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Direct synthesis of diphenyl carbonate by mediated electrocarbonylation of phenol at Pd²⁺-supported activated carbon anode

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ABSTRACT

Mediated electrocarbonylation of phenol to diphenyl carbonate (DPC) at a PdCl₂-supported activated carbon anode in 1 atm CO at 298 K was studied. A dry CH₂Cl₂ or CH₃CN solvent and a galvanostatic electrolysis of 1 mA were necessary for formation of DPC, while the addition of a base and a supporting electrolyte was also essential. A combination of triethylamine (Et₃N) and tetrabutylammonium perchlorate (Bu₄NClO₄) was suitable in various combinations. The addition of 2 equiv. of Et₃N to the electrolyte (C₆H₅OH/Bu₄NClO₄/CH₂Cl₂) at 1-h intervals was more efficient in the formation of DPC than a single initial addition of the same amount of Et₃N. The yield of DPC was 130% based on Pd and its current efficiency (CE) was 42% for 6 h. The CE of the CO₂ formation was only 3%. Sodium phenoxide (PhONa) showed dual functionality as a base and supporting electrolyte, DPC was produced in 172% yield and 40% CE for 6 h. The CE of the CO₂ formed continuously after a single initial addition of 4 equiv. of PhONa. Li or K phenoxide also worked as promoters for the mediated electrocarbonylation of phenol to DPC.

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1. Introduction

The demand for polycarbonates is growing worldwide because of their use as a transparent thermoplastic with the current rate of the production being three million tonnes per year. A majority of polycarbonates are manufactured by a phosgene process, i.e., interfacial polycondensation of bisphenol-A and phosgene. An alternative to this phosgene process is transesterification using bisphenol-A and diphenyl carbonate (DPC). DPC is a key material in the phosgene-free process. However, DPC is currently manufactured from phosgene and phenol (Eq. (1)) or dimethyl carbonate and phenol (Eq. (2)).

$$COCl_2 + 2C_6H_5OH \rightarrow (C_6H_5O)_2CO + 2HCl$$
(1)

$$(CH_3O)_2CO + 2C_6H_5OH \rightleftharpoons (C_6H_5O)_2CO + 2CH_3OH$$
 (2)

Direct synthesis of DPC has been studied for oxidative carbonylation of phenol with O_2 using Pd catalysts. The direct synthetic method is attractive from the viewpoint of green and sustainable chemistry because of its reduced energy consumption (CO₂ emission) and environmental safeguards [1]. This catalytic carbonylation is the primary alternative to the phosgene process.

Three decades ago, the stoichiometric carbonylation of phenol and CO to DPC using Pd²⁺ and trialkylamine at room temperature was reported (Scheme 1), wherein a phenoxide anion (PhO⁻) produced from phenol and trialkylamine promoted nucleophilic attack on CO [2]. Phenyl salicylate was produced as a byproduct. Here a key reaction was re-oxidation of Pd⁰ to Pd²⁺ with O₂ under catalytic conditions. The rate of the oxidation of Pd^0 to Pd^{2*} with O_2 was very slow; therefore, a Cu^{2+}/Cu^+ redox couple was used in the Wacker oxidation at 100 °C. In earlier attempts to achieve catalytic synthesis of DPC, a redox couple of Mn³⁺/Mn²⁺ or a twinredox couple of benzoquinone/hydroquinone and Co³⁺/Co²⁺ was reported for the re-oxidation of Pd⁰ to Pd²⁺ under CO and O₂ pressures >6 MPa at 100 °C [3–6]. The carbonylation activity of the Pd catalyst and the yield of DPC were considerably good in previous studies; however, water accumulation was a serious problem in the catalytic carbonylation of phenol with O2. A significant amount of the water formation in the mixture accelerates the hydrolysis of DPC to phenol and CO₂ and the direct oxidation of CO to CO₂. Therefore, suppression of unfavourable effects of accumulated water is very important in the oxidative carbonylation method.

The present study investigated the use of an electrochemical potential instead of O_2 for the re-oxidation of the Pd^{2+} -catalyst in the DPC synthesis. Water is not formed during the electrochemical oxidation of Pd^0 to Pd^{2+} and the oxidation potential is easily controlled. Mediated electrocarbonylation of phenol to DPC would occur at the Pd^{2+} -anode.

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 $\langle -\rangle$ -OH + R₃N \rightarrow $\langle -\rangle$ -O⁻ + R₃NH⁴ Refs. [2,3].

Scheme 1.

The use of the electrochemical potential for the re-oxidation of a Pd⁰ catalyst has been reported in pioneer studies on carbonylation of alkynes to unsaturated diesters [7], alkenes to esters [8] and aromatic amines to isocyanates [9]. These indirect electrocarbonylations were efficiently performed and produced high product yields.

Our research group has also reported the Wacker oxidation of ethylene and propylene at a Pd/C anode applying a fuel cell reaction [10-12] and electrocarbonylation of methanol to dimethyl carbonate in the gas phase at Pd/graphite and Cu/graphite anodes [13,14]. Electrocarbonylation activity of the Pd/C anode was improved by applying a three-phase boundary of CO (gas), methanol (liquid) and electrode (solid). A turnover number (TON) increased to 36 in 1 h and a CO selectivity increased to 90% [15]. Electrocarbonylation of methanol in the liquid phase was also improved by use of the Pd/C anode coupled with a Br⁻-mediator [16]. Electrocatalysis of gold for carbonylation of methanol was achieved in the liquid phase at 25 °C and the selectivity to dimethyl carbonate and dimethyl oxalate could be controlled by the anode potential [17,18]. These electrocarbonylation systems have been applied to carbonylation of phenol. However, carbonylation products such as DPC and phenyl salicylate have not been detected, whereas only black-brown unknown products (tar) have been obtained. It was concluded, therefore, that a stronger oxidation potential was unsuitable for the electrocarbonylation of phenol because an unselective oxidation of phenol proceeded and formed tar. We have recently applied mild electrochemical oxidation conditions to the carbonylation of phenol and have accomplished the first electrochemical synthesis of DPC at P(CO) = 1 atm and $25 \circ C$ [19]. The details of the electrocarbonylation of phenol to DPC were studied and the reaction paths for the DPC formation are discussed in this study.

