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Spectroscopic Investigation of the Electrosynthesis of Diphenyl Carbonate from CO and Phenol on Gold Electrodes

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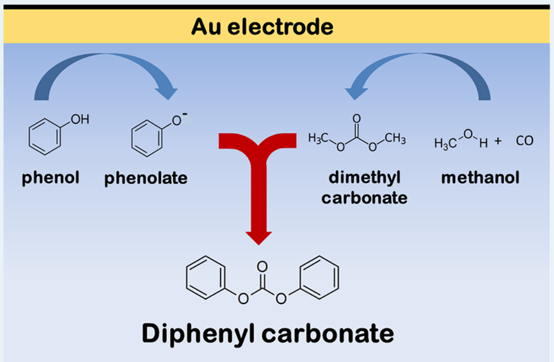
Supporting Information



ABSTRACT: In this work, we study the synthesis of diphenyl carbonate (DPC) from phenol and CO on gold electrodes studied by means of in situ Fourier transform infrared spectroscopy (FTIR). The results show that, on gold electrodes, the formation of DPC is observed at potentials as low as 0.4 V vs Ag/AgCl, together with the formation of dimethyl carbonate (DMC) from the carbonylation of methanol that was used as a solvent. The spectroelectrochemical results also suggest that the formation of DPC occurs via the replacement of the methoxy groups from DMC with phenoxy groups from phenol and not directly by the carbonylation of phenol. Although this transesterification process is known to occur with heterogeneous catalysts, it has not been reported under electrochemical conditions. These are interesting findings, since the direct DPC production by carbonylation of phenol to DPC is usually performed with Pd-based catalysts. With this reaction scheme of transesterification happening under electrochemical conditions, other non-Pd catalysts could be used as well for one-step DPC production from phenol and CO. These findings give important mechanistic insights into this reaction and open up possibilities to an alternative process for the production of DPC.

KEYWORDS: *carbonylation, methanol, electrosynthesis, diphenyl carbonate, Au catalysts*

The use of electrochemistry in the synthesis of organic molecules is a very promising methodology for future industrial applications. With the help of electrochemistry, it is possible to fulfill several requirements for the development of environmentally friendly industrial processes. One of the main contemporary advantages of electrochemistry is the use of sustainable energy utilizing electricity produced by renewable sources such as wind or solar.[1]

Electrochemical reactions typically occur at room temperature and the combination of low temperature and accurate control of the potential should, in principle, allow the selectivity of the process to be driven toward a specific desirable product. Moreover, electrocatalysts are generally “heterogeneous” electrode materials that will facilitate the separation and reuse of the catalyst. Successful examples of electrochemical processes in industry can be found in the Chlor-Alkali industry, and in aluminum or adiponitrile production.[2] These established electrochemical processes are undergoing constant improvement. A prominent example in chlorine electrolysis is the implementation of gas diffusion electrodes into aqueous electrolysis in 2003, enabling the use of gaseous reactant oxygen under high current density with electricity savings up to 30%.[3] There is great potential for electrochemical methods to help in the development of other green alternatives for the chemical industry, especially being that, with gas diffusion electrodes, the choice of reactants is now extended to gaseous reactants.

Diphenyl carbonate (DPC) is a key material in the solvent-free production of polycarbonates[4] through the transesterification of DPC with bisphenol A (BPA). However, the synthesis procedure occurs in several steps involving a high number of reactants and very particular conditions. First, dimethyl carbonate (DMC) is prepared via oxidative carbonylation of methanol, and then diphenyl carbonate (DPC) is synthesized from a two-step reaction consisting of transesterification of DMC with phenol into methyl phenyl carbonate (MPC), followed by disproportionation of MPC into DMC and DPC. Finally, DPC is reacted by transesterification with BPA in the melt phase, resulting in the formation of polycarbonate precursors.[4,5]

The world demand of polycarbonate increased up to 5 million tons in 2015,[6] making DPC a high-value building block to the chemical industry. The direct synthesis of DPC will bring several advantages such as reduced energy consumption and environmental benefits and sustainability.[5] The oxidative carbonylation of phenol has been the focus of intensive

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research in the past by the main polycarbonate producing companies, because the reaction pathway is very simple and uses commonly available chemicals. However, the expensive catalyst system with homogeneous Pd and a series of highly corrosive co-catalysts prevented industrial implementation of the technology.[7,8] The focus of the industrial research into DPC synthesis moved on to reaction pathways using detours and more exotic raw materials,[9] but electrochemistry can present several advantages, when compared with chemical oxidative carbonylation. First, the reaction temperature (that is between 100 °C and 200 °C for oxidative carbonylation[6]) can be decreased to room temperature without loss in efficiency or selectivity, which will represent significant savings, in terms of energy losses and higher energy efficiencies at the industrial level. Second, the oxidation reaction occurs at the electrode and there is no need for an oxidative gas, avoiding the use of explosive mixtures such as O_2 and CO. Moreover, with the appropriate catalyst, the usage of an inorganic co-catalyst (used in oxidative carbonylation to increase the reaction yield) can be avoided, reducing the number of chemical components in the process. Therefore, the electrochemical carbonylation of phenol (PhOH) with CO is one of the appealing alternative routes toward this goal. With gas diffusion electrodes for inclusion of CO as gaseous reactant, the hurdles for technical implementation nowadays are lower than in the past.

