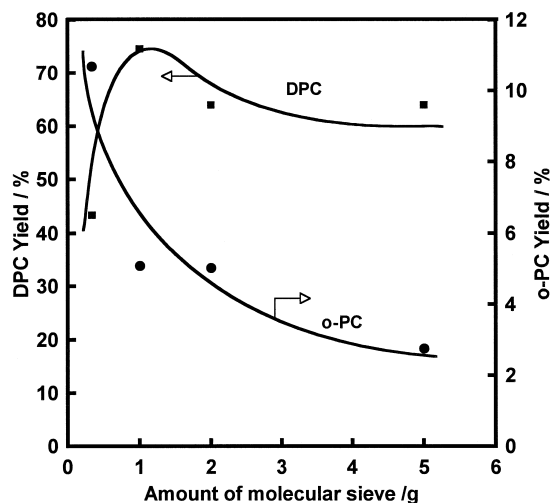


Fig. 2. Effect of amount of 3A molecular sieves on DPC and *o*-PC yields (phenol 8.33 mmol, PdCl<sub>2</sub> 0.0125 mmol, Cu(OAc)<sub>2</sub> 0.075 mmol, tetrabutylammonium bromide 0.375 mmol, hydroquinone 0.375 mmol, CH<sub>2</sub>Cl<sub>2</sub> 5 ml, CO 60 kg/cm<sup>2</sup>, O<sub>2</sub> 3 kg/cm<sup>2</sup>, temp. 100°C, time 24 h).

76% yield of DPC (Pd turn over number 600) as compared to 40% obtained by 4A molecular sieves. Further studies revealed that for 3A molecular sieves, 1 g was the optimum amount giving highest DPC yield (Fig. 2).

Besides improving DPC yield, molecular sieves were also effective in suppressing the side product formation which will be discussed in detail in a later section of this paper (Section 3.6).

### 3.5. Reaction conditions

In order to determine the optimum reaction conditions for obtaining maximum yield of DPC, reaction was carried out over a wide range of temperature, pressure, and time. Effect of reaction temperature on DPC yield was examined over a temperature range of 60 to 120°C and the results (Fig. 3) revealed that 90–100°C was the optimum temperature range for obtaining high DPC yield. Further increase in the temperature led to a decrease in DPC yield. This may be due to increased oxidation of phenol at higher temperature leading to various side products formation. To study the effect of CO and O<sub>2</sub> pressure

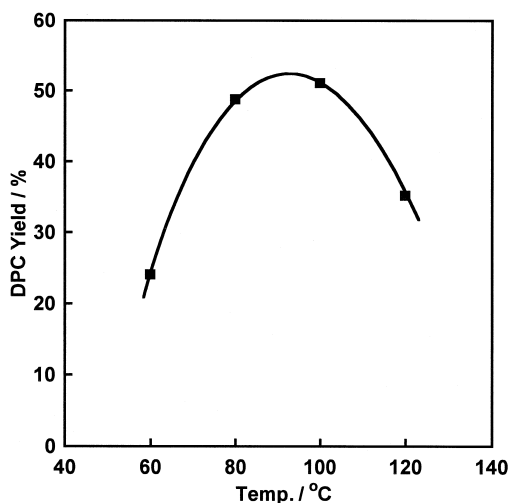


Fig. 3. Effect of temperature on DPC yield (phenol 8.33 mmol, PdCl<sub>2</sub> 0.0125 mmol, Cu(OAc)<sub>2</sub> 0.075 mmol, tetrabutylammonium bromide 0.375 mmol, hydroquinone 0.375 mmol, 4A molecular sieves 5 g, CH<sub>2</sub>Cl<sub>2</sub> 5 ml, CO 60 kg/cm<sup>2</sup>, O<sub>2</sub> 3 kg/cm<sup>2</sup>, time 24 h).

on DPC yield CO pressure was varied from 40 to 70 kg/cm<sup>2</sup> with O<sub>2</sub> pressure as 5 vol % of CO pressure and as shown in Fig. 4 higher pressure was beneficial for obtaining high catalytic activity along with high DPC yield. Influence of reaction time on DPC yield was studied