2. Experimental

2.1. Stoichiometric carbonylation

Stoichiometric carbonylation of phenol promoted by amine: stoichiometric carbonylation of phenol was confirmed and studied using PdCl₂ (1 mmol), phenol (30 equiv.), triethylamine (Et₃N, 7 equiv.) and CO (1 atm) in CH_2Cl_2 (0.030 dm⁻³, dried over MS-4A) at 25 °C. Water content in the dry CH₂Cl₂ solvent and in the reaction mixture were monitored using the Karl Fischer titration, and were controlled below 20 ppm. Stoichiometric reaction proceeded as follows; (i) introduction of CO into the mixture of PdCl₂, phenol, tetrabutylammonium perchlorate (Bu₄NClO₄) and CH₂Cl₂ for 1 h and (ii) addition of Et₃N and initiation of carbonylation by stirring with a magnetic spin bar for 1 h at 25 °C. Bu₄NClO₄ was added as a supporting electrolyte to ascertain its influence on the carbonylation. Other salts, such as Bu₄NBr, Bu₄NCl, Hx₄NClO₄ (Hx: hexyl) and Et₄NClO₄, as well as other amines, diethylamine (Et₂NH), diisopropylethylamine (*i*-Pr₂NEt), tributylamine (Bu₃N), triphenylamine (Ph₃N), diethylphenylamine



Fig. 1. Diagram of one-compartment electrolysis cell for DPC synthesis.

 (Et_2NPh) and N,N,N',N'-tetramethylethane-1,2-diamine (TMEDA) were used in this study.

Stoichiometric carbonylation of phenol promoted by PhONa: stoichiometric carbonylation of phenol by $PdCl_2$ using a solution of sodium phenoxide (PhONa, 4 equiv.), phenol (0.89 mol dm⁻³) and CH₃CN (0.030 dm⁻³, dried over MS-3A) was conducted in a similar manner as that described above.

Stoichiometric carbonylation of phenol promoted by CH_3CO_2Na : stoichiometric carbonylation of phenol by $PdCl_2$ using a solution of CH_3CO_2Na (2 equiv.), C_6H_5OH (0.89 mol dm⁻³) and CH_3CN (0.030 dm⁻³, dried over MS-3A) was conducted in a similar manner.

Stoichiometric carbonylation of cresol promoted by PhONa: stoichiometric carbonylation of cresol by $PdCl_2$ using a solution of sodium phenoxide (PhONa, 4 equiv.), $4-CH_3-C_6H_4OH$ (0.89 mol dm⁻³) and CH₃CN (0.030 dm⁻³, dried over MS-3A) was conducted in a similar manner.

All reagents were purchased from Aldrich Co. and Wako Pure Chemical Co., and required no further purification.

2.2. Mediated electrocarbonylation

2.2.1. Anode preparation

An electrocatalyst of PdCl₂/AC was prepared by impregnation of PdCl₂/2HCl aqueous solution on activated carbon (AC, Wako Pure Chemical Co.), followed by drying in air at 100 °C. An anode was prepared by the hot-press method, using 30 mg of PdCl₂/AC powder (Pd loading: 11 wt% and 30 μ mol), 125 mg vapour-grown carbon-fibre (VGCF, Showa Denko Co.) and 40 mg polytetrafluoroethylene (PTFE, Daikin Co.) [13–16]. Hereafter, the prepared anode is denoted as [PdCl₂/AC+VGCF]. The geometric area of the anode was 5 cm².

2.2.2. Electrolysis procedure

A one-compartment electrolysis glass cell was used for the carbonylation of phenol, as shown in Fig. 1. The [PdCl₂/AC+VGCF] anode was placed on the flat bottom of the cell, and a current collector made of Au wire and a PTFE rod were attached to the anode by physical pressing. A Pt-coil counter-electrode was also placed inside the cell. The distance between the anode and the counter-electrode was 1 cm. Pure CO (1 atm, dried using a cold trap at -76 °C) was introduced into the electrolysis solutions of phenol (1.0 mol dm⁻³)/Bu₄NClO₄ (0.1 mol dm⁻³)/CH₂Cl₂ (0.033 dm⁻³) for 1 h. Et₃N was added to the electrolyte and the solution was electrolyzed under galvanostatic conditions at 1 mA for 4 h at 25 °C. A HZ-5000 electrochemical instrument system (Hokuto Denko Co.) was employed for the galvanostatic electrolysis. A reference electrode was not used for the galvanostatic electrolysis to prevent contamination by additional water. Other electrolyte solutions of phenol (0.89 mol dm⁻³), PhONa (4 equiv.) and CH₃CN (0.033 dm⁻³) were used for carbonylation. Lithium and potassium phenoxides, PhOLi and PhOK, were also used instead of PhONa.

2.2.3. Alkali metal phenoxide synthesis and handling

PhOLi and PhOK were synthesized by a neutralization reaction between phenol and LiOH, and phenol and KOH, respectively. For PhOLi synthesis, 0.6 mol dm⁻³ phenol/H₂O solution (0.05 dm⁻³ and 2.0 mol dm⁻³ LiOH/H₂O solution (0.015 dm⁻³) were well mixed. This mixture was dried under pressure conditions at 25 °C A white solid powder (3.79 g) was obtained, which was identified as PhOLi 1.9H₂O using the elemental analysis and the Karl Fischer titration. In addition, PhOK 1.6H₂O (4.39 g) was obtained in a similar manner.

PhONa·2H₂O (Aldrich), PhOLi·1.9H₂O (synthesized) and PhOK·1.6H₂O (synthesized) reagents contained significant quantities of H₂O. Therefore, PhONa, PhOLi and PhOK were dissolved in dry CH₃CN and the solutions were dried using MS-3A. The dried 50 mM PhONa, PhOLi and PhOK/CH₃CN solutions (<20 ppm H₂O) were used as reagents in carbonylation study.

2.2.4. Open-yield

Stoichiometric reaction between phenol, CO and Pd^{2+} in the $[PdCl_2/AC+VGCF]$ anode proceeded under open-circuit conditions. Hereafter, the yields of DPC and CO_2 based on Pd^{2+} (30 µmol) are denoted as DPC open-yield and CO_2 open-yield.

