Oxidative carbonylation of phenol

A. L. Lapidus, S. D. Pirozhkov,[†] and V. V. Sukhov^{*}

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: (095) 135 5328. E-mail: albert@ioc.ac.ru

Oxidative carbonylation of phenol was studied. The activities of the catalysts and cocatalysts were compared. The effect of solvents and pressure on the yield of the target product was studied.

Key words: diphenyl carbonate, phenol, carbonylation.

Oxidative carbonylation of phenol (OCP) affords diphenyl carbonate (DPC), the intermediate of polycarbonates that are widely used in electrical technology, medicine, and optics.¹

Presently, DPC is obtained from phenol and highly toxic phosgene²

 $2PhOH + COCl_2 \rightarrow (PhO)_2CO + 2HCl$

and this reaction is accompanied by the formation of chlorinated waste. Oxidative carbonylation of phenol is an alternative method for manufacturing DPC

$$2PhOH + CO + 0.50_2$$
 Cat $(PhO)_2CO + H_2O.$

The purpose of this work is to study the effect of the nature of components of the catalytic system on the catalytic synthesis of diphenyl carbonate by OCP and search for optimum conditions for this process.

Palladium salts $PdCl_2$, $Pd(PhCN)_2Cl_2$, $Pd(NO_3)_2$, and $Pd(OAc)_2^3$ and palladium clusters⁴ can catalyze OCP. The data of the comparative study of the activity and selectivity of different palladium salts using $CuCl_2$

Table 1. Catalysts of oxidative carbonylation of phenol

Catalyst	Yield of DPC, η (%)	Selectivity, $\sigma_{\rm DPC}$ (%)	IUN
Pd(PhCN) ₂ Cl ₂ ^a	Absent		
$Pd(NO_2)_2$	26.1	68.1	17.7
PdCl	9.7	57.4	6.7
PdBr5	Traces	-	
$Pd(OAc)_{2}^{b}$	8.1	95.3	5.3
Pd(OAc) ₂	36.8	99.7	24.7
Note: CH_2Cl_2/Pl $T = 120 ^{\circ}C; t$ (mol.): $p = 130$	hOH = 5.55 (wt.) = 1 h; CuCl ₂ /C atm.	; $Bu_4NBr/Cat =$ at = 1; PhOH/0	5.55 (mol.); Cat = 127.5
^a Tar products an	re absent.		
^b Entry without	CuCl ₂ .		
† Deceased			

as the cocatalyst are presented in Table 1. They show that $Pd(OAc)_2$ and $Pd(NO_3)_2$ give the best results.

In the catalytic cycle of the formation of DPC, palladium changes oxidation state from Pd^{2+} to Pd^0 (see Refs. 3 and 5), and an oxidant is required to return it to the active form. Under conditions of this reaction, palladium is oxidized by molecular oxygen at a low rate, and hence, a catalyst of palladium oxidation is required, which is the cocatalyst in the process under discussion. Some compounds favoring the oxidation of palladium are listed in Table 2. CuCl and CuCl₂, which, as is known, perform efficiently in the re-oxidation of palladium in the "Wacker pro-

cess," ⁶ are the best of the cocatalysts checked. Good results were obtained with a complex cobalt compound with the tetradentate ligand



N, N'-bis(salicylidene)ethylenediamine (CoSalen, salcomine), which can be considered as a model of the

 Table 2. Effect of the nature of cocatalysts on the yield of DPC in the absence of ligands

Cocatalyst	Yield of DPC, n (%)	Selectivity,	TON
		o DbC (ve)	
	8.1	95.3	5.3
Co(OAc),	17.1	99.8	11.6
CoAcac,	21.8	93.2	14.8
CoSalen	37.0	87.2	25.36
MnAcac ₁	26.4	78.3	17.8
Pb(OAc),	27.1	86.6	18.3
CuBr ₂	13.6	99.8	9.1
CuBr	28.7	79.7	19.4
CuCl ₂	36.8	99.7	24.9
CuCl	41.6	93.1	28.1
Note: PhOH/	$Pd(OAc)_2 = 127.5$ (mol.); CH ₂ Cl ₂ /F	PhOH = 5.5
(wt.); cocata	$lyst/Pd = 2; Bu_4N$	Br/Pd = 5.55	(mol.); T =
120 °C; p =	130 atm; $t = 1$ h.		

