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Direct Synthesis of Diphenyl Carbonate by Electrocarbonylation at a Pd^{2+}-supported Anode

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The first electrochemical synthesis of diphenyl carbonate was accomplished using triethylamine/tetrabutylammonium perchlorate/phenol/dichloromethane or sodium phenoxide/phenol/acetonitrile electrolyte at a [$PdCl_2$/activated carbon and vapor grown carbon fiber] anode, 1 atm CO and 25 °C. Sodium phenoxide functioned as a promoter, triethylamine, and a supporting electrolyte, tetrabutylammonium perchlorate, for the carbonylation.

The majority of polycarbonates are manufactured by a phosgene process, interfacial polycondensation of bisphenol-A and phosgene. An alternative phosgene process is transesterification using bisphenol-A and diphenyl carbonate (DPC). DPC is the key material for the phosgene-free process of polycarbonates.[1] However, DPC is manufactured from phosgene and phenol (PhOH) or dimethyl carbonate and PhOH by an ester exchange reaction.

Three decades ago, the stoichiometric carbonylation of PhOH and CO to DPC using Pd^{2+} and triethylamine (Et_3N) was reported.[2] Here, a key reaction is the reoxidation of Pd^0 to Pd^{2+} with O_2 under the catalytic conditions.[3] The oxidation rate of Pd^0 to Pd^{2+} with O_2 is very slow; therefore, a redox couple of Mn^{3+}/Mn^{2+}, or a twin redox couple of benzoquinone/hydroquinone and Co^{3+}/Co^{2+}, were reported for the reoxidation of Pd^0 to Pd^{2+} under pressures of CO and $O_2 > 6$ MPa at 100 °C.[4–6] The catalytic carbonylation is the primary alternative phosgene process of the DPC production; however, water accumulation is a problem. The hydrolysis of DPC to PhOH and CO_2 and the direct oxidation of CO to CO_2 are accelerated by water. We have reported electrochemical system for carbonylation of methanol,[7–9] but it could not perform carbonylation of PhOH. We investigated electrosynthesis of DPC by Pd electrocatalyst in this work.

We confirmed stoichiometric carbonylation using $PdCl_2$ (1 mmol), PhOH (30 equiv), Et_3N (7 equiv), and CO (1 atm) in CH_2Cl_2 (30 mL, dried by MS-4A) at 25 °C. Products in the solution (DPC, phenyl salicylate, oxidation products of PhOH) and CO_2 in the outlet gas mixture were analyzed using GC and HPLC. Experimental error was ±5% for each product yield. Significant yields of DPC (31%) and CO_2 (25%), based on Pd^{2+}, and a trace of phenyl salicylate were obtained. In addition, black deposits assumed to be Pd^0 were observed after the reaction.

First, we studied the effects of the addition of supporting electrolytes, tetraalkylammonium perchlorate, chloride, or bromide (R_4N-ClO_4, -Cl, and -Br), to the stoichiometric carbonylation conditions on the DPC yield. DPC yields decreased in this order: 47% (n-Bu_4NClO_4) > 39 (n-Hx_4NClO_4) > 35 (Et_4N-ClO_4) > 31 (no addition) ≫ 0 (n-Bu_4NBr and n-Bu_4NCl). Second, the effects of the amount of Et_3N were studied on the DPC yield with n-Bu_4NClO_4. A higher DPC yield of 68% was obtained with 2 equiv of Et_3N. Furthermore, other amines (2 equiv) were used for the carbonylation. DPC yields decreased in this order 68% (Et_3N) > 47 (i-Pr_2EtN) > 18 (n-Bu_3N) ≫ 0 (Et_2HN). Thus, we chose Et_3N and n-Bu_4NClO_4 to conduct the electrocarbonylation.

A Pd anode (5 cm^2) was prepared from $PdCl_2$ (30 μmol) loaded on activated carbon ($PdCl_2$/AC), vapor grown carbon fiber (VGCF) as an electron conductor, and a PTFE binder by hot press.[7] Various electrolysis conditions for DPC formation were studied using the [$PdCl_2$/AC + VGCF] anode. We found that a galvanostatic electrolysis using a conventional one-compartment cell with a Pt-coil counter electrode and without a reference electrode was suitable for the formation of DPC. The electrolyte was 1000 equiv of PhOH, 2 equiv of Et_3N, and 0.1 M n-Bu_4NClO_4/CH_2Cl_2 (30 mL) dried over MS-4A. The solutions were electrolyzed under galvanostatic conditions with a low current of 1 mA after introduction of 1 atm CO.