Current efficiency: DPC was formed by 2-electron oxidation (Eq. (3)), with current efficiency (CE) as defined in Eq. (4).

$$2C_6H_5OH + CO \rightarrow (C_6H_5O)_2CO + 2H^+ + 2e^-$$
(3)

$$CE = \frac{(DPC yield)(2)(96, 485)(100)}{charge passed}\%$$
(4)

CE for CO₂ formation was calculated using Eqs. 5 and 6, similar to DPC formation.

 $CO + H_2O \to CO_2 + 2H^+ + 2e^-$ (5)

$$CE = \frac{(CO_2 \text{ yield})(2)(96, 485)(100)}{\text{charge passed}}\%$$
(6)

DPC and CO_2 formation rates correspond to their CEs in galvanostatic electrolysis. In other words, 1 mA electrolysis with 100% CE corresponds to a maximum formation rate of 18.7 μ mol h⁻¹ (DPC or CO₂).

2.3. Product analyses

Products in the solution were analyzed using GC and HPLC techniques. DPC and phenyl salicylate were analyzed using a Shimadzu GC-2010 (ZB-1 capillary column ($0.25\% \times 30$ m), FID detector, He carrier gas) and Agilent EZ Chrom and SS420X. The reaction mixture (5.0×10^{-4} dm⁻³) was introduced using a micro-syringe and an external standard solution of phenanthrene ($100 \,\mu$ mol)/CH₃CN (1.0×10^{-4} dm⁻³) was added. A 0.05 μ L sample was then injected to the GC and analyzed at 150 °C.

Other carbonylation or oxidation products of phenol could not be detected using GC and HPLC analysis. HPLC analysis was per-

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Stoichiometric carbonylation of phenol by metal salts at 25 $^\circ\text{C}$

	Metal salt	Additives	Product yield (%) ^a		
Entry		Base (equiv.), electrolyte	DPC ^b	PSc	CO ₂
1	PdCl ₂	Et ₃ N (7), –	30.5	0.8	24.6
2	$Pd(OAc)_2$	Et ₃ N (7), –	14.3	16.0	69.4
3	HAuCl ₄	Et₃N (7), –	0	0	0
4	CuCl ₂	Et ₃ N(7), –	0	0	0
5	PdCl ₂	Et ₃ N (7), Bu ₄ NClO ₄	46.6	0.4	24.9
6	PdCl ₂	Et ₃ N (7), Bu ₄ NCl	0	0	0
7	PdCl ₂	Et ₃ N (7), Bu ₄ NBr	0	0	0
8	PdCl ₂	Et ₃ N (7), Et ₄ NClO ₄	35.3	0.5	21.9
9	PdCl ₂	Et ₃ N (7), Hx ₄ NClO ₄	38.6	0.5	21.9

Metal salt 0.03 mol dm $^{-3},\ C_6H_5OH$ 1 mol dm $^{-3},\ electrolyte\ 0.1$ mol dm $^{-3},\ CH_2Cl_2$ 0.030 dm $^{-3},\ CO$ 1 atm, reaction time 1 h.

^a Product yield based on Pd²⁺.

^b Dipheny carbonate.

^c Phenyl salicylate.

formed using a Shimadzu 10VP system (UV–vis detector, DOS-3 column ($4 \varnothing \times 150$ mm), H₂O/CH₃CN solvent).

The outlet gas mixture (CO, CO₂ and H₂) was analyzed using an on-line GC (Shimadzu GC-8A, Porapak-Q column ($4 \varnothing \times 2 m$), TCD detector, He carrier gas) for CO₂ and CO, and another GC (Shimadzu GC-8A, Activated Carbon column ($4 \varnothing \times 2 m$), TCD detector, Ar carrier gas) for H₂. Experimental error was $\pm 5\%$ for each product yield.

3. Results and discussion

3.1. Stoichiometric carbonylation of phenol

Stoichiometric carbonylation of phenol to DPC with Pd²⁺ ((PhCN)₂PdCl₂) has previously been reported in an Et₃N/CH₂Cl₂ solvent at room temperature [2]. The conditions for stoichiometric carbonylation of phenol with PdCl₂ were studied and applied to the mediated electrocarbonylation (Table 1). No carbonylation products were confirmed in the stoichiometric reaction of $C_6H_5OH (1.00 \text{ mol } dm^{-3})/CH_2Cl_2 (0.030 dm^{-3}, dried \text{ over MS-4A}),$ $PdCl_2$ (0.0333 mol dm⁻³) and CO (1.00 atm) at 25 °C. The addition of 7 equiv. of Et₃N against Pd²⁺ resulted in a significant yield of DPC (30.5%) based on Pd^{2+} and a trace of phenyl salicylate, as indicated in entry 1. Black deposits of Pd⁰ were produced after the reaction. CO₂ (24.6% yield) was produced by the oxidation of CO with H₂O and Pd²⁺. Et₃N promoted the DPC formation by creating a supply of PhO⁻ (Scheme 1). Et₃N also enhanced the CO₂ formation due to stabilization of H^+ with Et_3N to yield Et_3NH^+ (Eq. (7)). The absolute amount of CO $_2$ produced (2.46 \times 10 $^{-4}$ mol) was larger than the H₂O content, approximately 0.40×10^{-4} mol (20 ppm) in 0.030 dm⁻³ CH₂Cl₂. Therefore additional water contamination of Et₃N could have contributed to the CO₂ formation.

$$CO + H_2O + 2Et_3N + Pd^{2+} \rightarrow CO_2 + 2Et_3NH^+ + Pd^0$$
 (7)

Other metal oxidants, such as $Pd(OAc)_2$, $HAuCl_4$ and $CuCl_2$ were tested for carbonylation of phenol with the addition of Et_3N in entries 2–4, respectively. As mentioned in the introduction, gold and copper are active for the electrocarbonylation of methanol [12,15]. DPC and phenyl salicylate were produced using $Pd(OAc)_2$, whereas Au^{3+} and Cu^{2+} were not efficient in the stoichiometric carbonylation of phenol. The product selectivity using $Pd(OAc)_2$ differed significantly from that using $PdCl_2$. Counter-anion species may have affected the carbonylation selectivity, but the total yields of DPC and phenyl salicylate were very similar in entries 1 and 2.