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cobalt analog of iron-containing porphyrins. The ability of the CoSalen complex to absorb dioxygen reversibly from the air (more than 3000 "oxygenationdesoxygenation" cycles per sample) makes it possible to perform the catalytic oxidation of various substrates under mild conditions and even at room temperature.⁷ It is known⁸ that CoSalen is capable of oxidizing phenols to benzoquinones. Trace amounts of benzoquinone are present in the products of OCP. Although the presence of palladium in the catalytic system prevents, most likely, the oxidation of phenol to benzoquinone, the latter is nevertheless formed. The $Pd^0 \rightarrow Pd^{2+}$ oxidation with benzoquinone is described in the literature.9 Considering the nature of the solvent, temperature, oxygen concentration, and structure of the ligands, the energy barrier of the oxidation of Pd⁰ with the CoSalen-O₂ system can be quite high. Accordingly, the three-step mechanism of palladium oxidation¹⁰ with dioxygen involving the CoSalen complex (Scheme 1, stages II-IV) can be envisaged.

The quaternary ammonium salt is an important component of the catalytic system without which DPC is virtually not formed. The data on the effect of tertiary amines and quaternary ammonium salts as well as their anions on the yield of DPC are presented in Table 3.

Table 3. Influence of the structure of amines and their salts in the catalytic system on the yield of DPC

Amine or ammonium salt	Yield of DPC, η (%)	Selectivity, ^o _{DPC} (%)	
Me ₄ NBr	Traces		
Mc ₄ NI	7.8	88.6	
Et,N	15.3	79.3	
ELNCI	7.3	76.8	
Et NBr	37.5	76.5	
ELNI	Traces		
Bu ₃ N	Traces		
Bu₄NBr	36.8	99.7	
$Bu_{2}N + BuBr$	4.0	78.9	
Bu ₄ NI	4.0	99.9	

Note: PhOH/Pd = 127.5 (mol.); $CH_2Cl_2/PhOH = 5.55$ (wt.); N/Pd = 5.55 (mol.); $CuCl_2$: Pd(OAc)₂ = 1 : 2 (mol.); T = 120 °C; p = 130 atm; t = 1 h. Et_4NBr and Bu_4NBr are the most efficient, whereas Me_4NBr has no positive effect on the oxidative carbonylation of phenol. The opposite situation is observed for iodides: Me_4NI is the best, and Et_4NI is inactive. Tertiary amines with bulky radicals are less favorable for the synthesis of DPC than Et_3N . It is most likely that the quaternary armonium salt does not decompose during the OCP process, because in the presence of its components the yield of DPC is an order of magnitude lower than in the presence of Bu_4NBr .

When such nitrogen-containing ligands as phenanthroline,¹¹ terpyridine,¹² etc. are introduced into the catalytic system, the yield of DPC increases significantly. The results obtained with ligands of the terpyridine series are presented in Table 4. In the absence of the cocatalyst, but in the presence of the ligand, the yield of DPC increases 1.5-fold (cf. the data in Table 1). In the presence of the cocatalyst, the ligand also provides an increase in the yield of DPC from 1.5 to 3 times. The ligand exerts the lowest effect when the copper salts are used, and the effect is the highest for the cobalt compounds. As the result of the introduction of the ligand, the efficiencies of catalytic systems with different cocatalysts become similar, and the yield of DPC is retained at a level of ~60%.

Evidently, during the oxidation in the catalytic cycle, the ligand favors the transition of palladium from a lower to a higher oxidation state.

Based on the foregoing, we suggested the scheme of oxidative carbonylation of phenol involving the catalytic system with palladium compounds (Scheme 2).

Complex 2 can be formed from the Pd^{2+} compound (1) by analogy with the alcoholate mechanism.¹³ Then inserting CO transforms complex 2 into the phenoxycarbonyl complex 3, followed by the attack of the phenolate ion on the carbonyl carbon atom. This attack can occur both through the five-coordinate transition complex and by the interaction of the phenolate ion with the external sphere of complex 3. As a result, the complex decomposes to diphenyl carbonate and the complex palladium compound in the oxidation state of 0 (4). The presence of the ligands does not allow palladium to aggregate, and it can rather easily be oxidized to Pd^{2+} to form the starting complex 1. The scheme sug-





HQ is hydroquinone, BQ is benzoquinone, CoL(ox) is the oxidized form of CoSalen, CoL(red) is the initial CoSalen complex present before the reaction with dioxygen occurs. and -C is part of the organic carbonate molecule.