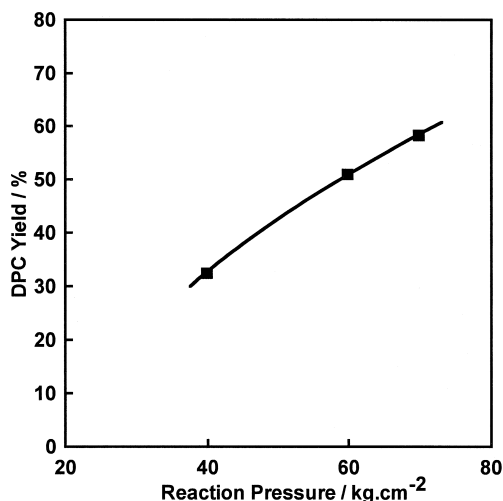


Fig. 4. Effect of pressure on DPC yield (phenol 8.33 mmol, PdCl<sub>2</sub> 0.0125 mmol, Cu(OAc)<sub>2</sub> 0.075 mmol, tetrabutylammonium bromide 0.375 mmol, hydroquinone 0.375 mmol, 4A molecular sieves 5 g, CH<sub>2</sub>Cl<sub>2</sub> 5 ml, O<sub>2</sub> 5 vol.% of CO, time 24 h, temp. 100°C).

with 3A and 4A molecular sieves both, which were found to behave differently in terms of DPC yield. Fig. 5 shows that with 4A molecular sieves, inspite of increasing the reaction time from 3 h to 24 h DPC yield remained unchanged at around 40%. However, with 3A molecular sieves (Fig. 6) when the reaction time was increased from 3 h to 24 h, DPC yield increased from 42% to 75% but any increase beyond 24 h led to a decrease in DPC yield, probably due to degradation.

### 3.6. Formation of side products

Under the present reaction conditions, oxidative carbonylation of phenol produced some side products along with DPC. The major side product was *o*-phenylene carbonate (*o*-PC) which was identified by GC mass spectroscopy. It is reported that tyrosinases (dinuclear copper containing monooxygenases) and their chemical mimics such as copper(II) amine complexes are capable of selective orthohydroxylation of phenols by molecular dioxygen into ortho quinones and the oxidation of ortho diphenols into ortho quinones [19,20]. Recently Maumy and Capde-

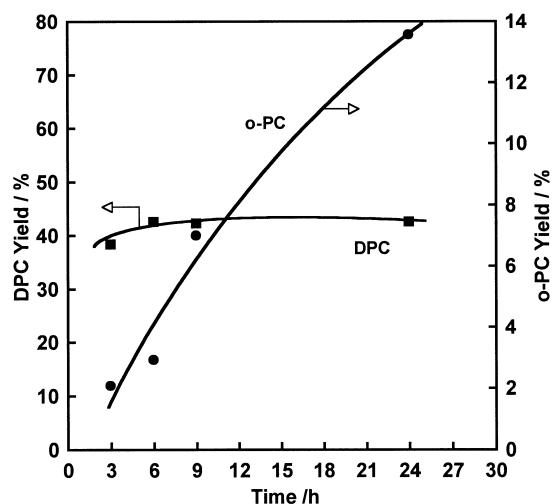


Fig. 5. Effect of time on DPC yield in the presence of 4A molecular sieves (phenol 8.33 mmol, PdCl<sub>2</sub> 0.0125 mmol, Cu(OAc)<sub>2</sub> 0.075 mmol, tetrabutylammonium bromide 0.375 mmol, hydroquinone 0.375 mmol, 4A molecular sieves 0.3 g, CH<sub>2</sub>Cl<sub>2</sub> 5 ml, CO 60 kg/cm<sup>2</sup>, O<sub>2</sub> 3 kg/cm<sup>2</sup>, temp. 100°C).