Next, the effects of adding a supporting electrolyte to the reaction mixture were studied on stoichiometric carbonylation of phenol in entries 5–9. The yield of DPC increased from 30.5%

Table 2
Effect of amines on stoichiometric carbonylation of phenol by $PdCl_2$ at 25 $^\circ C.$

Entry	Base (equiv.)	Product yield (%) ^a		
		DPC ^b	PSc	CO ₂
5	Et ₃ N (7)	46.6	0.4	24.9
10	Et ₃ N (2)	68.0	0.1	11.4
11	Et ₃ N(1)	41.2	0	6.1
12	$Et_2NH(2)$	0	0	22.4
13	$i-Pr_2NEt(2)$	47.3	0.3	4.2
14	$Bu_3N(2)$	18.4	0	4.6
15	$Ph_3N(2)$	0	0	0
16	$Et_2NPh(2)$	0	0	0
17	TMEDA (2)	1.1	3.1	0.8

 $PdCl_2~0.03~mol~dm^{-3}, C_6H_5OH~1~mol~dm^{-3}, n-Bu_4NClO_4~0.1~mol~dm^{-3}, various~amine, CH_2Cl_2~0.030~dm^{-3}, CO~1~atm, reaction~time~1~h.$

^a Product yield based on Pd²⁺.

^b Dipheny carbonate.

^c Phenyl salicylate.

to 46.6% with the addition of Bu_4NClO_4 , but the yield of phenyl salicylate decreased from 0.8% to 0.4%. On the other hand, the DPC and phenyl salicylate yields were zero following the addition of Bu_4NBr and Bu_4NCl , but several unidentified GC peaks were observed. Other tetra-alkylammonium perchlorates, Hx_4NClO_4 and Et_4NClO_4 , were tested in stoichiometric carbonylation solutions in entries 8 and 9, giving yields of DPC that were larger than those without electrolyte (entry 1). Therefore, tetra-alkylammonium perchlorate is able to enhance the stoichiometric carbonylation. In particular, Bu_4NClO_4 could be an efficient electrolyte for the carbonylation.

Furthermore, the effects of different quantities of Et₃N on DPC formation were studied by adding Bu₄NClO₄ in entries 10-12 (Table 2). The addition of 2 equiv. of Et₃N against Pd²⁺ obtained a higher DPC yield than the addition of any other quantity of Et₃N. The yields of CO₂ decreased as the amounts of Et₃N added decreased. As mentioned above, contamination of H₂O and stabilization of H⁺ by amines (Eq. (3)) should enhance the CO₂ formation. Furthermore, 2 equiv. of other amines, such as Et₂HN, *i*-Pr₂NEt, Bu₃N, Ph₃N, Et₂NPh and TMEDA were tested for carbonvlation in entries 13–17. *i*-Pr₂NETt and Bu₃N promoted the stoichiometric carbonylation of phenol significantly in contrast to other amines. Trialkylamines were suitable additives to enhance the carbonylation; in contrast, phenylamines were not found to be efficient. Therefore, we selected 2 equiv. of Et₃N and 0.1 mol dm⁻³ of Bu₄NClO₄ as additives for mediated electrocarbonylation of phenol at the [PdCl₂/AC+VGCF] anode.

3.2. Electrochemical re-oxidation of Pd⁰ under carbonylation conditions

If the black deposit of Pd were to oxidize with the electrochemical potential under stoichiometric carbonylation conditions, continuous electrocatalytic synthesis of DPC would occur. The [PdCl₂/AC+VGCF] anode (5 cm²) was applied for the carbonylation. Various electrolytic conditions for the DPC formation were studied using the [PdCl₂/AC+VGCF] anode. Reaction conditions consisting of galvanostatic electrolysis of solutions (1 mol dm⁻³ C₆H₅OH, 2 equiv. of Et₃N (60 µmol), 0.1 mol dm⁻³ Bu₄NClO₄ and 0.030 dm⁻³ CH₂Cl₂ dried over MS-4A), a low electrolysis current of 1 mA, and the use of a conventional one-compartment cell (Fig. 1) were found to be efficient in the DPC formation [17]. If a wet CH₂Cl₂ solvent (ca. 60,000 ppm H₂O) was used in these carbonylation conditions, DPC was not produced, with the primary product being CO₂.

Fig. 2 shows the time courses of the DPC formation under different conditions. First, the DPC open-yield and CO_2 open-yield were confirmed. As mentioned in Section 2, reactions between phenol,



Fig. 2. Time courses of DPC formation by mediated electrocarbonylation (1 mA) of $C_6H_5OH/Et_3N/Bu_4NClO_4/CH_2Cl_2$ at the $[PdCl_2/AC+VGCF]$ anode at 25 °C. Anode (5 cm²): PdCl_2 (30 μ mol)/AC (30 mg)+VGCF (125 mg)+PTFE (40 mg), Electrolysis solution: 1.0 mol dm⁻³ $C_{6}H_5OH$, Et_3N 0–8 equiv. 0.1 mol dm⁻³ Bu_4NClO_4 , CH_2Cl_2 0.033 dm⁻³, CO 1 atm. +: open circuit, Δ : initial addition of Et_3N (2 equiv.) at 0 h and additional Et_3N (2 equiv.) twice at 0 and 1 h, \bullet : intermittent addition of Et_3N (2 equiv.) at 0, 1, 2 and 3 h, \Box : initial addition of Et_3N (8 equiv.) at 0 h.

CO and Pd²⁺ in the anode proceed under open-circuit conditions. DPC formed smoothly ceasing after 30 min, giving a DPC openvield of 44% [19]. CO₂ was also formed by oxidation of CO with H₂O-contaminated solvent and Pd²⁺, giving a CO₂ open-yield of 35%. Next, the mediated electrocarbonylation with 1 mA was conducted at the flesh [PdCl₂/AC+VGCF] anode. DPC yield increased slightly after 30 min and was 54% at 120 min. When an additional 2 equiv. of Et₃N was added to the solution under open-circuit conditions, the DPC yield jumped to 73% as indicated (\triangle). Therefore, the mediated electrocarbonylation was conducted by adding 2 equiv. of Et₃N twice, at 0 and 1 h. The DPC yield increased linearly after 1 h and reached to a plateau after 2.5 h. When 2 equiv. of Et₃N was added in 1-h intervals (0, 1, 2 and 3 h), the DPC yield increased linearly after 4 h. The final DPC yield was 130% at 4 h based on Pd²⁺, which corresponds to a turnover number (TON) of 1.30. Phenyl salicylate and other oxidation products of phenol were not detected by GC and HPLC techniques. When a total of 8 equiv. of Et₃N was added simultaneously in the initial electrolysis solution, the DPC yield also increased linearly over 4 h but the yield was lower than that obtained with the 1-h interval addition of Et₃N. The interval addition of Et₃N was more efficient in the mediated electrocarbonylation than in initial single addition. These experimental results suggest that Et₃N enhances the mediated electrocarbonylation of phenol to DPC, but converts to an inactive form during electrolysis.