Similar to catalytic processes, the electrocarbonylation of phenol with CO has only been described in the literature for Pd-based catalysts, both metallic[10−12] and homogeneous.[13] For the heterogeneous catalysts, $PdCl_2$ (Pd^{2+}) supported on activated carbon[10] and Pd^0/Ketjenblack[11] were studied. In both systems, the yields for DPC were very dependent on the dryness of the solvents, and both sodium phenoxide (PhONa) and trimethylamine (Et_3N) additives have shown to be necessary for the reaction to proceed. The role of these additives was described as being H^+ acceptors from PhOH.

In this work, we use spectro-electrochemical techniques to access mechanistic information about the reaction pathways toward DPC starting from PhOH and CO at Au electrodes in methanol (MeOH) electrolytes.

Recently, our group reported spectro-electrochemical evidence for the synthesis of DMC at Au electrodes at low overpotentials (~0.4 V vs Ag/AgCl), revealing that there is no need for an oxidized surface in order to achieve this product from methanol carbonylation with CO.[14] Based on those findings, the electrosynthesis of DPC was also investigated on Au electrodes, using similar conditions. The experiments were performed with solutions of 0.1 M PhOH in MeOH with 0.1 M $LiClO_4$ as the supporting electrolyte in Ar and CO atmospheres under oxidative conditions using Au electrodes. The obtained cyclic voltammograms are presented in Figure 1.

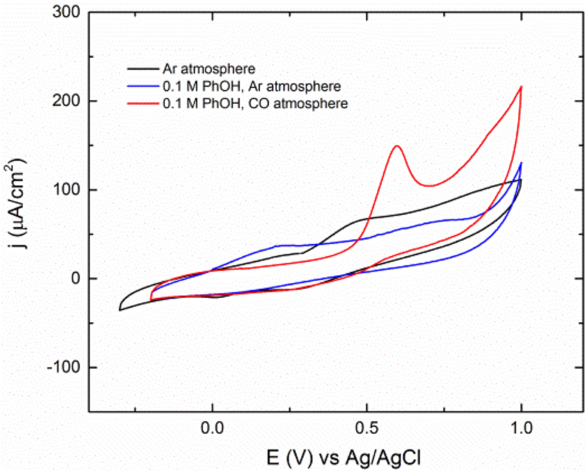

Figure 1. Cyclic voltammograms obtained at Au electrodes in 0.1 M $LiClO_4$ in MeOH with in Ar atmosphere (black line) and with 0.1 M PhOH with Ar (blue line) and CO atmosphere (red line).

The cyclic voltammograms show that, in the absence of phenol, Au oxidation (and, consequently, its reduction) is not observed at this potential range in MeOH. The black line in Figure 1 presents a small oxidation peak at potentials of ~0.4 V (vs Ag/AgCl), most likely due to MeOH oxidation on the Au electrode, as revealed by FTIR results previously reported.[14] When PhOH is added to the solution, this peak (as well as other oxidation currents at higher potentials) seems to be inhibited, most likely due to phenol adsorption on the electrode surface, as observed in aqueous solutions.[15,16] However, at ~0.2 V, a small oxidation peak, which is absent in pure MeOH can be observed. This peak can be related with the formation of PhO radicals, which are the first step for PhOH oxidation. Contrary to what is observed for aqueous solutions, further oxidation currents for PhOH are not observed, most likely because they are catalyzed by the presence of AuO,[15] which is absent in MeOH at the range of potentials used in this study. The cyclic voltammograms, where CO and PhOH are both present, show an increase in oxidation current with onset potential at 0.5 V, which are related (as explained further in combination with the in situ FTIR results) to the formation of both DMC and DPC (although CO oxidation cannot be excluded).