Cocatalyst	Ligand	Ligand : Pd (mol. : at.)	Yield of DPC, η (%)	Selectivity, ^o _{DPC} (%)	TON
CoSalen		1:1	63.6	95.4	43.1
CoSalen		1:1	59.2	90.1	40.0
CoSalen		1 : 1	59.6	90.7	40. i
CoSalen Co(OAc) ₂ CoAcac ₃ MnAcac ₃ CuCl ₂ CuCl	The same * * * * * * * *	I:2 I:1 I:1 I:2 I:2 I:2	58.8 63.7 61.7 49.7 62.1 53.4 12.8	86.0 87.2 84.1 86.0 83.2 89.4 90.1	39.9 43.1 41.8 33.2 42.1 36.1 8.5

Table 4. Yield of DPC in the presence of ligands of the terpyridine series

Note: PhOH/Pd(OAc)₂ = 127.5 (mol.); CH₂Cl₂/PhOH = 5.55 (wt.); Bu₄NBr/Pd = 5.55 (mol.); T = 120 °C; p = 130 atm; t = 1 h; Pd : cocatalyst = 1 : 1 (at.)



Scheme 2



gested can also include cluster palladium compounds as active intermediates.

Oxidative carbonylation of phenol can be performed both in the absence of the solvent and in an inert solvent (Table 5). In the absence of the solvent, a considerable amount of phenol converts to tars, and the selectivity does not exceed 50%. When MeCOEt is used as the solvent, the selectivity of the process is low, two byproducts are present in the reaction mixture, and their amount is comparable with that of DPC (DPC: $X_1: X_2$

Solvent	Yield of DPC, η (%)	Selectivity,
Without solvent	15.1	47.9
Methyl ethyl ketone	4.9	38.6
Tetrahydrofuran	13.3	99.9
N-Methylpyrrolidone	Traces	
N,N-Dimethylacetamide	Traces	
Methylene dichloride	35.1	93.6
Butyl acetate	36.2	72.8

Table 5. Effect of solvent on oxidative carbonylation of phenol

Note: $PhOH/Pd(OAc)_2 = 127.5 \text{ (mol.)}; CH_2Cl_2/PhOH = 5.55 \text{ (mol.)}; Bu_4NBr/Pd = 5.55 \text{ (mol.)}; T = 120 °C; p = 130 atm; t = 1 h; Pd/CuCl_2 = 1 : 2 (mol.); volume of the solvent, <math>V = 10 \text{ mL}$.

 Table 6. Effect of pressure on the yield of DPC

PCO	P02	Yield of DPC,	
atm		η(%)	
1.0	0.08	Traces	
40.0	3.0	20.2	
60.0	4.0	52.5	
120.0	8.0	59.6	
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Note: PhOH, 2.4 g; PhOH/Pd, 127.5 (mol.); Bu_4NBr/Pd , 5.55 (mol.); $Pd/CuCl_2$, 1 : 2 (mol.); volume of the solvent, V = 10 mL; t = 120 °C.

= 4.9:5:2). The oxidative carbonylation of phenol does not proceed in solvents of amide nature. CH_2Cl_2 and BuOAc are the best of solvents studied.

The effect of the CO pressure on the yield of DPC is shown in Table 6. When a $CO: O_2$ mixture is passed through the reaction mixture at atmospheric pressure, the catalytic systems under study did not exhibit sufficient activity, and only traces of DPC were observed among the reaction products. The yield of DPC increases as the initial CO pressure increases. A sharp rise in the yield of DPC is observed when the initial pressure is increased from 40 to 60 atm; the fact may be due to an increased solubility of CO in the reaction mixture and an rise in the rate of formation of intermediates.

The oxidative carbonylation of phenol occurs more efficiently in the presence of $Pd(OAc)_2$ and cocatalystoxidants, such as copper salts CuCl and CuCl₂ or the cobalt complex CoSalen. The presence of such ligands as terpyridine and its derivatives in the reaction system also enhances the efficiency of the process. The oxidative carbonylation of phenol does not proceed in the absence of the quaternary ammonium bromide salt. The best results were obtained in the presence of Bu₄NBr and an efficient drying agent. Removal of water from the reaction medium is very important, because water inhibits, most likely, the catalytic palladium complexes, occupying sites in the coordination sphere of palladium, and favors the non-productive oxidation of CO to form CO_2 .

This study outlined the optimum conditions for the formation of diphenyl carbonate in a 63% yield with a selectivity of 95%. This became possible when $Pd(OAc)_2$, CoSalen, and terpyridine were used as the catalyst, cocatalyst, and ligand, respectively, in the presence of the drying agent.

Experimental

Phenol (2.4 g), palladium acetate (0.045 g), calculated amounts of the cocatalyst and ligand, tetrabutylammonium bromide (0.36 g), methylene dichloride (10 mL), and a drying agent (1 g) were loaded into a 50-mL Hastelloy-C autoclave. Then an oxygen-helium mixture (80% O₂) calculated as a 1.5-fold excess of oxygen with respect to stoichiometry of the reaction (10 atm of the mixture) was transferred into the autoclave, and the pressure was brought to 130 atm of CO.