The CE calculated from the slope of Fig. 2 was 42% for the DPC formation by the interval addition of Et_3N . CO_2 production increased slightly using a 3% CE. On the other hand, the CE of DPC formed by the single addition of 8 equiv. Et_3N was 26% and that of the CO_2 formation was 29%. These CE data also clearly indicate that the interval addition of Et_3N was more efficient than the single initial addition for the DPC formation. The open-yields and the mediated electrocarbonylation activities of DPC and CO_2 are summarized in Table 3.

As described above, Et₃N was efficient for the electrosynthesis of DPC. The influence of substitution of the ethyl group of Et₃N by methyl, benzyl and phenyl groups on the mediated carbonylation was studied. Fig. 3 shows the mediated electrocarbonylation of phenol with addition of 2 equiv. of various amines, such as Me₂NEt, MeNEt₂, Me₂NBn or Me₂NPh at 1-h interval. The formation rates of DPC depended on the amines, such that Et₃N, MeNEt₂,



Fig. 3. Effects of amines on time courses of DPC formation by mediated electrocarbonylation (1 mA) of C₆H₅OH/amine/Bu₄NClO₄/CH₂Cl₂ at [PdCl₂/AC+VGCF] anode at 25 °C. Anode (5 cm²): PdCl₂ (30 μ mol)/AC (30 mg)+VGCF (125 mg)+PTFE (40 mg), Electrolysis solution: 1.0 mol dm⁻³ C₆H₅OH, intermittent addition of amine (2 equiv.) at each 1 h. 0.1 mol dm⁻³ Bu₄NClO₄, CH₂Cl₂ 0.033 dm⁻³, CO 1 atm. \bullet : Et₃N, \triangle : Me₂NEt, \bigtriangledown : Me₂NBn, \Box : MeNEt₂, \Diamond : Me₂NPh.

 $>Me_2NBn > Me_2NEt \gg Me_2NPh$. This order may indicate that the pKa values of their ammonium forms affect the formation rates of DPC. However, their pKa values in dry CH_2Cl_2 have not been reported.

As described above, the carbonylation activity was not sufficient, but it proves that the mediated electrocarbonylation of phenol to DPC can be accomplished under ambient conditions of P(CO) = 1 atm and 25 °C.

3.3. Mediated electrocarbonylation of phenol to DPC using PhONa

According a previous study, the function of Et_3N is to supply phenoxy anions (PhO⁻), as shown in Scheme 1 [1]. The nucleophilic phenoxy anion attacks CO on Pd²⁺, producing DPC. The supply of PhO⁻ may be essential for mediated electrocarbonylation of phenol to DPC. Thus, PhONa was used as a source of PhO⁻ and a supporting electrolyte instead of Et_3N and Bu_4NClO_4 , respectively, although, PhONa did not dissolve in the phenol/CH₂Cl₂ solution. Next, CH₃CN dried over MS-3A was applied to carbonylation. The water content was lower than 20 ppm, as determined using the Karl Fischer titration.

Fig. 4(a) and (b) shows time courses of carbonylation of phenol and CO₂ formation at the [PdCl₂/AC+VGCF] anode in various solutions, respectively. First, the open-yields of DPC and CO₂ were confirmed in a solution of PhONa (4 equiv.)/C₆H₅OH (0.89 mol dm⁻³)/CH₃CN (0.033 dm⁻³), CO (1 atm) and Pd²⁺ (30 μ mol) in the anode. CO₂ was immediately produced by addition of PhONa/CH₃CN at 0 min. The open-yields of DPC and CO₂ were considerably high, 50% and 23%, respectively, in 10 min.



Fig. 4. Effects of alkaline phenoxide (PhOX) on yields of DPC (a) and CO₂ (b) by mediated electrocarbonylation of C₆H₅OH/PhOX/CH₃CN at [PdCl₂/AC + VGCF] anode at 25 °C. Electrolysis solution: 0.89 mol dm⁻³ C₆H₅OH, PhOX 0.12 mmol, CH₃CN 0.033 dm⁻³, CO 1 atm. Using PhONa, ●: DPC, \bigcirc : CO₂; using PhOLi, ▲: DPC, \triangle : CO₂; using PhOK, ■: DPC, \Box : CO₂.

This indicates that PhONa can be used instead of Et₃N. Next, mediated electrocarbonylation using PhONa was conducted at the flesh [PdCl₂/AC+VGCF] anode with 1 mA for 6 h. PhONa functioned as a supporting electrolyte and DPC was continuously produced. The final yield was greater than 172% based on Pd²⁺ (1.72 TON). The CE for the DPC formation calculated from the initial slope of Fig. 4 was 40% after 1 h (Table 3). On the other hand, the yield of CO₂ increased to 50% within 1 h and slowly increased after 1 h. The CO₂ production ceased after 4 h and the final yield of CO₂ was 60% after 6 h. The time course of the CO₂ formation indicated that water contaminated from the electrolyte was consumed by oxidizing CO (Eq. (3)). The average CE of CO₂ formation was 10%, calculated from the yields between 10 min and 6 h, (Table 3). The formation of H₂ was confirmed during electrolysis. The formation rate of H₂ was constant for 6 h and its CE was 68%.

To understand the function of PhONa, i.e., PhO^{-} and Na^{+} , mediated electrocarbonylation of phenol was studied using PhOLi or PhOK instead of PhONa. The electrolysis solutions were dried over MS-3A to <20 ppm H₂O. Kinetic curves of the DPC formation in the two cases were very similar to those of PhONa (Fig. 4). The time courses of the CO₂ yield using PhOLi and PhOK differed from those using PhONa. However, the yield of CO₂ decelerated after 3 h, and on comparison, the reaction gave yields similar to that obtained

Table 3

Summarization of open-yields and CEs of DPC and CO2 formation at [PdCl2/AC+VGCF].

