

Letter

Palladium-lead catalyzed oxidative carbonylation of phenol¹

Masatoshi Takagi^{a,*}, Hidekazu Miyagi^b, Takahiro Yoneyama^a, Yuji Ohgomori^a

^a *Yokohama Research Center, Mitsubishi Chemical Corporation, 1000, Kamoshida-cho, Aoba-ku, Yokohama 227, Japan*

^b *Tsukuba Research Center, Mitsubishi Chemical Corporation, Tsukuba, Japan*

Received 2 June 1997; revised 4 August 1997; accepted 5 August 1997

Abstract

Oxidative carbonylation of phenol to form diphenyl carbonate (DPC) was examined. A novel catalyst of type Pd–Pb–NMe₄Br was found to show high activity and selectivity for the present reaction. The Pd species seems to work as an homogeneous catalyst. The rate of DPC formation was in first order with respect to P_{O₂} and [Pb], indicating that the oxygen activation with lead compound is the rate-determining step. Concomitant bromophenol formation was suppressed by Cu or Co additives and longer catalyst life was achieved with these additives. © 1998 Elsevier Science B.V.

Keywords: Diphenyl carbonate; DPC; Oxidative carbonylation; Redox catalysis; Palladium; Lead

Diphenyl carbonate (DPC) is an industrially important precursor for the production of the aromatic polycarbonate by melt polymerization process. Several methods have been developed or proposed for manufacturing DPC. Among them, oxidative carbonylation of phenol with CO and O₂ [1–6] is one of the most attractive methods, in that it is a one-step process with H₂O being the sole by-product, and the use of highly toxic phosgene can be avoided. The present reaction has already been reported to proceed with the catalyst composed of Pd compounds and metal additives such as Cu [2], Mn [2,3], Co [2,4] or Ce [5] compounds, and more

recently the related reaction adopting PhNO₂ as an oxidant instead of oxygen has appeared [6], although the reported catalytic activities are far from the industrial level. We present here that a novel Pd–Pb catalyst combination is found much more effective than previously reported ones.

Reaction procedure is as follows: In 50 ml Hastelloy-C autoclave was charged phenol (32 mmol, 3.01 g), 5% Pd/C (1.2 μg-atom, 2.55 mg), PbO (12 μmol, 2.68 mg) and NMe₄Br (0.24 mmol, 36.97 mg). The reactor was sealed and the mixture was exposed to CO (60 kg/cm²) and air (30 kg/cm²) for 3 h at 100°C. DPC was formed in 9.55% yield (1.53 mmol, turnover number (TON) of Pd = 1273) accompanied by phenyl salicylate (PS, 0.005 mmol), *ortho*- and *para*-brominated phenols (BP; 0.097 mmol, ca. 2:1 mol ratio) and CO₂ (0.47 mmol), as by-products which were determined by GLC and GC/MS analyses.

* Corresponding author. Tel.: +81-45-9633177; fax: +81-45-9633974; e-mail: 3805591@cc.m-kagaku.co.jp

¹ Part of this work has appeared in a patent literature. M. Takagi, H. Miyagi, Y. Ohgomori, H. Iwane, US Patent 5498789.

Table 1
Oxidative carbonylation of phenol^a

Run	Metal additives (48 μ mol each)	DPC (%/PhOH)	TON	PS (%/DPC)	BP (%/Br ^c)	CO ₂ (%/DPC)	Select. ^b (%)
1	PbO	9.55	1273	0.34	40.3	31	78.8
2	Mn(OAc) ₂	1.60	217	4.50	48.7	500	5.9
3	Co(OAc) ₂	1.10	150	7.10	0	51	43.9
4	Co(smdpt) ^d	0.46	63	3.54	0	880	2.3
5	Ce(OAc) ₃	4.26	577	2.77	8.9	22	42.8
6	PbO + CuO	9.63	1302	0.54	19.2	26	63.8
7	PbO + Co(OAc) ₂	1.06	142	2.30	0	24	
8	PbO + Co(trop) ₂	4.12	550	1.35	0	20	
9	PbO + Co(pic) ₂	3.51	475	2.23	0	44	

^aReaction conditions are shown in the text.

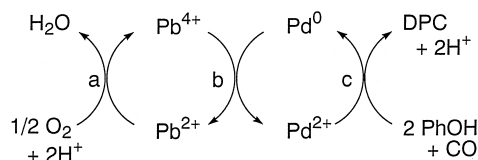
^bDPC percentage in the products evaluated from the peak areas on liquid chromatogram. Column: ODS; Eluent: MeCN/H₂O; Detector: UV (210 nm).

^cMolar ratio of bromophenols/NMe₄Br, used.

^dBis(salicylideniminato-3-propyl)methylaminocobalt(II), see Ref. [4].

The results for the Pd–Pb system are shown in Table 1 together with those for the previously reported catalysts under the same reaction conditions (runs 1–5). It is apparent that the present Pd–Pb catalyst system gives a much higher DPC yield and selectivity based on phenol than the others. Not only Pd/C but Pd(OAc)₂ or Pd(dba)₂ (dba = dibenzylideneacetone) can be used as the catalyst precursor, and a variety of lead compounds such as Pb₂O₃, PbO₂, Pb(OAc)₂ were found to be used as the Pb component. Furthermore, a wide variety of tertiary ammonium or phosphonium bromides were also useful instead of NMe₄Br.