The reaction was carried out with stirring at 120 °C for 1-6 h, noting the reading of a manometer initially at 15-min intervals and then at 30-min and 1-h intervals. After the end of the reaction, the autoclave was cooled, and the pressure was reduced to atmospheric. The reaction mixture was removed into a receiver, weighed, and analyzed.

The yield of DPC was determined from the ratio of its content in the reaction mixture to the theoretical content upon complete conversion of phenol and 100% selectivity:

$$\eta_{\text{DPC}} = \frac{a_{\text{DPC}} 2M_{\text{PhOH}}}{a'_{\text{PhOH}} M_{\text{DPC}}} 100(\%),$$

where a_{DPC} and a'_{PhOH}/g are the content of diphenyl carbonate in the reaction mixture and that of phenol in the substrate, respectively; M_{PhOH} and M_{DPC} are the molecular weights of phenol and diphenyl carbonate.

The conversion of phenol was determined from the ratio of the difference between the concentrations of phenol in the reaction mixture and substrate to the content of phenol in the substrate:

$$\chi_{\text{PhOH}} = \frac{a'_{\text{PhOH}} - a_{\text{PhOH}}}{a'_{\text{PhOH}}} 100(\%)$$

where a'_{PhOH} and a_{PhOH}/g are the concentrations of phenol in the starting and reaction mixtures, respectively.

Selectivity was calculated as the ratio of the yield of diphenyl carbonate to the conversion of phenol

$$\sigma_{DPC} = \frac{\eta_{DPC}}{\chi_{PbOH}} 100(\%)$$

The number of catalytic cycles of the catalyst was calculated as the ratio of the amount of the product formed to the amount of the catalyst (mol mol^{-1}).

$$TON = n_{DPC}/n_{Cat}$$

Procedure of chromatographic analysis. The reaction mixture was weighed, 1 g of the product was taken, and dodecane (0.1 g) was added to it as the internal standard. Analysis was carried out on an LKhM-8 temperature-programmed chroA steel column with a length of 1 m and a diameter of 4 mm, 15% SE-30 on Chromaton as the chromatographic phase, and helium as the carrier gas (flow rate 30 mL min⁻¹) were used.

References

- Entsiklopediya polimerov [Encyclopedia of Polymers], Sovetskaya Entsiklopediya, Moscow, 1974, 2, 840 (in Russian).
- E. Abrams, in *Encyclopedia of Chemical Technology*, Ed. Kirk-Otmer, Vol. IV, 3rd, edn., Wiley, New York, 1979, p. 758.
- 3. J. E. Hallgren and R. O. Matthews, J. Organomet. Chem., 1979, 175, 135.
- I. Moiseev, M. N. Vargaftik, T. V. Chernysheva, T. A. Stromnova, A. E. Gekhman, G. A. Tsirkov, and A. M. Makhlina, J. Mol. Catal., A: Chem., 1996, 108, 77.

- 5. J. E. Hallgren, G. M. Lucas, and R. O. Matthews, J. Organomet. Chem., 1981, 204, 135.
- 6. P. M. Maitlis, *The Organic Chemistry of Palladium*, Vol. 2, Academic Press, New York, London, 1971, p. 82.
- 7. G. Henrici-Olive and S. Olive, Coordination and Catalysis, Verlag Chemie, Wienna-New York, 1977.
- Du Wen, Wang Guixia et al., Fenzi Cuihua, 1990, 4(4), p. 306 (Chem. Abstrs., 114, 246885).
- 9. I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, Dokl. Akad. Nauk SSSR, 1960, 130, 820 [Dokl. Chem., 1960 (Engl. Transl.)].
- J.-E. Backval, R. B. Hopkins, H. Grennberg, M. M. Mader, and A. K. Awasthi, J. Am. Chem. Soc., 1990, 112, 1560.
- 11. US Pat. 1994, 5,284,956 (Chem. Abstrs., 120, 216957).
- 12. Eur. Pat. 1994, 583,938 (Chem. Abstrs., 120, 298247).
- 13. O. N. Temkin, O. L. Kaliya, L. N. Zhir-Lebed', V. A. Golodov, L. G. Bruk, and N. G. Mekhryakova, in *Tr. IOKE AN KazSSR. Gomogennoe okislenie [Works of IOKE Acad. Sci. KazSSR. Homogeneous Oxidation]*, Nauka, Alma-Ata, 1978, **17**, 5 (in Russian).

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