-	-				-					
Reactivities	2 eq. \times 4 Et ₃ N ^a		8 eq. Et ₃ N ^b		4 eq. PhONa ^c		4 eq. PhOLi ^c		4eq. PhOK ^c	
	DPC	CO ₂	DPC	CO ₂	DPC	CO ₂	DPC	CO ₂	DPC	CO ₂
Open-yield/% ^d	44	28	43	40	50	23	57	13	50	11
CE/% ^e	42	3	26	29	40	10	41	10	31	10

^a 2 equiv. Et₃N \times 4 times addition + Bu₄NClO₄.

^b Initial addition of 8 equiv. Et₃N + Bu₄NClO₄.

^c Initial addition of 4 equiv. PhONa, PhOLi or PhOK.

^d Yield based on Pd supported on AC.

^e CE calculated from the slope by mediated-electrocarbonylation with 1 mA.



Fig. 5. Effects of quantities of PhONa addition on (a) mediated electrocarbonylation of phenol (1 mA) and (b) open-yield at $[PdCl_2/AC + VGCF]$ anode at 25 °C. Electrolyte: 0.89 mol dm⁻³ C₆H₅OH/PhONa/CH₃CN (0.033 dm⁻³), CO 1 atm. Anode (5 cm²): PdCl₂ (30 μ mol)/AC (30 mg) + VGCF (125 mg) + PTFE (40 mg), Stoichiometric yield, \bigcirc : DPC, \Box : CO₂; electrochemical formation rate, \oplus : DPC, \blacksquare : CO₂.

using PhONa. The open-yields and CEs of DPC and CO_2 using PhOLi or PhOK are listed in Table 3. The alkaline cations, Na⁺, Li⁺, or K⁺, did not have significant influence on the mediated electrocarbonylation of phenol to DPC. Although alkaline cations may have affected the formation of CO_2 at an early stage of the reaction but the final yields of CO_2 were very similar.

When the galvanostatic current was increased to 3 mA, the DPC yield increased slightly, 206% based on Pd^{2+} (2.06 TON), compared to that at 1 mA [19]. The CEs of the DPC and the CO₂ formations were only 17% and 11%, respectively. A higher electrolytic current did not favour the DPC formation at the [PdCl₂/AC+VGCF] anode; no other products or reactions were detected that could account for the current of approximately 72% CE.

3.4. Influence of reaction conditions on DPC formation

The effects of various PhONa concentrations on mediated electrocarbonylation of phenol to DPC at the [PdCl₂/AC+VGCF] anode were studied. The reaction conditions were the same as that used for Fig. 4, except for the addition of PhONa. All electrolytic solutions (PhONa; 0–16.7 equiv.) were dried over MS-3A to <20 ppm H₂O. Electrolysis did not proceeded without the addition of PhONa.

Fig. 5a shows the DPC and CO₂ formation rates under the mediated electrocarbonylation with 1 mA. The formation rates of products corresponded to their CEs because the current was constant. The maximum formation rate of DPC or CO₂ was $18.7 \,\mu$ mol h⁻¹ in the mediated electrocarbonylation with 1 mA, as described in Section 2. Mediated electrocarbonylation could not proceed in the steady state at 0 mol dm⁻³ PhONa because PhONa functions as a promoter and electrolyte. Therefore, data of the formation rate (CE) of DPC and CO₂ were not at 0 mol dm⁻³. The formation rate (CE) of DPC increased with the PhONa addition and showed a maximum (40% CE) at 4.0 of equiv. PhONa concentrations higher than 6 equiv. were not efficient for the DPC formation (<20% CE). Therefore, the addition of 4.0 equiv. of PhONa was selected in later



Fig. 6. Effects of concentration of phenol on (a) mediated electrocarbonylation of phenol (1 mA) and (b) open-yield at $[PdCl_2/AC+VGCF]$ anode at 25 °C. Electrolyte: $C_6H_5OH/4$ equiv. PhONa/CH₃CN (0.033 dm⁻³), CO 1 atm. Anode (5 cm²): PdCl₂ (30 µmol)/AC (30 mg)+VGCF (125 mg)+PTFE (40 mg). Stoichiometric yield, \bigcirc : DPC, \Box : CO₂: electrochemical formation rate, O: DPC, \blacksquare : CO₂.

experiments. The formation rate (CE) of CO₂ was almost constant ($15 \pm 3\%$ CE).

Fig. 5b shows the open-yields of DPC and CO_2 extrapolated from time courses of the product formation at 0 min. The DPC open-yield increased with addition of PhONa and showed a maximum of 56% at 6 equiv. The DPC open-yield decreased slightly with excess additions of PhONa. In contrast, the CO_2 open-yield was almost constant with the addition of PhONa.

Fig. 6 shows the effect of varying phenol concentrations from 0 to 0.89 mol dm⁻³ on the mediated electrocarbonylation of phenol to DPC at the [PdCl₂/AC+VGCF] anode. In the electrochemical reaction shown in Fig. 6a, the formation rate (CE) of DPC sharply increased with the concentration of phenol and reached a constant formation rate (ca. 40% CE) above 0.05 mol dm⁻³. Interestingly, DPC was produced in significant quantities with 11% CE at 0 mol dm⁻³ phenol. The formation rate of CO₂ was very high, i.e., 75% CE at 0 mol dm⁻³ phenol. The formation rate of CO₂ (CE) decreased with increasing phenol concentration. These facts indicate that the carbonylation of phenol to DPC and the oxidation of CO by water to CO₂ were competitive.

In Fig. 6b, DPC open-yield at $0 \mod dm^{-3}$ phenol was zero. The DPC open-yield increased with the concentration of phenol and reached a constant yield of approximately 50% above 0.20 mol dm⁻³. The CO₂ open-yield was almost constant at 25% for all concentrations of phenol.