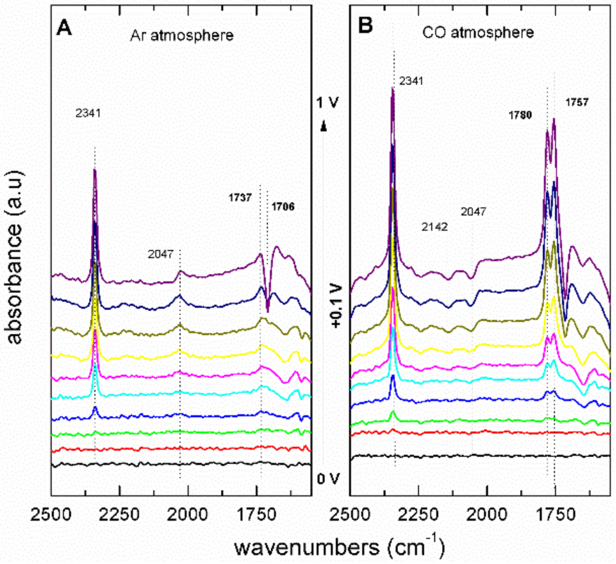

Figure 2. FTIR spectra obtained for Au electrode in 0.1 M $LiClO_4$ in MeOH with 0.1 M PhOH saturated with (A) Ar and (B) CO. Background was obtained at 0 V.

The spectra presented in Figure 2A (Ar atmosphere) show bands at 2341, 2047, 1737, and 1706 cm^{-1}. These bands correspond to CO_2 formation (2341 cm^{-1}), MeOH (2047 cm^{-1}), methyl formate (MF) formation (1737 cm^{-1}) and lithium methoxide consumption (1706 cm^{-1}), which are due to methanol decomposition/oxidation, as described in our recent publication (which also contains further reference spectra).[14]

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The addition of PhOH does not appear to change the reaction pathway for MeOH oxidation. Moreover, the spectra do not show any evidence of PhOH decomposition or oxidation to products other than CO_2. However, even its decomposition to CO_2 is not clear, because this product is also observed for MeOH oxidation and a clear distinction from its origin cannot be made. Nevertheless, the intensity of the band for MF, which is the major MeOH oxidation product on Au,[14] are less intense than previously reported. Consistent with the observations on the CVs, we can attribute this decrease in intensity to some blocking of the Au electrode by adsorbed PhOH or its radical.

After the solution was saturated with CO (Figure 2B), two new bands for product formation (positive bands) are observed in the spectra at potentials of >0.4 V (vs Ag/AgCl). A band at 1757 cm^{-1} arises with increasing potential; this band has been previously attributed to the formation of dimethyl carbonate (DMC).[14] At the same time, a second band appears in the spectra at 1780 cm^{-1} that can be due to the formation of other carbonate, DPC or methyl phenyl carbonate (MPC).

To shed light onto the nature of the compound giving rise to the band observed at 1780 cm^{-1} formed from the reaction of PhOH with CO in MeOH, transmission spectra for solutions of different carbonates and their mixtures in MeOH solution containing the supporting electrolyte were obtained and are plotted in Figure 3.

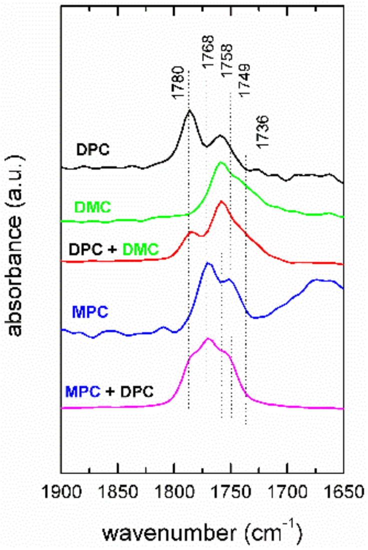

Figure 3. Transmission spectra for 0.1 M DPC, DMC, MPC and correspondent mixtures in 0.1 M $LiClO_4$ in acetonitrile. Background obtained with 0.1 M $LiClO_4$ in MeOH.

The results show that DPC presents vibration features at 1780 and 1758 cm^{-1}, while DMC shows only one band at 1758 cm^{-1}. The mixture of the two compounds presents bands at the same wavenumbers but with different relative intensities (red line in Figure 2). For the case of the MPC solution, it also presents two vibrational bands but at slightly shifted wavenumbers (1768 and 1749 cm^{-1}), when compared with DPC and DMC. However, for the mixture of DPC and MPC, the bands overlap and appear at very similar wavenumbers, compared to the individual compounds (1780, 1768, and 1758 cm^{-1}).