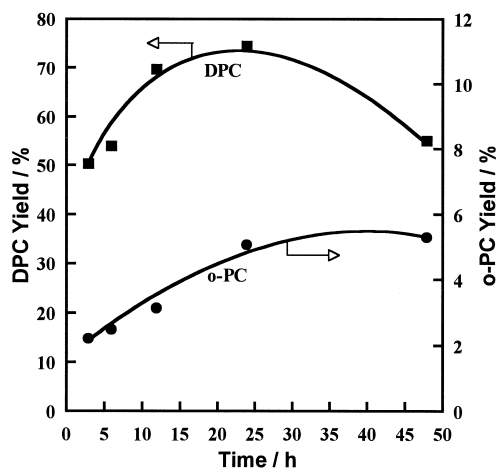


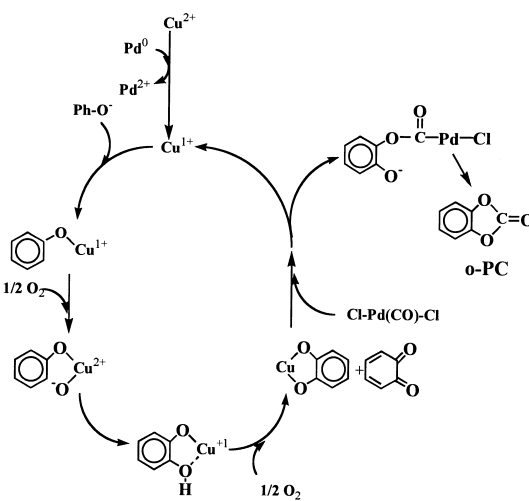
Fig. 6. Effect of time on DPC yield in the presence of 3A molecular sieves (phenol 8.33 mmol,  $\text{PdCl}_2$  0.0125 mmol,  $\text{Cu}(\text{OAc})_2$  0.075 mmol, tetrabutylammonium bromide 0.375 mmol, hydroquinone 0.375 mmol, 3A molecular sieves 1 g,  $\text{CH}_2\text{Cl}_2$  5 ml,  $\text{CO}$  60  $\text{kg}/\text{cm}^2$ ,  $\text{O}_2$  3  $\text{kg}/\text{cm}^2$ , temp. 100°C).

vielle [21] proved that this ortho oxidation of phenols yields catechols as primary products. As the system under investigation fulfils all the requirements for ortho hydroxylation of phenols, it can be assumed that Cu is catalysing Cu catecholate formation which in turn is being converted to *o*-phenylene carbonate by Pd (Scheme 2). To confirm that Pd is responsible for the carbonylation of Cu catecholate and not Cu, reaction was carried out in the absence of Pd catalyst and it was found that no *o*-PC was formed. This observation confirmed the role of Pd as carbonylation catalyst in this reaction too.

Reaction time influenced the *o*-PC formation and its yield was found to increase with an increase in reaction time from 3 to 24 h (with 3A as well as 4A molecular sieves). In case of 4A molecular sieves (0.3 g) though the increase in reaction time could not improve DPC yield, it accelerated *o*-PC formation and its yield increased to 13.6% from 2.11% with an increase in reaction time to 24 h from 3 h (Fig. 5). With 3A molecular sieves (1 g) also even though the DPC yield decreased on increasing the time beyond 24 h, *o*-PC yield kept increasing (Fig. 6).

Though DPC and *o*-PC formation both are carbonylation reactions, it was observed that molecular sieves favored only DPC formation while *o*-PC formation was suppressed in the presence of molecular sieves. Figs. 3 and 4 show that increase in the amount of 4A or 3A molecular sieves led to a decrease in *o*-PC formation. On increasing the amount of 3A molecular sieves from 0.3 g to 5 g (reaction time 24 h), *o*-PC yield decreased from 10.7 to 2.77%. Another important observation made was that whereas 3A molecular sieves were found to be more effective than 4A molecular sieves in terms of DPC yield, no such difference was observed for *o*-PC formation. In 24 h, 1 g of both 3A as well as 4A molecular sieves resulted in 5.09% *o*-PC. Similarly in 24 h, 5 g of 3A or 4A molecular sieves led to a decrease in *o*-PC yield to 2.77%. This trend indicates that molecular sieves did not play a direct role in decreasing *o*-PC formation. However, the substantial anhydrous conditions provided by molecular sieves favored more DPC formation, thereby decreasing the phenol availability for *o*-PC formation.