A possible reaction mechanism is proposed in Scheme 1. The Pd²⁺ species, formed in situ from the catalyst precursor, is reduced to Pd⁰ during the DPC formation from two molecules of phenol and one molecule of carbon monoxide. The Pd⁰ thus formed is then oxidized with Pb⁴⁺ to form Pd²⁺ and Pb²⁺, and the latter can



Scheme 1. Proposed mechanism for the oxidative carbonylation of phenol.

be reoxidized by O₂. Redox potential for Pb⁴⁺–Pb²⁺ in acidic aqueous solution (1.65 V) is reported to be higher than that for Pd²⁺–Pd⁰ (0.92 V) [7], indicating that Pb⁴⁺ has an ability to oxidize Pd⁰ to Pd²⁺. However, to our knowledge, no literature has appeared which describes the catalytic activity of Pd–Pb couple for such type of oxidation reactions.

Preliminary kinetic study shows that, the initial rate of DPC formation correlates in first-order with respect to P_{O₂} and [Pb], and is independent of P_{CO}, [Pd], and [NMe₄Br]. This indicates step a in Scheme 1 is the rate-determining step. On the other hand, in the case of the Pd–Mn, Pd–Co or Pd–Ce systems, we found the rate depends on [Pd], that means the rate-determining step is the DPC formation step (step c). High rate of DPC formation by the Pd–Pb system can be explained in this context. The lower PS/DPC ratio also indicates that step c is relatively fast in our Pd–Pb catalysis, since PS is reported to be obtained through *o*-hydroxyphenylpalladium(II) intermediate formed by rearrangement of phenoxypalladium(II) species [1]. Nevertheless, the detailed mechanism, particularly the role of NMe₄Br, remains yet unclear.

Decreasing rate of DPC formation was observed at early stage of the reaction along with

formation of BP. In order to suppress the BP formation, adding further metal compounds to the Pd–Pb system was examined (Table 1, runs 6–9). Adding Cu compounds was found to reduce BP formation to about 1/2 amount with slightly higher DPC yield. However, the time course of the reaction² revealed that the rate of DPC formation still decreased gradually, and at the same time decrease of the Pd concentration in the reaction mixture, which was measured by ICP analysis of the reaction mixture filtered through a 2 μm sintered metal filter, was also observed. At 8 h Pd concentration was < 1 ppm and the reaction completely stopped.

On the other hand, Co additives completely suppressed BP formation. Unfortunately, Co reduces the rate of DPC formation, but some compounds possessing organic ligands such as tropolonate (trop) and pyridine-2-carboxylate (pic) gave rather high yield of DPC (Table 1, runs 7–9). It is noted that the Pd/C–PbO–Co(trop)₂–NBu₄Br system exhibits a large amount of the soluble Pd, and the catalytic activity retains at least within 20 h³ (Fig. 1). This indicates that the Co additives inhibit deposition of Pd. Up to this time, attempts to assign the deactivated Pd species were unsuccessful, but

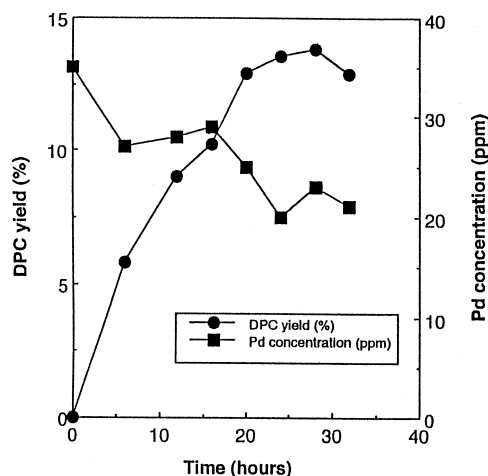


Fig. 1. Oxidative carbonylation of phenol catalyzed by Pd/C–PbO–Co(trop)₂–NBu₄Br system.

possibly the basic compound, typically NMe₄OPh, formed by the reaction of NMe₄Br with phenol to liberate BP, causes the Pd deposition.

References

- [1] J.E. Hallgren, R.O. Matthews, J. Organomet. Chem. 175 (1979) 135.
- [2] J.E. Hallgren, G.M. Lucas, R.O. Matthews, J. Organomet. Chem. 204 (1981) 135.
- [3] J.E. Hallgren, G.M. Lucas, J. Organomet. Chem. 212 (1981) 135.
- [4] R.P. Joyce, J.A. King, Jr., E.J. Pressman, US Patent 5231210.
- [5] H. Iwane, H. Miyagi, S. Imada, S. Seo, T. Yoneyama, US Patent 5543547.
- [6] I.I. Moiseev, M.N. Vargaftik, T.V. Chernysheva, T.A. Stromnova, A.E. Gekhman, G.A. Tsirkov, A.M. Makhlina, J. Mol. Catal. 108 (1996) 77.
- [7] J.A. Dean (Ed.), Lange's Handbook of Chemistry, 13th ed., McGraw Hill, New York, 1985.

² Reaction procedure is as follows: In a 500 ml continuous gas-flow reactor, were charged phenol (1.1 mol, 103.5 g), 5% Pd/C (36 μg -atom, 76.62 mg), PbO (0.36 mmol, 80.35 mg), CuO (0.36 mmol, 28.63 mg) and NBu₄Br (21.6 mmol, 6.96 g). Reaction was performed at 100°C with a continuous flow of CO and air (2:1 mixture, 500 ml/min) under 90 kg/cm² pressure.

³ The same procedure with ² was applied, except for using Co(trop)₂ (0.36 mmol, 108.4 mg) instead of CuO.