When no phenol was added (0 mol dm⁻³), it was observed that the DPC formation with 11% CE and the lack of DPC with 0% open-yield contradicted each other. To resolve this discrepancy, the time courses of the products were studied during the electrolysis of the 4 equiv. of PhONa/CH₃CN (0.033 dm⁻³) solutions at the [PdCl₂/AC+VGCF] anode with 1 mA, as shown in Fig. 7. CO₂ was produced at 0 min, 20% open-yield of CO₂. However, DPC was not formed at 0 min, demonstrating that the DPC open-yield was zero using PhONa/CH₃CN solution. The major product, CO₂, was produced linearly during electrolysis, whereas DPC was produced slowly after 2 h. An induction period was observed during for the DPC formation from PhONa. This unusual result may be due to phe-



Fig. 7. Time courses of DPC and CO₂ formation by mediated electrocarbonylation of PhONa/CH₃CN at [PdCl₂/AC+VGCF] anode at 25 °C. Electrolysis current 1 mA, electrolysis solution: PhONa 0.12 mmol, CH₃CN 0.030 dm⁻³, CO 1 atm. \bullet : DPC, \blacksquare : CO₂.

nol formation during the oxidation of CO with H_2O (Eq. (8)). The accumulated phenol formed DPC by the mediated electrocarbonylation after 2 h.

 $CO + H_2O + 2PhONa \rightarrow CO_2 + 2PhOH + 2Na^+ + 2e^-$ (8)

3.5. Function of PhONa

As described in Fig. 6, PhONa did not directly produce DPC by Pd²⁺ at the anode and mediated electrocarbonylation. These results indicate that PhOX (X: Na, Li, K) promotes Pd²⁺-catalysed the carbonylation of phenol to DPC. To obtain more detailed information regarding the function of PhONa, advanced stoichiometric reactions were studied in the dry CH₃CN solvent, as shown in entry 18-22 in Table 4. Entry 18 was the result of a standard stoichiometric carbonylation of phenol with PhONa and significant yields of DPC and CO₂ were produced. Entry 19 was the result of a stoichiometric reaction using PhONa, CO and PdCl₂ and a major product was CO₂ and a trace amount of DPC was produced. Entry 20 is a stoichiometric carbonylation of phenol with CH₃CO₂Na. DPC was produced in 24% yield. CH₃CO₂Na functioned as the promoter instead of PhONa during the formation of DPC. Entry 21 was the result of carbonylation of p-cresol with PhONa. $(4-CH_3-C_6H_4O)_2CO$ was produced in 72% yield by the stoichiometric carbonylation of *p*-cresol with PhONa. DPC was not produced in entry 21. Entry 22 was the result of carbonylation of phenol with sodium p-cresolate. DPC was produced in 51% yield by the stoichiometric carbonylation of phenol with sodium p-cresolate. (4-CH₃-C₆H₄O)₂CO was not produced in entry 22.

Table 4

Effects of additives on stoichiometric carbonylation phenols in CH_3CN by $PdCl_2$ at $25\,^\circ C.$

Entry	Reactant	Promoter	Product yield (%) ^a		
			DPC ^b	$(4-CH_3-C_6H_4O)_2CO$	CO ₂
18	Phenol	PhONa	70.1	-	29.3
19	-	PhONa	1	-	87.1
20	Phenol	CH ₃ CO ₂ Na	23.9	-	25.6
21	p-cresol	PhONa	0	71.5	20.9
22	Phenol	4-CH ₃ -C ₆ H ₄ ONa	51.3	0	47.7

 $PdCl_2~0.03~mol~dm^{-3},~C_6H_5OH~or~4-CH_3-C_6H_4OH~1~mol~dm^{-3},~promoter~(2~equiv),~CH_3CN~0.030~dm^{-3},~CO~1~atm,~reaction~time~1~h.$

^a Product yield based on Pd²⁺.

^b Dipheny carbonate.



RONa (Proton accepter): Sodium Phenoxide, Sodium Acetate, Sodium Cresolate.

Scheme 2.

The value of pKa of phenol (9.95) is larger than that of CH_3CO_2H (4.76); therefore, PhONa should not be produced in the mixture of phenol and CH_3CO_2Na in entry 20. When a mixture of C_6H_5OH and CH_3CO_2Na was analyzed using a GC technique, CH_3CO_2H was not detected. These facts suggest that CH_3CO_2Na functions as a H⁺ acceptor and promotes carbonylation, as indicated in Eq. 9.

$$2C_{6}H_{5}OH + CO + Pd^{2+} + 2CH_{3}CO_{2}Na \rightarrow (C_{6}H_{5}O)_{2}CO + Pd^{0} + 2CH_{3}CO_{2}H + 2Na^{+}$$
(9)

If the Eq. (9) is correct, PhONa also functions as the H^+ accepter in the same way as CH_3CO_2Na (Eq. (10)).

$$2C_{6}H_{5}OH + CO + Pd^{2+} + 2PhONa \rightarrow (C_{6}H_{5}O)_{2}CO$$

+ $Pd^{0} + 2PhOH + 2Na^{+}$ (10)

According to Eq. (10), the stoichiometric carbonylation of *p*-cresol produced $(4-CH_3-C_6H_4O)_2CO$ and did not produce DPC in entry 21. Sodium *p*-cresolate also functioned as the H⁺ accepter and $(4-CH_3-C_6H_4O)_2CO$ was not produced in entry 22.

3.6. Reaction scheme

Based on these experimental observations, we propose the following reaction scheme for the mediated electrocarbonylation of phenol to DPC at the [PdCl₂/AC+VGCF] anode (Scheme 2).

First, the Pd²⁺-catalysed the stoichiometric carbonylation of phenol proceeds in which PhONa promotes the carbonylation. PhONa functions as the H⁺ accepter because of the following reasons: (i) CH₃CO₂Na promotes the stoichiometric carbonylation, (ii) DPC is not directly produced from PhONa and (iii) (4-CH₃-C₆H₄O)₂CO is produced from the solution of cresol and PhONa. After the promoting this reaction, PhONa is converted to phenol and Na⁺ (Eq. (10)).

Next, Pd^0 at AC was electrochemically oxidized to regenerate Pd^{2+} . Then, H_2 was produced by phenol reduction at the Pt-wire cathode and PhONa was possibly reproduced. Therefore, a single initial addition of PhONa was efficient in the mediated electrocarbonylation of phenol to DPC.