We have recently described the reaction scheme for the formation of DMC from MeOH carbonylation with CO at Au electrodes.[14] The formation of methoxy intermediates, which are necessary for the carbonylation, was shown to be closely related with the electrode ability to oxidize MeOH to methyl formate. Moreover, the metal needs to bind CO with an intermediate binding strength in order to allow the reaction to proceed. The FTIR spectra presented in Figure 2 show no evidence for the direct formation of DPC from phenoxy carbonylation with CO, and the formation of DMC is observed simultaneously. Moreover, it is know that the transesterification of DMC with PhOH can occur when proper temperature and catalysts are used.[17]

In order to understand the role of DMC in the formation of DPC, the following experiments were performed. The solvent was replaced with acetonitrile (MeCN) to avoid the formation of any intermediate coming from MeOH oxidation and no CO was present in solution. Only 0.1 M of DMC and 0.1 M of PhOH were added to the acetonitrile solution containing 0.1 M of $LiClO_4$ as a supporting electrolyte. The spectroelectrochemical results for the Au electrode are presented in Figure 4.

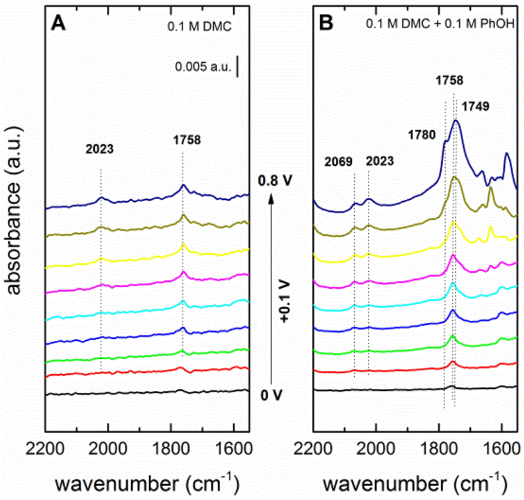

Figure 4. FTIR spectra obtained by scanning toward positive potentials at Au electrode in 0.1 M $LiClO_4$ in MeCN with (A) 0.1 M DMC and (B) 0.1 M DMC + 0.1 M PhOH. Background obtained at 0 V.

The spectra obtained when only DMC is present in the solution (Figure 4A) shows small bands at 1758 cm^{-1} due to DMC in the thin layer. In addition, a positive band for CO (2023 cm^{-1})[18] can be identified as a consequence of DMC oxidative decomposition.[19] After the addition of PhOH (Figure 4B), some changes are observed in the spectra. The most notable difference is visible in the 1750−1790 cm^{-1} region, where new bands rise at ~0.6 V (vs Ag/AgCl). In this region, three bands are observed at 1780, 1758, 1749 cm^{-1}. Analyzing these bands based on the transmission spectra plotted in Figure 3, we can attribute them to DPC, DMC, and MPC, respectively. As DMC is already in solution, we suggest that the exchange of a methoxy group by a phenoxy group is occurring. These results are strongly supported by the observation of MPC for which only one of the methoxy groups has been replaced.

Based on these findings, the following reaction pathway for the formation of DPC from PhOH in methanol electrolyte can be suggested. As a first step, DMC is formed from the carbonylation of the methoxy groups from MeOH and CO.

Next, the replacement of the methoxy groups with phenoxy occurs. It must be mentioned that the reaction does not occur if there is no applied potential, most likely because the polarization of the CO of the DMC to more positive values is needed, so the nucleophilic attack of PhO− can occur, and MeO− is substituted.

It is interesting that transesterification of DMC by PhOH can occur under electrochemical conditions at Au electrodes without the need of high temperatures and using the same catalyst as for the synthesis of DMC. However, the exact nature of this transesterification under electrochemical conditions currently remains unknown.

Through this process, it is possible synthesize, in one step, DMC and directly convert it to DPC. In situ FTIR spectroscopy is an excellent tool for mechanistic studies and for identification of species and intermediates involved on the electrochemical reactions. Unfortunately, one of its major drawbacks is that the results are only qualitative and do not allow quantification of the products. However, the findings on this work provide deeper understanding of the reaction and a new electrochemical path for the direct production of DPC than can be further studied and optimized for future industrial application.

In summary, with this work, we show a direct path for the electrochemical synthesis of DPC starting from CO, MeOH, and PhOH on Au electrodes. By using in situ FTIR, we observed that DPC can be obtained on Au electrodes at low overpotentials (0.5 V vs Ag/AgCl) through an indirect electrochemical path where DMC is synthesized and readily converted to DPC in an "electro-transesterification" step, at room temperature. For the first time, DPC is obtained electrochemically without the presence of palladium-based catalysts. With this report, important insights on the electrochemical synthesis of DPC are given, especially concerning the reaction intermediates, opening new possibilities for the design of alternative processes and routes for the electrochemical synthesis of DPC that can become industrially competitive.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b04204.

Materials and experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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