Figure 1 shows time courses of the formation of DPC under different procedures. First, stoichiometric carbonylation of PhOH by $PdCl_2$/AC in the anode was studied under open circuit conditions. DPC formed smoothly increasing after 30 min; a final yield of 44% was obtained based on Pd^{2+}. CO_2 also formed by stoichiometric oxidation among CO, contaminated H_2O and Pd^{2+} (34% yield). Second, galvanostatic electrolysis of 1 mA was applied at the [$PdCl_2$/AC + VGCF] anode, and the DPC yield slightly increased to 54% after 2 h. Then another portion of 2 equiv of Et_3N was added to the solutions; the DPC yield jumped to 73%. Therefore, electrolysis was performed over a long period of time, adding 2 equiv of Et_3N every 60 min. The DPC yield linearly increased with the reaction time. A current efficiency (CE) of 42% for the DPC

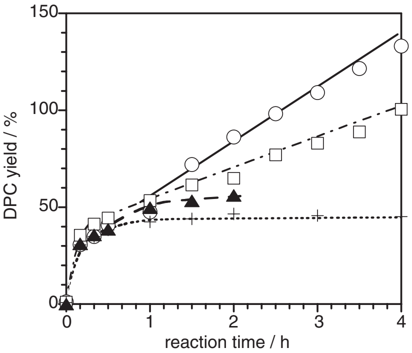

Figure 1. Time courses of DPC yield based on Pd by galvanostatic electrolysis (1 mA) of phenol/Et_3N/n-Bu_4NClO_4/CH_2Cl_2 at the [$PdCl_2$/AC + VGCF] anode at 25 °C. Electrolyte: 0.12 M phenol, Et_3N, 0.1 M n-Bu_4NClO_4/CH_2Cl_2 (30 mL), CO 1 atm. +: open circuit, ▲: initial addition of 2 equiv of Et_3N, ○: intermittent addition of 2 equiv of Et_3N at every 1 h, □: initial addition of 8 equiv of Et_3N.

Table 1. Summarization of stoichiometric and electrochemical carbonylation of PhOH by a [$PdCl_2$/AC + VGCF]

Carbonylation activity/%	2 equiv × 4 Et_3N^a		8 equiv Et_3N^b		4 equiv $PhONa^c$	
	DPC	CO_2	DPC	CO_2	DPC	CO_2
Stoichiometric yield[d]	44	28	43	40	48	35
Electrochemical CE[e]	42	3	26	29	40	26

Additives: [a]2 equiv of Et_3N × 4 times + n-Bu_4NClO_4. [b]8 equiv of Et_3N + n-Bu_4NClO_4. [c]4 equiv of PhONa. [d]Yield based on Pd-supported AC. [e]CE calculated from the slope by galvanostatic electrolysis with 1 mA in Figures 1 and 2.

formation was calculated from the slope of Figure 1. The yield of CO_2 did not increase by the electrolysis. The stoichiometric and electrochemical carbonylation activities were summarized in Table 1. We could not detect other products using GC and HPLC. A total amount of 8 equiv of Et_3N was added once in the initial electrolyte, and the electrolysis was conducted. A DPC yield linearly increased with 26% CE which was lower than 42% CE obtained by the intermittent Et_3N addition; on the other hand, a CO_2 yield increased with 29% CE (Table 1). The carbonylation activity is not efficient but proves the first electrocatalytic carbonylation of PhOH to DPC at $P(CO) = 1$ atm and 25 °C.

According to the previous study, the function of Et_3N should be to generate phenoxy anion (PhO^-) from PhOH.[2] Thus, we used sodium phenoxide (PhONa) as a source of PhO^- instead of Et_3N and as a supporting electrolyte instead of n-Bu_4NClO_4, and CH_3CN solvent instead of CH_2Cl_2.