The addition of Et₃N is expected to promote the DPC formation and to form Et₃NH⁺ (Eq. (12)). However, when a mixture of phenol, Et₃N and CH₂Cl₂ were added, Et₃N and phenol were detected, and the neutralization of phenol and Et₃N to (C₆H₄O⁻)(Et₃NH⁺) did not proceed or was very slow under our reaction conditions.

$$2C_6H_5OH + CO + Pd^{2+} + 2Et_3N \rightarrow (C_6H_5O)_2CO + Pd^0$$

+ $2Et_3NH^+$ (12)

 Et_3NH^+ was not able to regenerate Et_3N and $Et_3NH^+PhO^-$ accumulated because of the formation of H_2 at the cathode, as indicated

in Eq. (13). Therefore, the addition of Et₃N at 1-h intervals was efficient in the mediated electrocarbonylation.

$$2C_{6}H_{5}OH + 2Et_{3}NH^{+} + 2e^{-} \rightarrow H_{2} + 2Et_{3}NH^{+}C_{6}H_{5}O^{-}$$
(13)

As summarized in Table 3, the electrolysis systems using Et₃N, PhONa, PhOK and PhOLi showed very similar CEs for the DPC formation. The CEs of the combination of DPC and CO₂ were ca .50%. The products accounting for 50% CE could not be identified in the liquid phase using GC or HPLC techniques. We speculated that an oxidative oligomerization of phenol proceeded and oligomer deposited on the carbon surface. To achieve a more selective and active carbonylation of phenol, the electrocatalysis of the Pd anode must improve to suppress the unselective oxidation of phenol.

The anode potential was not monitored during the electrolvsis to suppress water contamination because dry electrolyte solutions were essential for our system. In a separate experiment, we measured the $[PdCl_2/AC + VGCF]$ anode potential using an Ag/Ag^{+} (0.01 mol dm⁻³ Ag(NO₃)/0.1 mol dm⁻³ Bu₄NClO₄/CH₃CN) reference electrode. The anode potential was +0.5 V (Ag/Ag⁺) for 1 mA of electrolysis and the applied voltage between the anode and the cathode was approximately 3 V.

This reaction system has a strong reductive atmosphere of 1 atm CO and no oxygen. The AC surface had strong adsorption and reduction abilities owing to the free electrons. The reduction rate of Pd²⁺ by carbonylation can be calculated from stoichiometric reaction rate under the open-circuit condition, as shown in Fig. 4. The reduction of 30 µmol Pd²⁺ was completed in 10 min, which corresponded to 10 mA. Thus, the reduction rate was 10 times faster than the electrochemical oxidation rate of Pd⁰ (1 mA). Therefore, Pd⁰ is more stable than Pd²⁺ on the AC surface during the mediated electrocarbonylation at 1 mA.

4. Conclusions

The mediated electrocarbonylation of phenol to DPC with P(CO) = 1 atm at the [PdCl₂/AC + VGCF] anode and 25 °C was studied, although the maximum TON and yield were not excellent. The use of a dry solution (<20 ppm H₂O) and the addition of either trialkylamine (Et_3N) and phenol or alkaline metal phenoxide (PhOX, X; Li, Na and K) were efficient in DPC formation and a lower electrolysis current (1 mA) was favoured. PhOX worked as the promoter and the supporting electrolyte for the mediated electrocarbonylation of phenol to DPC. We proposed that PhONa and Et₃N functioned as the H⁺ accepter from phenol but not from a simple base during carbonylation to produce phenoxide. An indirect electroorganic synthetic mechanism for the DPC formation, consisting of stoichiometric carbonylation of phenol to DPC by Pd²⁺ and the electrochemical oxidation of Pd⁰ to Pd²⁺, was proposed. To develop an efficient alternative to the phosgene method for DPC production, we must further accelerate the oxidation rate of Pd⁰ to Pd²⁺ (electrolysis current) while simultaneously suppressing the direct oxidation of phenol and the formation of a by-product (tar) at the anode.

References

- [1] J. Gong, X. Ma, S. Wang, Appl. Catal. A: Gen. 316 (2007) 1.
- [2] J.E. Hallgren, R.O. Mathews, J. Organomet. Chem. 175 (1979) 135.
- [3] J.E. Hallgren, G.M. Lucas, R.O. Mathews, J. Organomet. Chem. 204 (1981) 135. [4] M. Takagi, H. Miyagi, T. Yoneyama, Y. Ohgomori, J. Mol. Catal. A: Chem. 129
- (1998) L1. [5]
- A. Vavasori, L. Toniolo, J. Mol. Catal. A: Chem. 139 (1999) 109.
- [6] H. Ishii, M. Ueda, K. Takeuchi, M. Asai, J. Mol. Catal. A: Chem. 144 (1999) 369. F.W. Hartstock, L.B. McMahon, I.P. Tell, Tetrahedron. Lett. 34 (1993) 8067.
- [8] D.D.M. Wayner, F.W. Hartstock, J. Mol. Catal. 48 (1988) 15.
- [9] F.W. Hartstock, D.G. Herrington, L.B. McMahon, Tetrahedron. Lett. 35 (1994) 8761.
- [10] K. Otsuka, Y. Shimizu, I. Yamanaka, J. Chem. Soc, Chem. Commun. (1988) 1272.
- K. Otsuka, Y. Shimizu, I. Yamanaka, J. Electrochem, Soc. 137 (1990) 2076. [11]
- [12] I. Yamanaka, Y. Nabae, K. Otsuka, J. Electrochem, Soc. 150 (2003) D129.
- [13] K. Otsuka, T. Yagi, I. Yamanaka, Electrochim. Acta 39 (1994) 2109.
- [14] K. Otsuka, T. Yagi, I. Yamanaka, I. Electrochem. Soc. 142 (1995) 130.
- [15] I. Yamanaka, A. Funakawa, K. Otsuka, J. Catal. 221 (2004) 110.
- [16] A. Funakawa, I. Yamanaka, K. Otsuka, J. Electrochem. Soc. 153 (2006) D68.
- [17] A. Funakawa, I. Yamanaka, S. Takenaka, K. Otsuka, J. Am. Chem. Soc. 126 (2004) 5346.
- [18] A. Funakawa, I. Yamanaka, K. Otsuka, J. Phys. Chem. B 109 (2005) 9140.
- [19] T. Murayama, Y. Arai, T. Hayashi, I. Yamanaka, Chem. Lett. 39 (2010) 418.