Besides *o*-PC, small amounts of phenyl acetate and traces of phenyl salicylate, *m*-bromophenol, and few oxidation products of phenol were also observed during GC analysis.



Scheme 2.

To study the presence and amount of gaseous side product, CO<sub>2</sub>, GC analysis of residual gaseous mixture was carried out. The reactions with molecular sieves did not reveal the formation of CO<sub>2</sub> because molecular sieves are capable of selectively absorbing it. Therefore, to investigate it further, DPC synthesis was carried out in the absence of molecular sieves and the residual gaseous mixture was analysed by GC. The results established the formation of 0.49 mol% of CO<sub>2</sub>.

#### 4. Conclusions

Direct synthesis of DPC by oxidative carbonylation of phenol could be carried out successfully by using catalytic amounts of Pd. A combination of inorganic and organic redox co-catalysts, i.e., Cu(OAc)<sub>2</sub> and hydroquinone helped in regeneration of active Pd species thereby increasing its catalytic efficiency. Under optimum conditions of temperature and CO pressure, Pd turnover number up to 250 giving 76% DPC yield could be achieved. Anhydrous condition was a major requirement for this reaction because the presence of molecular sieves as desiccant improved DPC yields drastically. Besides the main product, diphenyl carbonate, *o*-phenylene carbonate was found to be the major side product.

#### References

- [1] K. Kondo, S. Sonoda, T. Tsutsumi, *Tetrahedron Lett.* (1971) 4885.
- [2] T. Saegusa, T. Tsuda, K. Isayama, K. Nishijima, *Tetrahedron Lett.* (1968) 831.
- [3] D.M. Fenton, P.J. Steinwand, *J. Org. Chem.* 39 (1974) 701.
- [4] M. Graziani, P. Uguagliati, G. Carturan, *J. Organomet. Chem.* 27 (1971) 275.
- [5] W. Schoeller, *Chem. Ber.* (1920) 2144.
- [6] B.K. Nefedov, N.S. Sergeeva, Y.T. Eidus, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1972) 1635.
- [7] I.L. Mador, A.U. Blackham, U.S. Patent 3,114,762 (1963).
- [8] J.E. Hallgren, U.S. Patent 4,201,721 (1980).
- [9] C.T. Chin-The, *Eur. Patent* 0,350,697 A2 (1990).
- [10] H. Kezuka, F. Okuda, *Eur. Patent* 0,508,340 A2 (1992).
- [11] R.P. Joyce, J.A. King, E.J. Pressman, U.S. Patent 5,231,210 (1993).
- [12] H. Iwane, H. Miyagi, S. Imada, S. Seo, T. Yoneyama, *Eur. Patent* 0,614,876 A1 (1994).
- [13] J.E. Hallgren, G.M. Lucas, R.O. Matthews, *J. Organomet. Chem.* 204 (1981) 135.
- [14] I.I. Moiseev, M.N. Vargaftik, T.V. Chernysheva, T.A. Stromnova, A.E. Gekhman, G.A. Tsirkov, A.M. Makhlina, *J. Mol. Cat. A: Chem.* 108 (1996) 77.
- [15] Schnabel, E. Kober, *J. Organomet. Chem.* 19 (1969) 455.
- [16] J.E. Hallgren, A.O. Matthews, *J. Organomet. Chem.* 175 (1979) 135.
- [17] K. Nakata, Y. Yamaoka, T. Miyata, Y. Taniguchi, K. Takaki, Y. Fujiwara, *J. Organomet. Chem.* 473 (1994) 329.
- [18] K. Nakata, T. Miyata, Y. Taniguchi, K. Takaki, Y. Fujiwara, *J. Organomet. Chem.* 489 (1995) 71.
- [19] D.A. Robb, in: R. Lontie (Ed.), *Copper Proteins and Copper Enzymes*, Vol. 2, CRC Press, Boca Raton, 1984, 207.
- [20] W. Brackman, E. Havinga, *Rec. Trav. Chim.* 74 (1955) 937, 1021, 1070, 1100, 1107.
- [21] M. Maumy, P. Capdevielle, *J. Mol. Cat. A: Chem.* 113 (1996) 159.