Figure 2 shows the time courses of the carbonylation of PhOH at the [$PdCl_2$/AC + VGCF] anode in solutions of PhONa (4 equiv)/PhOH (1000 equiv)/CH_3CN (30 mL). First, a stoichiometric carbonylation of PhOH was performed in the solution with $PdCl_2$/AC. A fairly high DPC yield of 48% based on Pd^{2+} and a CO_2 yield of 35% were obtained within 10 min. Second, galvanostatic electrolysis of 1 mA was conducted for 6 h. DPC was produced continuously with 40% CE. The yield of CO_2 also linearly increased with 26% CE (Table 1). Continuous formation of H_2 with 68% CE was confirmed during the electrolysis of 1 mA for 6 h. When the galvanostatic current increased to 3 mA, the DPC yield slightly increased as compared to that at 1 mA. The CEs for the DPC and CO_2 formation were only 17 and 11%, respectively. A higher electrolytic current did not favor the DPC formation; however, PhONa functioned as a promoter and supporting electrolyte. Electrooxidation of PhOH at the anode may inhibit the electrocarbonylation at a higher current.

To clarify the function of PhONa, three experiments were conducted as follows: (1) PhOLi and PhOK were used for the electrocarbonylation of PhOH instead of PhONa. The DPC formation in the two cases was the same as that shown in Figure 2. We observed hardly any significant influence of alkali cations on the carbonylation. (2) A stoichiometric reaction using PhONa (4 equiv)/CH_3CN (30 mL) solution, $PdCl_2$, and CO was conducted but products were not produced. This indicated that PhO^- did not directly produce DPC. (3) Another stoichiometric reaction was conducted using CH_3CO_2Na (4 equiv)/PhOH/CH_3CN (30 mL) solution, $PdCl_2$, and CO. To note, DPC was produced with 24% yield. A mixture of PhOH and CH_3CO_2Na does not generate PhO^- because the pK_a of PhOH (9.95) is larger than that of CH_3CO_2H (4.76). However, CH_3CO_2Na promotes the DPC formation.

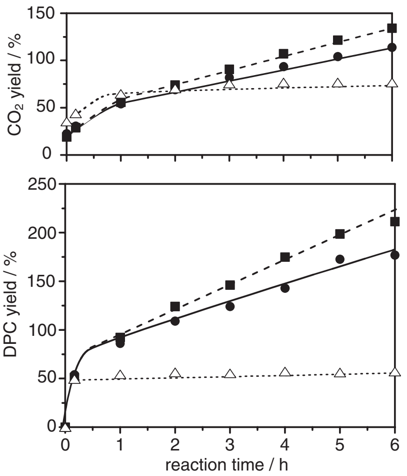

Figure 2. Time courses of DPC and CO_2 yields based on Pd by galvanostatic electrolysis of phenol/PhONa/CH_3CN at the [$PdCl_2$/AC + VGCF] anode at 25 °C. △: open circuit, ●: 1 mA, ■: 3 mA.

We can propose the following reaction scheme for the electrocarbonylation of PhOH to DPC at the [$PdCl_2$/AC + VGCF] anode. First, the stoichiometric carbonylation of PhOH proceeds with Pd^{2+}/AC in which PhONa promoted the carbonylation. PhONa may function as H^+ acceptor in the carbonylation (eq 1), because DPC was not produced from PhONa without PhOH and CH_3CO_2Na promoted the formation of DPC. Pd^0 on AC electrochemically oxidized to Pd^{2+}. H_2 was produced at the Pt-wire cathode, and PhONa was possibly reproduced (eq 2).

$$\begin{aligned} &\mathrm{PhOH} + \mathrm{CO} + \mathrm{Pd}^{2+} + 2\mathrm{PhONa} \\ &\quad \rightarrow \mathrm{DPC} + \mathrm{Pd}^0 + \mathrm{PhOH} + 2\mathrm{Na}^+ \qquad (1) \end{aligned}$$

$$2\mathrm{PhOH} + 2\mathrm{Na}^+ + 2e^- \rightarrow 2\mathrm{PhONa} + \mathrm{H}_2 \qquad (2)$$

We accomplished the first electrocarbonylation of PhOH to DPC with 1 atm CO at a [$PdCl_2$/AC + VGCF] anode and 25 °C in this work, though the yields were not excellent. Dry solution (<50 ppm H_2O) and copresence of promoter (Et_3N, PhONa, CH_3CO_2Na, and so on) are essential for the efficient formation of DPC, and a lower electrolysis current (1 mA) is favored.

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